

The**SPEX**

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Speaker

FOURIER TRANSFORM SPECTROSCOPY

GAS chromatography can be downright frustrating. Run two organic samples showing slightly different properties and, sure enough, an extra peak percolates out of one. The additional component thus indicated, the adventure begins; how to identify the microgram or less of material represented by that peak? More generally, how does one analyze such small quantities of pure substances which march off the GC gangplank every 10 to 30 seconds?

A rapid-scan IR spectrophotometer would be the preferred analytical tool for the job. An IR spectrum is unique for every compound and, equally important, most labs have access to almost 100,000 spectra against which to match their unknowns. But the GC-IR gap has not yet been bridged, overall performance of the best spectrophotometers falling well below the stiff demands. Even with slits spread to a spectral bandpass of 20 cm^{-1} , where many IR peaks blur beyond recognition, the miniscule GC fractions slip by undetected.

So potentially valuable are such analyses that even partial solutions have found acceptance. One manufacturer offers an instrument which stops the GC after each peak to give the spectrophotometer adequate time for tracing its scan. Other devices have been constructed to store the effluent fractions so they can be run later. And some chemists have opted for a mass spectrometer. Despite their high cost (upward of \$70k), their hearty appetite for large blocks of computer time per sample and complex software to accompany them, GCs are now piped to mass spectrometers in a number of labs. But MS data are hardly conclusive. The computer grinds out only an intelligent guess as to the number of carbon, oxygen, hydrogen, nitrogen, etc. atoms in the GC fraction. From there, it's up to old *Homo sapiens* to narrow down the eligible molecular candidates. As an interim measure, MS has earned its credentials; but, in the long run, it may be pre-empted by a newcomer, Fourier Transform Spectroscopy.

S. K. Freeman (1) of International Flavors & Fragrances, Inc. parries the question nicely:

"If the present efforts devoted to optimizing FT spectroscopy continue unabated, the routine and rapid attainment of IR spectra of submicrogram quantities of liquids and vapors is within sight. However, the present state of the art does not permit a confident prediction that a GC-IR system soon will rival the commercially available GC-MS devices in sensitivity (<1 nanogram), speed ("on the fly") or in convenience of operation."

Is an "on the fly" GC-IR system on the way through FT spectroscopy? Prospects seem bright. Analytical instrumentation is exquisitely simple, relatively inexpensive and, most important, the output data from FT spectroscopy can be generated at an exceedingly rapid clip. Like IR, FS provides molecular fingerprints rather than reports concerning the number of different atoms in the molecule. An inexpensive, dedicated computer — not the Herculean time-shared computer required by MS — processes and presents the analyses. Hopefully in pace with an operating GC, those data may shortly be rolling off at least one commercial system.

FT spectroscopy blends an old optical instrument, somewhat older mathematical principles and a new computer approach. In 1823, Fourier devised his famous treatment of curves, concluding that all periodic shapes, regardless of their complexity, could be transformed into a number of sine or cosine curves. In the 1890s, Michelson, who invented an interferometer for the express purpose of measuring the speed of light, realized that its output could be unscrambled into a spectrum when subjected to Fourier analysis. Without a modern digital computer, however, the unwieldy calculations hampered acceptance of the interferometer as a practical means of characterizing compounds.

To those of us brought up on spectroscopy, the concepts of interferometry are at first almost incomprehensible. Bearing no resemblance whatever to and appearing much less complex than a spectrogram, an interferogram seems incapable of accommodating the detailed information for unambiguously portraying each compound. Yet, the information is all there. In fact there is no theoretical reason for converting the interferogram to a spectrogram. FT instrument manufacturers have gone to a great deal of trouble to add this conversion faculty to placate that nostalgic majority of oldtimers homesick for the familiar landscape of mountains and valleys.

A grating or prism spectrometer disperses radiation in terms of frequency; an interferometer is entirely non-dispersive. Regardless of the region of the electromagnetic recorded spectrum, a spectrogram is a presentation of frequency vs. energy. The energy may be absorbed, emitted, excited, fluoresced, or reflected. Readout may be exposed on a photographic plate, traced by a recorder, or printed out by a computer. But always one winds up with energy vs. frequency or, for convenience, some related parameter.

By contrast, an interferogram is a display of the distance traversed by a mirror vs. energy. A seemingly irrelevant parameter, this traverse distance (or the time taken to traverse that distance at a fixed velocity) defines the envelope of curves which must be sorted out to isolate and evaluate the data.

The basic equation in Fourier interferometry is:

$$I(X) = B(\nu) \cos(2\pi X\nu)$$

where $I(X)$ is the intensity of the output beam as a function of mirror displacement X ; $B(\nu)$ is the intensity of the spectrum of the source as a function of frequency ν .

The equation applies to two stationary mirrors in a Michelson interferometer. When one mirror is displaced over a fixed distance, the equation is simply expanded to the definite integral over that distance. The greater the distance, the greater is the information contained within the interferogram, *i.e.*, the greater the resolution that can be extracted from it. In practice, the moving mirror is started slightly inside the point where the two mirror distances are exactly equal and moved out to 0.5 cm or more. The mirror may be stepped along with readings taken at distance increments, or it may be driven smoothly, readings taken at time intervals.

The single frequency ν of a monochromatic beam gives rise to an interferogram consisting of a single cosine wave. The frequency of the cosine wave — let's call this the modulation frequency to avoid confusion — is generally in the audio range. With a mirror velocity of 0.5 cm/sec, a 1000 cm^{-1} infrared frequency is converted to a cosine wave of frequency 500 Hz, some 11 decades lower.

In practice, a polychromatic source — any absorption spectrum — produces a number of overlapping, intertwined cosine waves. It is the function of the Fourier transform to untangle these waves, determine the intensity of each and elegantly present the data as a familiar spectrum. Fig. 1, a diagram of a Michelson interferometer, indicates how this is accomplished. A beamsplitter sends half of the radiation it receives to a moving mirror M1, the other half to a stationary mirror M2. Upon re-

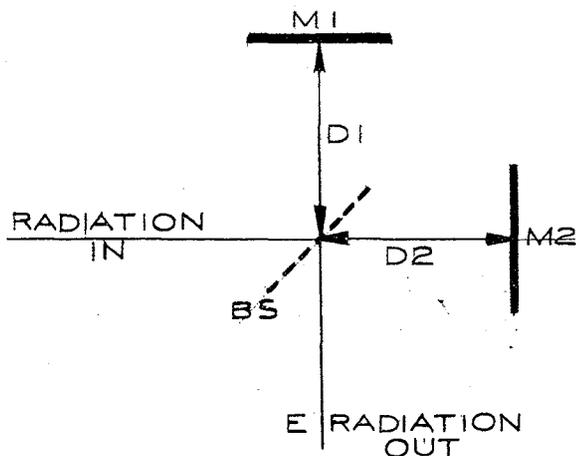


Fig. 1 Simplified layout of a Michelson interferometer. Radiation split by a semi-reflecting mirror is reflected by two mirrors into a single, recombined beam. Small differences in the two path lengths result in patterns of constructive and destructive interference.

