Application of Raman Spectroscopy to Analytical Chemistry: A New Type of Spectrograph.

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APPLICATION OF RAMAN SPECTROSCOPY TO ANALYTICAL CHEMISTRY:

A NEW TYPE OF SPECTROGRAPH

by

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Introduction

One of the reasons for the resurgence of Analytical Chemistry to a prime position in the field of chemistry in both academic and industrial circles was the addition of instrumental analytical methods to its procedures; the most widely known of these being spectroscopy. For many years the analytical chemist had been using a closely related field in his colorimetric methods but this was of small importance compared to gravimetric and volumetric analysis. However, the need for rapid accurate means of analysing large numbers of samples, many of them not easily handled by the older methods, led him in the direction of physical rather than chemical analysis, principally optical methods. In this he was greatly aided by the wartime researches leading to the improvement in optical instruments and materials.

The broad field of spectroscopy can be divided into several branches, one of them being Raman. Raman spectroscopy is applicable to both qualitative and quantitative analysis and it is a means of improvement in the latter, through the building of a new type of spectrometer, that was the object of the research leading to this thesis.

The quantity of a compound present in a mixture is determined in this, as well as all other spectroscopic branches, by comparing the intensity of a line in its spectrum with the intensity of the same line in the spectrum of the pure compound. In Raman work this is not easy to do as the absolute line intensities must be used and these cannot be duplicated with the precision demanded for accurate analysis. Research has provided instruments which will improve this precision over a short period of time but it has not supplied a spectrograph that will reproduce today's intensities next year.

A better method of approaching the problem is to use relative rather than absolute intensities in the comparison. In this manner it would not be essential to eliminate operating condition fluctuations as these fluctuations would affect the intensities of the standard and sample lines to the same degree with the result that the intensity ratio would always be constant. This poses the problem of what line to use for the comparison standard. In infra red, for example, the standard is the source radiation after it is passed through a blank cell. In Raman this is impractical because the Raman line intensities are only a small fraction of that of the source and thus a small but significant variation in the Raman intensity would escape detection.

Another way would be to run a standard sample before the unknowns and compare all unknown spectra lines to one line of the standard spectrum. However, if any fluctuations occur in operating conditions between the standard and sample runs these ratios would give results little more accurate than the results obtained by using absolute intensities.

A variation of this idea appears to provide the desired method. If the standard and sample were run at the same time they would be run under the same conditions and the ratios should be independent of the operating fluctuations. This procedure requires the design and building of a new type of Raman spectrograph - one utilizing a double beam principle. If this can be accomplished and the results obtained are as predicted the analytical chemist would have a new reliable method of quantitative analysis.

This thesis is a summary of the work done and the results obtained in the construction of such an instrument.

Chapter I

The Raman Effect and Its Application to Analytical Chemistry

In an address to the South Indian Science Association at Bangalore in March of 1928, Sir C. V. Raman announced the results of investigations carried out by himself and his associates. The address, entitled "A New Radiation", told of a new type of secondary radiation which has come to be known as the Raman Effect in his honor and is considered to be an optical analogue of the Compton Effect.

While this discovery was not essentially new, it had been referred to or theoretically predicted in some manner by Smekal, Lallemand, Landsberg and Mandestam and was implied in the quantum theory of Kramers and Heisenberg, it remained for Raman and his co-workers to experimentally prove its presence. They had been working on this idea since 1920 and had noticed secondary scattering of wave lengths different from the source on several occasions. This scattering could not be traced to either impurities in the sample or to its fluorescence. It was not until they added a mercury vapor lamp source and a spectroscope to their apparatus that they came to realize the true nature and spectral character of this phenomenon.

Upon Raman's announcement of his findings the phenomenon became the subject of wide spread investigations in almost every country of the world and since that time over two thousand articles or books have been published on it. The effect is of interest and use to both the physicist and chemist and has been a contributing factor in the introduction of modern physics and physical methods into the field of chemistry. The subject has been treated theoretically both mathematically and mechanically, but it is with conclusions based on empirical observations that the chemist is chiefly interested. The effect is shown to some extent by all forms of matter be they liquid, solid or gas.