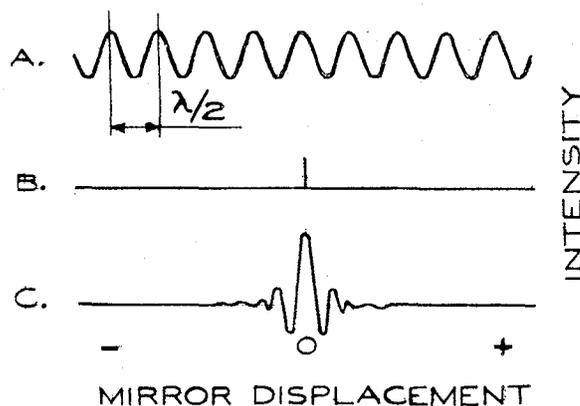


Fig. 2 Michelson interferogram from monochromatic source of radiation is a cosine wave (A); from a continuum it is a single line (B) at the point where the two beam distances are exactly equal; when a substance absorbs radiation from a continuum, the interferogram consists of a number of overlapping cosine waves of different period and intensity (C).

flection from the mirrors, the two beams are constrained to recombine at E. If the distances from M1 and M2 to the beam splitter are exactly equal, the emerging beams reinforce one another; they constructively interfere. Should the distance $D1$ be increased or decreased so that it equals $D2 \pm n\lambda/2$, where λ is the wavelength of the monochromatic beam, the emerging beams again reinforce one another. In the simplest case, with monochromatic radiation of frequency $f \text{ cm}^{-1}$, the output at E is a cosine wave of frequency $2fv$ Hz, where v is the velocity of the moving mirror in cm/sec.

At the opposite extreme, white light interferes with itself so thoroughly that most of its interferogram huddles together into a single line at the point where the mirror-to-beamsplitter distances are exactly equal.

Both monochromatic and white radiation are, of course, trivial with respect to spectrometric applications. Meaningful cases lie in between and a typical spectrum of a substance absorbing white light is shown in Fig. 2c. Fig. 3 shows a real interferogram and its computer-traced transformation into a spectrum.

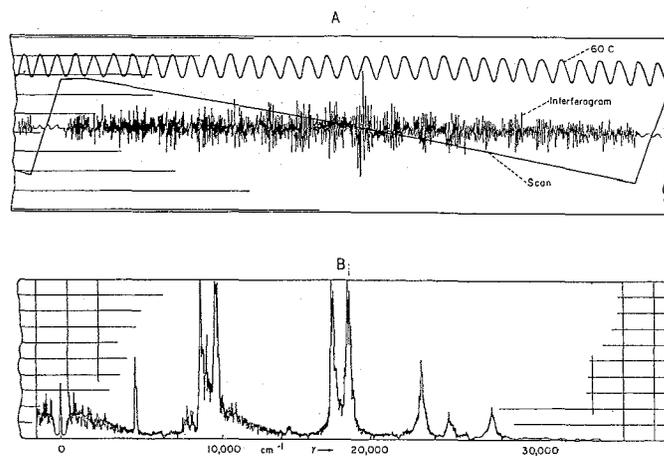


Fig. 3 Transformation of an interferogram in (A) to a spectrum in (B). The cosine wave in the upper part of (A) from a monochromatic source serves to trigger the readout times of the digitizer. The sloping straight line follows the displacement of the mirror.

Information from an interferometer is generated in analog form along both the intensity and displacement axes. The simplest way of manipulating these data is to leave them in this form and, indeed, this constituted the earliest approach to FT spectroscopy. An ordinary audio frequency or wave analyzer was used. Though demonstrably feasible, the approach does not lend itself to high-speed data reduction and lacks provisions for conversion of the information to a traditional ratioed spectrum.

Both objections can be simultaneously overcome by digitizing the data, turning it ultimately over to a digital computer. The computer has additional talents: it can manipulate, refine, correct, and ratio the data, then evaluate their reliability.

One of the first corrections needed involves the beamsplitter of the interferometer. For the ordinary infrared, the beamsplitter is usually a flat KBr plate coated with an evaporated film of germanium. The two interfering paths are thus not exactly identical, one passing through a KBr plate, the other not. To compensate for this difference a similar plate of KBr is introduced into the second path. To the extent that the dispersion of this plate varies with wavelength, the resulting interferogram becomes non-symmetrical. Further, the moving mirror can never be made to move perfectly uniformly in speed. The result? lopsided cosine waves.

Suitably configured, the digital computer can correct for such asymmetries. The computer can also provide double-beam data, subtract out the spectra of interfering substances, average out repeat runs, furnish the operator with statistical data. Little wonder then that the current trend in FT spectroscopy is to hitch on a dedicated computer permanently.

Before it can get to work, however, the computer must be fed digitized raw material. The intensity of the bundle of cosine waves must be measured and carefully digitized. Since the dynamic range of the interferogram is great and small differences are meaningful, this is done with high-speed A-to-D converters having resolution in the order of 12 to 15 bits. That is, the intensity of each peak is measured to a precision of at least one part in 2^{12} . From here the digitized intensity data are sent together with the digitized displacement data to the computer.

Computer programming has developed into such a competitive and proprietary art that little can be told about how the information is processed in commercial instruments. One thing is certain. Ordinary Fourier transform mathematics has been supplanted by algorithms, simplifications resulting in faster processing of the data.

The mesmeric attractant of FT spectroscopy, first to dozens of prominent researchers and later to the inevitable entrepreneurs waiting in the wings, is its incomparable "speed" potential. By speed is meant the time taken to obtain FT spectra of equivalent quality with ordinary IR. Speed comprises two parts; first, in the optical component itself: how efficiently it gathers the incoming radiation, converting it to a signal of a stated resolution. This is termed throughput, luminosity or *étendue*. Secondly, speed consists of the means of measuring

that optical signal: how efficiently it is converted to a datum point — analog or digital — ultimately to be logged by the analyst.

The throughput advantage has been theorized by Jacquinot (2) but its extent is the subject of a controversy which we plan judiciously to avoid. In principle, he started with the well known premise that the amount of light collected by an optical instrument is a product of the solid angle of collection and the area of the source being viewed, the latter proportional to the slit size in the system. Commercial spectrometers capable of resolving 0.1 cm^{-1} have a slit area about 1 mm^2 . FT instruments have a circular aperture around 50 mm diameter. From these two factors, one might estimate a throughput advantage of 2000 times. The possibility of scanning in less than one second what formerly took hours raised a lot of anticipatory eyebrows.

Practice is something else again because in FT spectroscopy the incoming radiation must be so highly colimated that the solid angle factor in the throughput formula is not the same as in conventional spectrometry. Until definite comparisons are made, most people in the field seem content to avoid a showdown. Whether or not Jacquinot's advantage proves to be as large practically as it is theoretically remains to be demonstrated.

Fellgett's advantage is, unlike Jacquinot's, widely accepted. It is real and significantly large. Fellgett (3) pointed out by a simple mathematical treatment how signal-to-noise may be improved by looking at all wavelengths in the entire spectrum of interest simultaneously instead of point-by-point. In a scanning spectrometer, only one resolution element is examined at any one time. During the entire time the sample is illuminated, its entire spectrum is being produced in space; the detector, however, is measuring an exceedingly small portion of that spectrum. Wasteful of time and therefore throughput, it is like taking a drink from the side of a firehose stream while the mainstream is directed to a sewer. If the resolution unit or bandpass is 1 cm^{-1} and the spectrum of interest covers 3800 cm^{-1} ($200\text{-}4000 \text{ cm}^{-1}$), the efficiency of a prism or grating spectrometer is a pitiful 0.26%. By contrast, an interferometer has an advantage of $3800^{1/2}$ or 62 times as great. An equivalent spectrum in terms of resolution and S/N should be obtainable by interferometry in $1/62$ of the time required by a spectrometer. Further, the greater the spectral span and the tighter the resolution demands, the greater is the Fellgett advantage.

Though treated rigorously for the first time in 1952, Fellgett's advantage has long been known intuitively to every emission spectrographer. He can photograph a spectrum of iron with a resolution of 0.1Å in one second but to scan a spectrum photoelectrically and obtain a similarly resolved and peaked spectrum might take upward of an hour.

In the interest of rigor, it should be stated that Fellgett's advantage is fully applicable to most infrared detectors but only partially to photomultipliers. The criterion hinges on whether the detector's noise goes hand in hand with the level of the signal. Thermal devices used in the infra-

red have a constant noise level irrespective of the signal level. The noise in photomultipliers, comprising several ingredients, tends to rise somewhat with increasing signal level.

If one person is to be credited with the renaissance of FT spectroscopy, it is H. A. Gebbie who in 1955, working under the tutelage of Prof. John Strong at Johns Hopkins University, took note of the compound advantages of Fellgett and Jacquinot and recognized that the main limitation of FT spectroscopy lay in the decoding operation. Gebbie constructed a Michelson interferometer and programmed a digital computer to present the data in spectrum form (4). Upon his return to England, he was fortunate in having the opportunity to extend his work at the National Physical Laboratory in Teddington. The implications of his new instrument were enthusiastically appreciated by Sir Gordon Sutherland, UPL's director, well known in his own right as a spectroscopist. Sir Gordon invited Grubb Parsons & Company Ltd. to see the instrument, benefit from Gebbie's experience and knowledge, and produce a commercial model. Later, a second company, Research & Industrial Instruments Company was invited to participate as well. Soon both companies had developed a far IR FT spectrometer, RIIC incorporating a dedicated computer in theirs in the early '60s. Further impetus to commercial development came from additional successes by Gebbie especially that which showed that FT spectroscopy could yield data unattainable by conventional techniques. In 1957 he produced a spectrum of the atmospheric absorption of solar radiation in the difficult region $300\text{-}1000\mu$ (5). In 1961, he went on to presage the exploitation of IR emission spectroscopy in the normal IR ($2\text{-}12\mu$), an application only now gaining a foothold.

Back in the United States, Block Engineering became active in FT spectroscopy, delivering their first instrument in 1960 to the University of Michigan. Rather than concentrate on the far IR, however, they have preferred to exploit the normal IR which they feel has more sales potential.

Both Grubb Parsons and RIIC are still deeply involved in FT spectroscopy in the far infrared. They have brought this difficult region—harboring vital information for characterizing organic and especially metallo-organic compounds—out of the hands of a few patient, dedicated and courageous fundamental researchers into the hands of a sizable number of more practical minded chemists. Grubb Parsons' Mark II interferometer, in the \$12-\$14,000 range, is based on the Gebbie design. Powered by a stepping motor, it generates a punched tape and the company offers the software necessary for plugging the tape into a large digital computer. RIIC's current model, FS-720, has a 75-mm diameter aperture and a mirror traverse distance up to 100 mm; a synchronous motor moves the mirror at a rate of 0.5 to 500 microns per second. Plastic film beamsplitters from 6 to 50 microns thick are manually interchanged to optimize analysis in the region from $10\text{-}50\text{ cm}^{-1}$. In FT spectroscopy one cannot rely on the constancy of speed of even a synchronous motor and more accurate techniques for

telling the electronics when to take a reading must be devised. For the purpose, the FS-720 incorporates a Moire grating. Attached to the moving mirror, it generates a series of fringes related to the distance displaced. The intensity peaks of these fringes trigger the electronics, instructing the lock-in amplifier when to take readings. A pneumatic Golay detector picks up the absorbed radiation after it is condensed by a plastic lens and light pipe. A type of bolometer, the Golay detector is uniformly responsive over the entire infrared region. Its detectivity (D^*) value is around 10^9 , comparable to the best detectors, but its thermal time constant is slow, around 0.1 sec. This limitation will be expanded upon further when we discuss the new pyro-electric detectors which are capable of keeping abreast of modulating frequencies in the order of 2000 Hz.

In the very far IR ($<30\text{ cm}^{-1}$), plastic film beamsplitters have turned out to be less than satisfactory. Poor transmittance properties of materials waste much of the total available energy and, secondly, multiple interference effects within the films impair the quality of the final spectra. A variation of the Michelson design, a lamellar grating interferometer, has turned out to be superior for work in this extremely-limited spectral region, (Fig. 4).

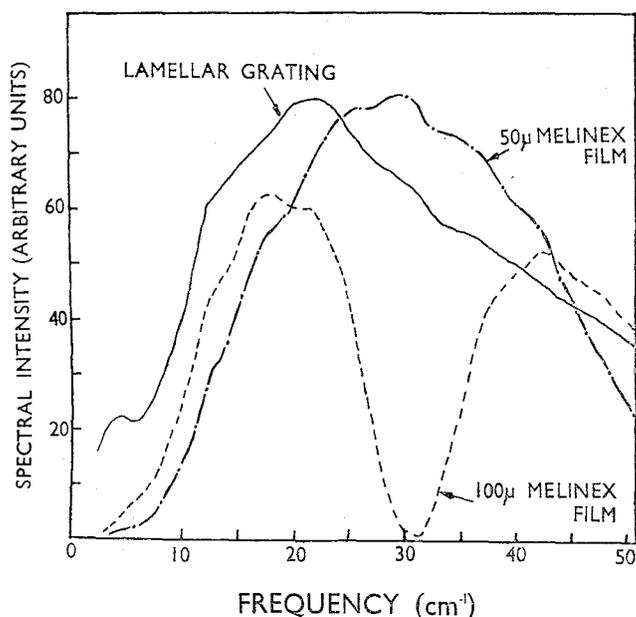


Fig. 4 Comparison between the intensity produced by an ordinary Michelson and a lamellar grating interferometer. Below 30 cm^{-1} , the latter is obviously the better choice. The graph also points up one shortcoming in FT measurements in the far IR, the need to switch beamsplitters where they run out of steam at certain frequencies, (courtesy Beckman-RIIC Ltd.).