Theory and Origin of the Raman Effect:

When a beam of radiation is allowed to impinge on a mass of matter one or more of the following events can occur depending on the wave length (or frequency) of the radiation and the optical characteristics and physical shape of the mass. The radiation may be transmitted if the mass is transparent to those wave lengths; it may be reflected if the mass is a reflector; if the mass is a black body for these wave lengths they will be absorbed; the beam may be broken up into its component parts if the mass is of the proper shape and is transparent; or it may be scattered due to interaction and collision with the particles making up the mass. It is the latter event in which we are interested.

The scattering may assume one of three forms: Rayleigh scattering in which it may be scattered through all angles, due to collision with the particles, and emerge with its wave length unchanged; fluorescence in which it is absorbed by the particles and re-emitted with either the same or different wave lengths; or Raman scattering in which it interacts with the particles upon collision and is scattered with new wave lengths. These new wave lengths can be longer or shorter than that of the illuminating beam, depending on the energy of the mass particles. This wave length change is called the Raman shift and is characteristic of the mass matter and not of the radiation. The lines on a photographic plate caused by the longer wave length radiations are called Stokes lines and those of shorter wave length Anti-Stokes lines. In Raman work their wave length is usually recorded in wave numbers.

That this shift is a function of the matter, called the sample, and not of the incident radiation can be proven by a simple experiment. If a sample is placed in the path of a monochromatic beam of light of wave number $\tilde{\nu}_1$ and the light emerging from the sample at right angles to the incident beam is passed through a monochrometer and then photographed, there will be found a line of wave number $\tilde{\nu}_1 + \Delta \tilde{\nu}_1$ another at $\tilde{\nu}_1 + \Delta \tilde{\nu}_2$ etc. If now the wave number is changed to $\tilde{\nu}_2$ the lines on the photographic plate will be found at $\tilde{\nu}_2 + \Delta \tilde{\nu}_1'$; $\tilde{\nu}_2 + \Delta \tilde{\nu}_2'$ etc. but it is also found that $\Delta \tilde{\nu}_1 = \Delta \tilde{\nu}_1'$ and $\Delta \tilde{\nu}_2 = \Delta \tilde{\nu}_2'$. This could be continued with light of any other wave number and $\Delta \tilde{\nu}_1''$ would still equal $\Delta \tilde{\nu}_1$ and $\Delta \tilde{\nu}_2''$ would be equal to $\Delta \tilde{\nu}_2$. Thus no matter what the wave number of the incident light the shift would always be the same.

However, if now instead of varying the incident illumination we vary the sample we will find that the lines no longer appear at the same relative position and $\Delta \tilde{\nu}_1 \neq \Delta \tilde{\nu}_1' \neq \Delta \tilde{\nu}_1''$ etc. Every time the sample is varied a new series of $\Delta \tilde{\nu}$'s is found. These shifts could be negative as well as positive, as stated above, but would not be of the same intensity. The series of lines with higher wave numbers is weaker than the series with lower wave numbers than the incident beam.

It has been proven that the sample factor involved in these interactions is the vibrational and/or rotational energy of the atoms or atom groups making up the sample molecules. Thus, the last phenomenon mentioned above becomes obvious if we consider it in the light of this fact and the Boltzman energy distribution curve. From the latter it can be seen that there are many more molecules in the normal than in excited states. As the intensity of a line is in part dependent on the number of molecules involved in interactions with the incident radiation, the intensities of the two lines should vary directly as the number of molecules present in that energy state. Thus as there are more normal than hot molecules those lines produced by the normal molecules should be the most intense. That these are the lines with higher wave numbers is shown as follows:

The energy of the molecule before collision is represented by E_1 and that after collision by E_2 and the frequency of the incident radiation as ν_1 and that of the resultant radiation as ν_2. Assuming the corpuscular theory of radiation, the

Einstein equation and the law of the conservation of energy to hold:

$$E_1 + h\nu_1 = E_2 + h\nu_2$$

where h is Planck's constant. Collecting like terms on the same side of the equation:

$$E_1 - E_2 = h\nu_2 - h\nu_1 = h(\nu_2 - \nu_1)$$

$E_1 - E_2 = \Delta E$ the change in energy of the molecule due to the interaction and