A lamellar grating interferometer achieves varying interference with a series of intermeshing reflecting plates; no transmission occurs. Like the teeth of one comb passing through those of another, one set of plates is displaced with respect to the other. Collimated radiation striking the lamellar grating is thus reflected from two intermeshed, segmented surfaces. The effect is a pair of reflections which interfere with one another, in contrast with a reflection and a transmission in the ordinary Michelson design.

RIIC's LR-100 is a lamellar grating instrument consisting of 9 stationary plates intermeshed with 8 moving plates, each 4.7 mm wide by 80 mm high. Machining and construction of the unit is, of course, tricky. The plates must be ground and lapped together so that all are coplanar within small fractions of a micron. Then the moving plates, as a rigid unit, must maintain their formation and their parallelism to the stationary plates. In the RIIC design, the traversing mechanism is powered by a stepping motor which rotates a micrometer drive in increments of 5 to 80 microns. Total traverse distance is 50 mm and the pause period between steps may be adjusted from 0.5 to 34 seconds. A single sweep is made to obtain the interferogram; should the best resolution of 0.1 cm^{-1} be sought, the sweep time is set to several hours. During this time, the digitizer and computer are kept whirring so the final curve is drawn almost immediately upon conclusion of the scan.

Although non-dispersive FT instruments are available for the far IR, their acceptance has been limited, the time-saving advantage over dispersive instruments turning out to be overly optimistic if existent at all. With either type of instrument, obtaining spectra is a long, frustrating job. Another setback for FT spectroscopy in the far IR occurred with the advent, about three years ago, of laser-Raman spectroscopy. Almost overnight, it became the fastest and simplest way of obtaining data down to 20 cm^{-1} . Though scattering and absorption data are complementary rather than identical, the ease in running Raman experiments tends to encourage research by this method which neatly circumvents the problem of weak energy in the far IR by taking signals not from the frequency itself but from changes in the frequency. Instead of laboring with frail sources and poor detectors, so characteristic of the 20-400 cm^{-1} region, investigators enjoy the power of ion gas lasers and highly efficient photomultipliers operating in the visible region.

But whatever the eventual outcome of instrumentation for the far IR, the normal IR retains its dominance. The region is home for thousands of spectrochemists. At a glance they can correlate a spectrum with its probable compound. And here even a 50-fold improvement in analytical speed is an exciting prospect; anything that can reduce time and maintain resolution is appealing.

Aware of this, Block Engineering recently announced their FTS-14, a Fourier Transform instrument designed principally to hasten analyses in the normal IR. Assuming that its in-lab performance matches the specifications nutshelled in Table 1, another barrier in analytical instrumentation will have been hurdled.

Claims for this FT spectrometer include obtaining a Class II spectrum in about 11 minutes as compared with upward of 5 hours for dispersing spectrophotometers. Before showing how this time is broken down, let us review the criteria laid down by the Coblenz Society for Class II spectra. In this category fall spectra produced by "the best currently available commercial infrared grating spectrophotometers, operating at maximum efficiency under conditions consistent with acceptable laboratory practice." Resolution and signal-to-noise separate the best instruments from those in the next tier. Resolution

Table 1. Comparison between planned commercial FT spectrometer and "best" current commercial grating instruments.

Parameter	Non-Dispersive	Dispersive
Speed	300X	X
Resolution, cm^{-1}	<0.5	<0.5
Spectral coverage, cm^{-1}	<10-10,000	200-5000
Stray light, %	0.03	0.2
Signal averaging	Yes	No
Wavenumber accuracy, cm^{-1}	<0.1	0.04-1
Cost	\$65K	\$30K

must be better than 2 cm^{-1} through at least 80% of the spectrum and at no place should it exceed 5 cm^{-1} . As for noise, "it should not exceed 1% of average peak-to-peak."

With the FTS-14 a resolution of 0.5 cm^{-1} is claimed on a routine basis. Theoretically, resolution of an interferometer is a function only of the traverse distance of the mirror. A 1-cm movement is equivalent to about 0.5 cm^{-1} resolution in the Block instrument. Alternatively, the drive excursion can be extended to 4 cm which is equivalent to a resolution of 0.13 cm^{-1} . Incidentally an FT spectrometer has been constructed in France having a 2-meter traverse with which a resolution of 0.005 cm^{-1} was demonstrated (6). Noise can be evaluated in the Block instrument by having it plot a reference spectrum alone. In a single run, under the worst noise conditions, random fluctuations plotted on the chart paper are shown at about 10% of full scale. Therefore, 100 runs should reduce the noise level to the specified 1% in accordance with accepted statistical principles, (Fig. 5).

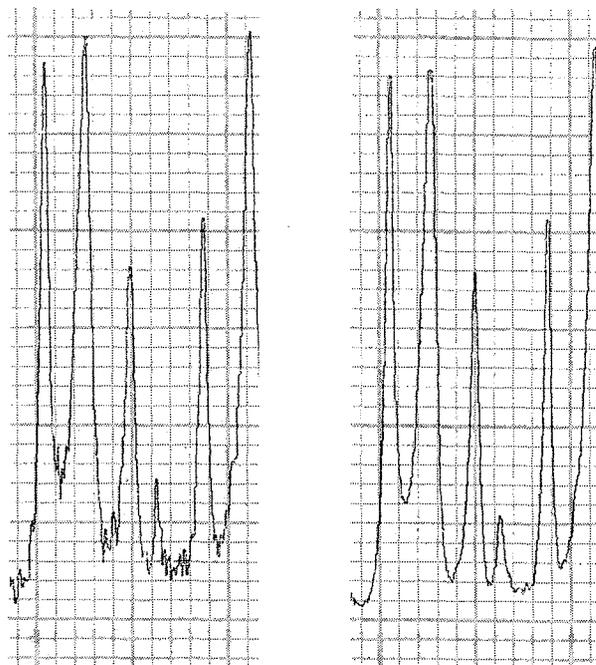


Fig. 5 Two computer-traced spectrograms from an FT instrument illustrate the S/N improvement attainable by increasing the number of scans. The left trace is of a single scan; the right of 16 scans of the same sample of indene in the 1200 cm^{-1} region, (courtesy Block Engineering Co.).