$\nu_2 - \nu_1 = -\Delta\nu$ the change in frequency of the radiation due to the interaction. Substituting in the above equation:

$$\Delta E = -h\Delta\nu$$

ΔE can be positive or negative but is always the opposite of $\Delta\nu$, i.e., the molecule gains energy if the frequency of the radiation decreases or loses energy if the frequency increases. As molecules in the normal energy state can only gain energy the frequency must decrease for these molecules while it will increase when excited molecules lose energy.

As the frequency, wave length and wave number are all related as follows:

$$\lambda = \frac{c}{\nu} = \frac{1}{\tilde{\nu}}$$

it can be seen that the wave number will change in the same direction as the frequency. Therefore, what was said about the relationship of the gain or loss of energy by the molecule to the decrease or increase of the radiation frequency will also be true if wave number is used instead of frequency.

Another factor which should be mentioned is that Δ E and $\Delta \nu$ have finite values. Thus the energy gained or lost by the molecule must be in discrete quanta and the spectrum will be a line or band spectrum and not a continuum. That this is so can be seen by an examination of a spectrogram where the dispersed resultant radiation appears as a series of lines or bands and not a continuum.

Raman Spectra and Spectrograms:

As stated above, if the light emerging from the sample at right angles to the incident beam is passed through a monochrometer and photographed the developed plate will be a series of lines or bands. These lines are the Raman lines, the whole series is the Raman spectrum of the sample and the picture is a Raman spectrogram. An examination of a spectrogram will reveal the following features:

First, there will be seen in the center of the series of lines a line much more intense and broader than the others. It is the line due to Rayleigh scattering and has the same frequency as the incident radiation. Should the incident radiation be polychromatic there will be one Rayleigh line for each frequency in the incident radiation.

Second, there is a continuum attached to the sides of the Rayleigh line. It appears as winglike formations stretching out from both sides of the line and attached to it. The origin of these continua is unknown and they vary in size and intensity with the sample material. According to Bhagavantam it is possible to resolve them in gases but not in liquids or solids. He further states that in very impure or viscous liquids these continua may be broad and intense enough to completely mask the Raman lines.

Third, on either side of this central group are a series of lines or bands. These are the Raman lines. They are of weak intensity and may appear on the long wave length (low frequency or wave number) side of the Rayleigh line only. Under proper conditions it is possible to resolve them into multiplets.

Fourth, a feature of the Raman effect not shown by the spectrograms which should also be mentioned, although no use of it was made in this research, is the fact that the scattered radiation may be highly polarized. This polarization applies only to the Raman lines themselves and not to either the wing-like continua attached to the Rayleigh line or the Rayleigh line itself. The amount of polarization varies from compound to compound and a measure of it, called the "depolarization factor", is sometimes used as a method of qualitative analysis. While this factor is useful in many cases it will not be discussed here and has no bearing on the problem.

As was implied in a previous section each incident frequency is a potential source of its own series of Raman lines. Although the lines from all frequencies give the same series of Raman shifts, the various series may overlap and thus the lines belonging to any given series would be difficult to sort out. This complication makes necessary the use of monochromatic illumination except where the polychromaticity falls into one of the two following classes: 1. The source line may be so weak that no visible Raman lines result from it; and 2. The source lines are so widely separated that the Raman spectra do not overlap. Polychromatic illumination can usually be rendered sufficiently monochromatic by the use of filters.

Intensity of the Raman Lines:

According to Bhagavantam the Raman line intensities are only several hundredths that of the Rayleigh while the Rayleigh line intensity has the same relation to the incident radiation. Thus to get intense Raman lines demands the presence of a very intense source and an efficient spectrograph. The latter is necessary to keep light losses to a minimum as all light lost, either by reflection from the elements or by falling on dead spaces in the instrument, decreases the intensity of the spectrum. The reflected light losses may also help fog the spectrum by falling on the film as stray light.