Unlike ordinary spectrophotometry where the infrared spectrum is traced out simultaneously with the rotation of the grating, a number of sequential steps are needed in FT decoding. The 11-minute total allotted for a resolution of 0.5 cm^{-1} at a 1% noise level is broken down:

100 scans	120 sec
100 retraces (time to return the mirror to starting position)	30 sec
Rerun of the above for reference beam which is alternated with sample beam	150 sec
Computer time	80 sec
Plotting time	240 sec

This technological breakthrough appears to have developed from no single achievement but, rather, the care taken to optimize each component. A formidable difficulty with interferometer design is to so bridle the mirror that it moves smoothly at a constant speed. In earlier instruments, a synchronous motor or stepping motor was the choice but the positional accuracy demanded in interferometry taxes the capabilities of ordinary motors. Their angular displacement with each pulse or change in polarity of the ac main depends on the accuracy with which the motor is constructed. If the poles in the motor are not uniformly separated, every angular jump will differ in amplitude. Block's design appears to offer the mirror a smoother and more uniform ride. A voltage applied to a loud-speaker coil pulls a piston inside of a closely fitting cylinder. Meanwhile an annular stream of air between the piston and cylinder wall at once cushions the piston, keeps it centered and acts as an air damper.

Taking a cue from grating ruling engine technology, interferometer manufacturers first assure themselves that their product is made as carefully as possible, specifying grinding, polishing and lapping to the closest tolerances they dare demand from machinists. And then they proceed to apply corrections. In short, they do not depend on a time-distance relationship with respect to the moving piston. For, only to the extent that the scans are all reproducible will the actual resolution approach theoretical. Again borrowing from grating ruling technology, Block designers resorted to interference fringes to find the exact position of the moving mirror at any time.

A source of monochromatic radiation (small He-Ne laser) functions as a referencing trigger. As pointed out earlier, monochromatic light gives rise to a perfect cosine wave train in an interferometer. Instead of instructing the digitizer interface of the computer to take signals at fixed time intervals, the digitizer takes its instructions from the cosine wave of the laser. When the peak intensity of each cycle is reached, a pulse is directed to the digitizer ordering it to take a reading. The reference laser beam rides astride a secondary interferometer mirror rigidly attached to the primary mirror. Any deviations from linear displacement are thus reflected as a deviation from a true cosine function. The laser reference serves still another purpose. Through a servo loop, it controls the speed with which the piston holding the mirror actually moves. This combined technique should prove capable of compensating for and correcting velocity changes.

The secondary interferometer is illuminated by an incandescent lamp as well as a laser. The purpose of the white light is to provide a pulse at the same starting line in each traverse. Since a moving object must be given time to accelerate up to speed, the piston must first be returned to a position behind the starting point. As it reaches the invisible starting gate, the interferogram of the incandescent lamp—a sharp line—instructs the computer to start taking the next cycle of data.

CONTRIBUTING heavily to the wave of progress promised by the FTS-14 is a remarkable new type of infrared detector based on the pyro-electric effect. In all ferro-electric materials a change in spontaneous polarization occurs with changes in temperature. In principle then, such materials can operate as bolometers. That is, they function through a change in their internal temperature rather than through some interaction with the oncoming radiation. Although known for some time, the pyro-electric effect had two drawbacks: the polarization change was small and it could not be measured directly. At least three manufacturers have found new materials of extraordinary sensitivity and, equally important, a means for converting the polarization to an easily measured electrical parameter.

The best pyro-electric material available thus far commercially is triglycine sulfate (TGS). When a wafer of TGS is coated on both sides with a conducting material, it becomes a capacitor. Temperature changes induce polarization changes in the capacitor which, in turn, produce a charge on the electrodes. This is readily measured as a flow of current in an external circuit.

What is remarkable about these new pyro-electric devices is a combination of three properties. Like bolometers and thermopiles, they appear to be uniformly responsive throughout the IR and far IR. In fact, their range has been shown to extend into the microwave region. Unlike bolometers and thermopiles, their performance is not drastically degraded with an increase in modulating frequency. Because the modulating frequency range of practical FT instruments operating in the IR reaches 1-2 kHz, bolometers are virtually inapplicable. They like to operate around 13 Hz, well below their reciprocal thermal time constants. Strangely, pyro-electric devices perform equally well above their thermal time constants. Both the responsivity and the noise drop at about the same rate so that the noise equivalent power remains essentially constant to 100 Hz. Up to 2 kHz, the NEP remains sufficiently low that TGS is still excellent. The third advantage of TGS is its properties at room temperature. At 300°K , its detectivity (D^*) is only one order of magnitude poorer than the peak detectivity of PbS submerged in liquid nitrogen. While photoconductors are restricted to a rather narrow band, PbS cutting off sharply at 4.5 microns, TGS can operate over the complete IR and far IR (Fig. 6).

Achieving a 40-second computation program appears to be the most significant time-cutter in the FTS-14 and, understandably, Block engineers are not telling all they know. Obviously, they are not working with the ordinary Fourier transform and, very possibly, even the Cooley-Tukey (7) fast-Fourier transform has been improved upon.

By now, it is a well-known truism that programming a small computer efficiently is a lot trickier and a lot more important than doing the same for a large computer. The forgiveness aspect of a large computer is its tremendous speed: if the program has several additional steps than actually needed, the large computer runs through them so fast that it makes but a few seconds difference in actual computation time. To a small computer, however, each operation is often measured in seconds rather than microseconds. Minimizing the number and complexity of the steps is often the key to the successful application of a small, dedicated computer.

ALREADY noted is the tremendous potential of FT spectroscopy for the analysis of fractions in real time as they are separated by a gas chromatograph.

The overall speed advantage of FT spectroscopy has been exploited elsewhere where conventional techniques have proved disappointing. Low and Clancy (8) have shown that the plume from a smokestack can be analyzed

Curve 1—InSb, 77°K, 60° FOV
 Curve 2—PbS, 300°K, 2° FOV
 Curve 3—InSb, 77°K, 2° FOV
 Curve 4—Cd HgTe, 77°K, 60° FOV
 Curve 5—Ge:Hg, 35°K, 60° FOV
 Curve 6—Ge:Cu, 4.2°K, 60° FOV
 Curve 7—(scale $\times 0.1$) InSb, 300°K, 2° FOV
 Curve 8—(scale $\times 0.1$) TGS bolometer