The intensities in addition to being partially a function of the intensity of the source are also functions of the sample material and of the incident frequency. Experiment shows that the intensity varies inversely as a high power of the frequency. Thus the higher the source frequency the greater the intensity of the spectrum. It would seem that the intensities could always be increased by increasing the frequency of the source. There is a practical limit to this increase, however, due to the fact that above some frequency the radiation possesses sufficient energy to either decompose the sample or to cause it to fluoresce. This upper or limiting value varies from compound to compound but is usually some where in the ultraviolet.

As a result of this factor and of the types of illumination available the frequency usually chosen is the blue line of the mercury spectrum (wave length 4358 Å). However, should the samples be able to resist decomposition and not fluoresce a better source, and one frequently used in such cases, is the mercury vapor line at 2537 Å.

To a lesser extent the line intensities are also affected somewhat by temperature fluctuations. The higher the temperature the larger the number of excited molecules in the sample and the more intense the anti-Stokes(or higher wave number) lines and the less the intensity of the Stokes lines.

Applications:

The Raman effect is useful to chemists in all branches of chemistry. A partial list of its uses includes: The determination of the structure of a compound; proof of the reliability of the Boltzman energy distribution law; proof of the presence of two forms of hydrogen; to distinguish between isotopes; to follow the course of reactions; to some degree in explaining the specific heats of compounds, especially gases; in determining the effects of hydrolysis; and in qualitative and quantitative analysis. These latter two are of special interest to the analytical chemist.

As has been stated or implied several times in previous sections, each compound gives its own spectrum, which is different in some way from those of all other compounds. Thus it affords a rapid and simple method of qualitative analysis. A comparison of the sample spectrum with those of known pure compounds allows the trained spectroscopist to detect which compounds are present.

However, despite the fact that the spectrum for each compound is different there are certain similarities in the spectra of compounds falling in a given series. Take the carbonyls for example: If this group is present in an acid the line shifts so that it is about 1700 cm^{-1}; for an aldehyde it is about 1720 cm^{-1}; it is the same for an ester but changes to about 1770 cm^{-1} for an anhydride and to about 1710 cm^{-1} for a ketone. Thus it can be seen that a line due to $C=O$ in any of these compounds always shows up some where between 1700 and 1790 cm^{-1}. The following table taken from Page 277 of Brode's "Chemical Spectroscopy" gives further illustrations.

Table I

Group or Linkage		cm^{-1}
C-H	aliphatic	2800-2970
	aromatic	3054
C-C	aliphatic	800-1000
	aromatic	1580-1608
C=C		1600-1650
C=C		2100-2250
C-OH		820-880
C=O	acid	1700
	ketone	1710
	aldehyde	1720
	ester	1720
	anhydride	1770
OH		3400
S-H		2570
C-S		645
NO	nitrate	1640
	nitrite	1660
	nitro	1565
C=N		1650
C-N		2110
C-N	nitro	910-930
	amine	880
NO		1000-1080
C-Cl		650-710
C-Br		570-600
C-I		500-530

For quantitative analysis these spectrograms should furnish a rapid, reliable and accurate analytical method. In fact, the same spectrogram should furnish both a qualitative and quantitative analysis of the unknown sample. Quantitative analysis in this case is based on the fact that the spectrum intensity is a function of the quantity of the sought for compound present in the sample. The per cent of compound present can be computed from the ratio obtained by comparing the intensity of a line of the compound in the sample mixture spectrogram with the intensity of the same line when the sample is the pure compound. The accuracy of this method should exceed that of wet chemicalanalysis as it is shorter and involves fewer operations. It is best adapted to components of the sample present in fairly large quantities. A valuable feature of this method of analysis is that water solutions can be used as samples.

Chapter II

Spectrographs

Sir Isaac Newton laid the foundations of spectroscopy when, in 1704, he secured a prism "to try the phenomena of color". In the course of his experiments he assembled the first crude spectrograph by cutting a slit in a window shutter and placing the prism behind it. Using the sun as a source he observed that the white light entering the prism was sorted out and emerged as a series of colored bands. Later he improved the purity of the spectrum by placing a lens between the slit and the prism. Unfortunately he spoiled this excellent beginning by dabbling in speculation on color and its source and thereby delayed spectroscopic progress by over a century.