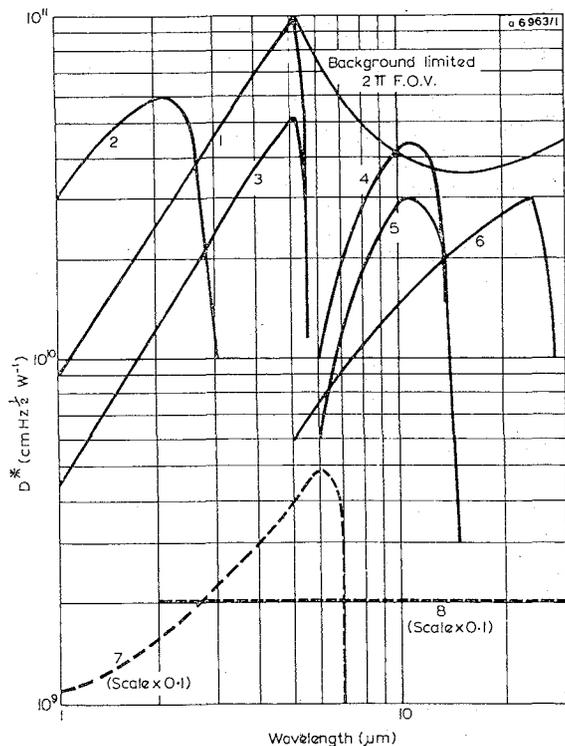


Fig. 6 At room temperature, triglycine sulfate, a pyro-electric detector, is shown to have uniform D^* with wavelength at a level not too far below the peaks of semiconductor devices which mostly must be operated at liquid nitrogen temperatures and below, (courtesy Mullard Ltd.).

at a distance of 600 feet. By mounting an FT instrument on an 8" reflector telescope, they were able to pick up SO_2 and CO_2 in the plume. Background from the sky was subtracted out by running it first and storing its data on tape.

Last year Low showed how conveniently FT spectroscopy could characterize coatings non-destructively without removal from their original base (9). By a reflection technique, he obtained easily identifiable spectra of paints, lacquers, polystyrene, nail polish.

Thus far emission IR spectroscopy has not been successful because of its inherently poor intensity. Although all materials emit radiation at the same frequency with which they absorb radiation, the temperature to which the materials must be raised in order to yield acceptable spectra is usually in excess of 100° . Thermal degradation of most organic materials—and of nearly all biological tissue—precludes the application of such temperatures. For this reason, living biological materials cannot be analyzed with dispersed IR through their emission spectra. Simulating body temperature, Low (10) obtained excellent interferometric data from organic materials. He has also (11) demonstrated differences in the IR emission from normal and psoriasis-infected skin by making FT measurements on the subject.

Compactness of instrumentation, simplicity of operation, excellence of optical speed and ease of telemetry of FT have made this approach a natural for space exploration. Already, the earth's emission has been surveyed by vehicles in the Gemini series (Gemini Mid-program Conf., NASA report SP-121, 1966). Spectra of Mars, Jupiter and a few bright stars have also been recorded (12). On the other hand, Mariner probes which reached Mars during this summer carried dispersion, not interferometric, spectrometers. Apparently, there are still two schools of thought concerning which technique is superior for space exploration. No doubt military files somewhere contain reports on the detection of nuclear explosions and monitoring of rocket exhausts by FT methods.

The pace quickens and another dead-end sign is being relocated, the digital computer finds one more small world to conquer.

—AJM

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NEW GRINDING VIALS FOR THE FREEZER/MILL

How to grind samples at liquid nitrogen temperatures without organic contamination was one recent challenge; another, how to grind and blend small quantities of material for the preparation of KBr pellets, again free from organics. Because some of the polycarbonate in the center tube of the 6701 Grinding Vial might rub off during the reciprocating end-to-end poundings by the impactor we have eliminated any possibility of organic pickup by replacing the polycarbonate cylinder with a Cr-Ni stainless steel tube. Though the impact loses some of its magnetic virility because of eddy-currents, enough power remains to grind most materials in two minutes or less.

For organic-free KBr work with micro samples, we are providing a set of much smaller vials, also of all-metal construction. Three samples may be ground simultaneously in a special holder.

So, if you wish to make powders of plastics, elastomers, biological tissue (including cartilage, bone, teeth) and other substances—the manifest has grown to hundreds—at a temperature where they are immune from thermal degradation, here's your chance.

- 6700 Freezer/Mill**, impact grinder for operation in a self-contained liquid nitrogen bath, 115 V, 50-60 Hz. each \$620.00
- 6701 Grinding Vial**, 10 ml maximum grinding capacity each \$ 35.00
- 6702 Center Cylinder**, stainless steel, for 6701 grinding vial. each \$ 15.00
- 6703 Grinding Vial Set**, 0.6 ml each maximum grinding capacity; set of three in special holder. set \$ 75.00



WESTERN REGIONAL SALES OFFICE

Philip Warren, who has been managing the West Coast region for us for the past year from our home office in New Jersey will henceforth do business from:

SPEX INDUSTRIES, INC. Phone: (408) 246-2333
129 Arcadia Avenue
Santa Clara, Calif. 95051

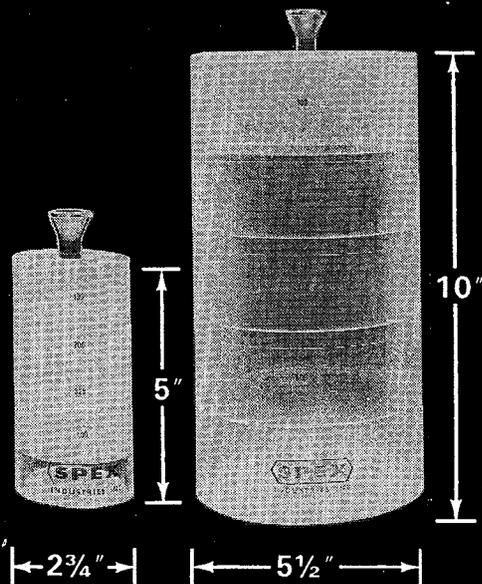
His territory includes Alaska, Arizona, British Columbia,

California, Colorado, Idaho, Hawaii, Montana, Nevada, New Mexico, Oregon, Utah, Washington and Wyoming.

Although Phil will be at your service for technical information concerning all products, we recommend that quotation requests and orders for chemicals, standards and supplies be mailed or phoned directly to our main office in Metuchen where stock is maintained so delivery information and shipments can be handled most promptly.

2 = 8

Rate this
new product
by its size



5 1/2" ϕ All Plastic

SIEVE SET

Eliminate metallic contamination when high purity materials are being screened. This new 120 mm i.d. Sieve Set, when you get down to business, means 8 times the capacity of our popular 57 mm i.d. version. The four sieves, 100, 200, 325, and 400 mesh monofilament nylon cloth, are each stretched on an "embroidery" frame of telescoping methacrylate cylinders which stack over a receiving tray. The screens meet ASTM specification E11-58T for size and uniformity of mesh, can be quite easily replaced when worn or to avoid inter-contamination of materials and are available in packages of pre-cut circles. The whole assembly slips apart for easy cleaning.

- 3536 Sieve Set**, consisting of 4 frames and 1 tray with 1 each of the screens listed below. set \$ 48.00
- 3530 Sieve Frame**, consisting of two telescoping methacrylate rings 57 mm i.d. x 25 mm high, specify for 100, 200, 325 or 400 mesh. each \$ 12.00

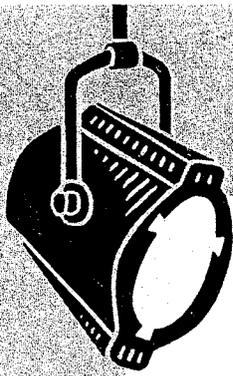
Screens, nylon monofilament cloth 88 mm ϕ

- | | |
|--|---------|
| 3531 100 mesh screen (12) | \$ 6.50 |
| 3532 200 mesh screen (12) | \$ 9.00 |
| 3533 325 mesh screen (6) | \$ 6.50 |
| 3534 400 mesh screen (3) | \$ 9.00 |
| 3535 Tray, 67.5 ml, 57 mm i.d. x 25 mm high | \$ 5.50 |

- 3546 Sieve Set**, consisting of 4 frames and 1 tray with 1 each of the screens listed below. set \$99.00
- 3540 Sieve Frame**, consisting of two telescoping methacrylate rings 120 mm i.d. x 50 mm high, specify for 100, 200, 325 or 400 mesh. each \$22.00

Screens, nylon monofilament cloth 150 mm ϕ

- | | |
|---|---------|
| 3541 100 mesh screen (12) | \$12.00 |
| 3542 200 mesh screen (12) | \$18.00 |
| 3543 325 mesh screen (6) | \$18.00 |
| 3544 400 mesh screen (3) | \$18.00 |
| 3545 Tray, 540 ml, 120 mm i.d. x 50 mm high. | \$25.00 |



SPEX PRESENTS

Source and Sample Chambers

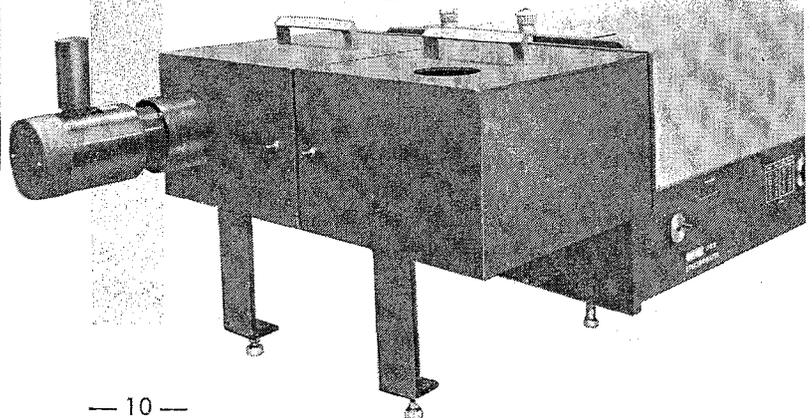
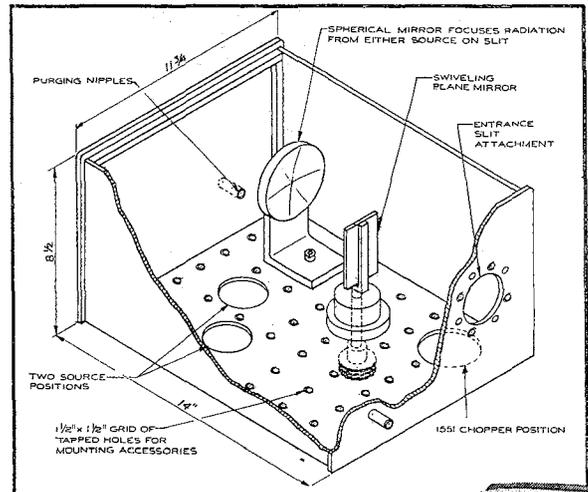
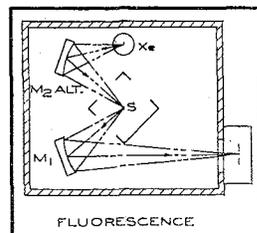
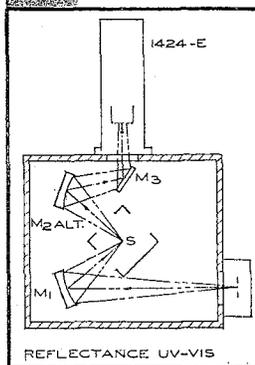
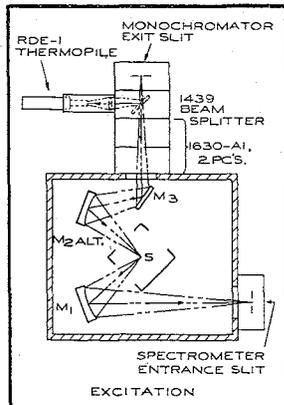
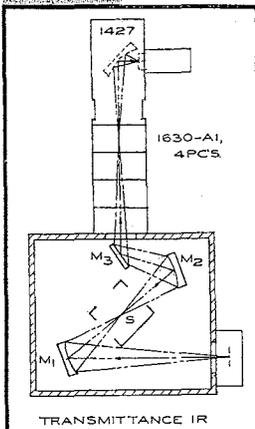
Not often do accessories merit star billing alongside the lead player, nor are SPEX UVISIR® SPECTROMETERS easily upstaged. But these two characters, having taken their bows for a few previews, rated so many curtain calls that they deserve a spotlight of their own.

Bravos go out for their great promise of flexibility, versatility and adaptability. They pose here with our 1702 Spectrometer, surrounded by some of their starlets.

Attached to the entrance slit, the #1550 SOURCE CHAMBER may be outfitted with any two of a repertory of sources extending from 1600A to 25 microns, our unique twirling light Chopper (#1551) and/or an 8-position Filter Wheel (9021).

The set-it-yourself #1570 EXPERIMENT CHAMBER on the exit slit includes set backdrops for absorption, reflectance, fluorescence or excitation spectroscopy at ambient, low or high temperatures. Performer creativity is inspired by the several strategically placed ports and the floor grid of tapped holes.

Previews are completely sold out but SRO is still available for matinee and evening performances at the Electro-Optical Systems Design Conference, New York City Coliseum, September 16, 17, 18, 1969. If you cannot attend that week send for detailed specs or phone and talk over your ideas with one of our sales engineers.



tricks of the trade

CALIBRATING WAVELENGTH READOUT

Well known to infrared spectroscopists, but possibly less familiar to those working in the ultraviolet and visible, is a very simple application of a Fabry-Perot *étalon* for calibrating and measuring periodic errors in spectrometer drive systems.

When a Fabry-Perot *étalon* is illuminated with a continuum and the transmitted light is viewed through a grating (or prism) spectrometer, the spectrum consists of bright fringes separated by intervening dark spaces (channeled spectrum). Separation between the observed fringes is constant in wavenumber for any given spacing between the Fabry-Perot plates and is inversely proportional to this spacing.

The test for periodic error in a scanning spectrometer is made photoelectrically, recording the channeled spectrum over at least 2 full rotations of the spectrometer leadscrew. Simple measurement of positions of the transmission maxima will reveal the magnitude of any periodic errors. Regular cycles of compression alternating with expanded regions, varying at the screw rotation rate, are a dead giveaway about periodic system errors.

In recent tests on our new 1702 and 1704 wavelength spectrometers no evidence of periodic error in the drive mechanism was found. Our fringe spacing was 3.9 cm^{-1} in the experiment (about 0.96A at 5000A) and we recorded 200A or 2 full turns of the screw. Any residual periodic error in the drive was less than the error of the measurements, $\pm 0.06A$ (1st order, 1200 groove/mm grating, 5000A region).

A METHOD OF SEMIQUANTITATIVE ANALYSIS

J. J. Johnson of Westinghouse's Atomic Power Division, Box 158, Madison, Penna. 15663, has worked out a comprehensive procedure for the analysis of samples of known matrix based on Spex G Standards. Although prepared back in May 1966 in a form typical of Mr. Johnson's admirable ability to get the facts down straight and concisely, the report has not been formally published. He has kindly offered to send a copy to anyone requesting it. Included is a sheet of special graph paper he has devised for plotting %Transmission vs %Concentration of the standards.

SUGGESTIONS ON OUR NEW SEMIQUANTITATIVE STANDARDS

"I read with interest your latest Spex Speaker, Vol. XIV No. 1, about semiquantitative standards.

"We have had very good results in using your semiquantitative standards. By a combination mixture of the Master-49, noble metal and rare earth standards we are able to report semiquantitative values for 60 elements in a single analysis of a sample with a precision of $\pm 20\%$ to $\pm 50\%$, using a 1:9 dilution of the sample with graphite. Our standard plate (20 in. spectrum) contains 16 standards from 0.0005% to 1.0%.

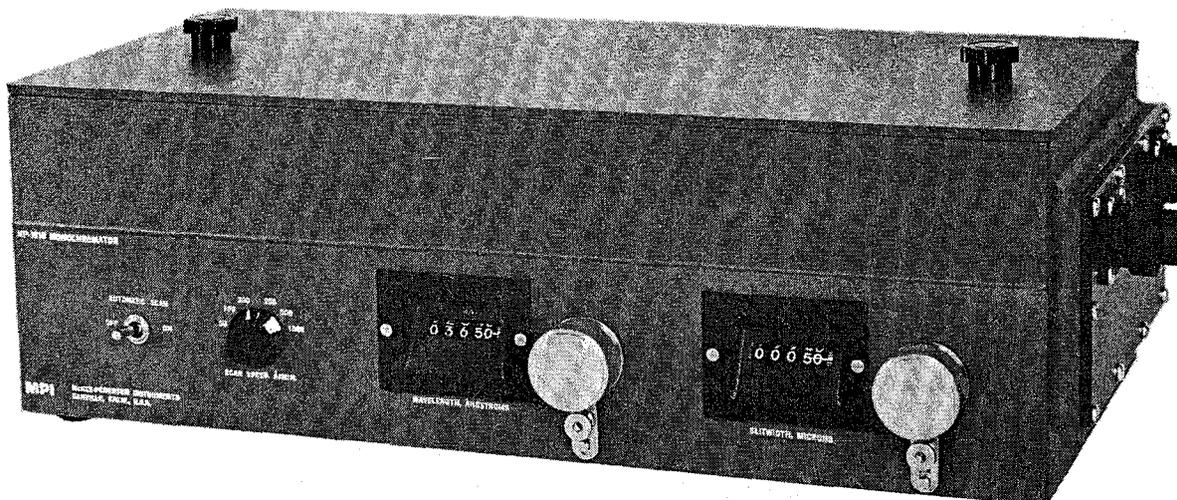
"Enclosed are some comparison results of NBS standards which confirm your reported results. Our purpose for doing the comparison studies was to find the type of sample that should not be analyzed by a graphite dilution semiquantitative method. The following is a list of materials that cannot be analyzed. These materials were rejected because 10% of the elements detected did not have precision or accuracy values of better than $\pm 50\%$: Al_2O_3 ; Na, Li, K, Rb, halides; Ta, W, B, Si, carbides; Fe, U, Th, some rare earths, and steel oxides.

"Results for steel oxide can be reliably determined if correction factors are applied to the final elemental results. The factors we found are 1.25 for Co and Mo; 1.5 for Cr, Ni, Si, Ti, V; and 2.0 for Cu and Mn.

"In every Spex Master-49 I have purchased, copper is the only element that does not grade down reliably in a prepared set of standards, especially from 100 ppm to 1 ppm in a graphite base. I have found other people who have had the same problem."

C. L. Chaney
Gulf General Atomic Inc.
San Diego, Calif. 92112

Ed. Note: Early complaints about copper inconstancy in our standards were traced to "nesting" in the graphite powder. This refers to impurity pockets in the material. It is suspected that nesting may occasionally occur in electrodes themselves although purity of commercial graphite has steadily improved.



MP-1018 MONOCHROMATOR
 Czerny-Turner Grating Monochromator for Ultraviolet,
 Visible, and Near Infrared.

MP MODULAR INSTRUMENTATION SYSTEM

Offering the maximum advantages of a modular system of electro and photometric instrumentation, McKee-Pedersen Instruments Company provides basic building blocks, the heart of which is their operational amplifier, which can be interconnected with patchcords to perform electrical measurements, control potentials or currents, carry out mathematical operations on signals, provide amplification, switching and other instrument and control functions limited only by your own imagination.

Compatible with the MP-1018 Monochromator described here is an array of some thirty modules including sources, detectors, a recorder, electrometer, integrator, power supplies, filters and the consoles that can house them all. And to give you an idea of the sound economy the system presents, the double-beam photometer can convert a monochromator into a double-beam spectrophotometer for just \$990.00.

If you thought your ideas were too plump for this year's tight budget try them once more with this sleek little monochromator and let us send you details of all the conveniences you can plug in now or later.

The MP-1018 Czerny-Turner monochromator is ruggedly built on a single aluminum sand casting. It may be used over a wide range of wavelengths by appropriate choice of diffraction grating. Gratings are available for use from 2000A to 15 microns. The wavelength counter reads directly in Angstroms when 590 line/mm gratings are used. The slit width is read in microns. Slits are adjustable in unison from 5 to 5000 microns. Slit height may be reduced by inserting baffle plugs. All optics are kinematically mounted. The stepper scan drive has six switch-selected speeds. Integrated circuits digitally control the speed. By using different drive motors, other sets of six speeds are available. Wavelength may also be changed manually, even while the electronic scan is operating. Both ends of the leadscrews are accessible for connection of retransmitting potentiometers, slit programming motors, etc.

MP-1018 Monochromator, designed to operate on 115V, 60 Hz; supplied with 590 grooves/mm grating blazed for 4000A. **\$ 995.00**
 Above unit supplied with different grating **1070.00**

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