It was not until 1814 that any improvements were made in the spectroscope. In that year Fraunhofer started a detailed study on the solar spectrum and in the course of his experiments added a telescope to the instrument. The telescope was set up to observe the slit and in this way he found the spectrum to be crossed with "an almost countless number of strong and weak vertical lines". During further experiments and in attempting to improve the manufacture of optical instruments he observed the diffraction pattern of fine slits and was led to the discovery of the transmission grating.

In 1870 the dry gelatine photographic plate was developed and the visual observations of previous years were replaced by photographic recordings. This improvement led to greater accuracy in spectrum measurements. About the same time Rowland greatly improved gratings and also discovered the concave reflection grating.

The introduction of the above elements plus the collimating lens added by Babinet in 1839 gave us our modern spectrograph. Since then photographic recording has been replaced to a large degree by photoelectric recorders. Also, except for a few instruments used in making solar measurements, the sun has been replaced as the source of the light.

The spectrograph of today consists of a source, slit, collimating and camera lenses, dispersive element and recorder. If the recording system is replaced with an eye piece the instrument becomes a spectroscope. Also a condensing lens may be used in conjunction with the source.

Spectrographs can be divided into two general classifications - prism instruments and grating instruments. As it was decided to build a prism spectrograph (for reasons listed in Chapter III) only this type will be discussed here. As there are many treatises available on theoretical optics the following discussion will deal only with the types of elements used and the problems involved in a general manner.

Source and Condensing Lens System:

There are two general types of sources - the continuous variety and the discontinuous variety. The former shows an uninterrupted series of wave lengths with no perceptible division anywhere in the spectrum. The latter yields a spectrum of sharp lines or bands with dark spaces of varying width between them.

Continuous sources are illustrated by incandescent solids, high pressure discharges and certain gaseous discharges. These sources are used in absorption spectroscopy, as for example infra red where the source is a globar or Nernst glower.

Discontinuous sources are furnished by atoms and molecules in their vapor state. They are used in emission and scattering (Raman) spectroscopic work. Examples of such sources are vaporization of materials in flames, arcs and sparks and in electric discharge tubes.

The illuminating radiation in Raman spectroscopy is usually provided by one or more mercury vapor arcs placed around the sample tube. As a powerful source is needed the light from the lamps is usually concentrated in the sample tube by elliptical reflectors and liquid lenses. The reflectors are so placed that the lamp is at one focus of the elipse and the sample tube at the other. The liquid lenses serve as both condensing lenses and light filters and are usually cylinderical. It is also possible to use a helix lamp with the tube, surrounded along its entire length by the light filter, in its center.

The illuminating system is always so set up that the sample tube is illuminated at right angles to the direction of the light beam entering the spectrograph slit. This reduces the amount of source illumination entering the monochrometer to a minimum.

Condensing lenses are used to focus the Raman rays at some point in the spectrograph if the source itself is of insufficient extent or is otherwise incapable of providing maximum illumination. It must be remembered, however, that they cannot provide an image of greater brightness than the source.

In sources of negligible depth this maximum is attained when the collimating lens is filled with light. If the source is of sufficient size to do this and is uniform, a condensing lens is of no value. It can, however, increase the spectrum intensity if the source is too small or correct its nonuniformity.

In sources of finite depth, such as Raman tubes, a condensing lens will probably be necessary. This problem has been treated by J. R. Nielsen from the viewpoint of geometric optics. His treatise (see bibliography) deals primarily with the type of system used in Raman work and was used to determine the final position of the condensing lens in the new spectrograph. In it he provides proof of the correct lens position and means for calculating it.

The Slit:

The slit is a narrow rectangular opening which admits light to the monochrometer. In photoelectric recording instruments a slit is also placed between the monochrometer and the recorder. The lines on the spectrogram are images of the slit, consequently its design and construction is of utmost importance to the success of the instrument.

The slit can be fixed in length and width or adjustable continuously in width and step wise in length. Fixed slits are either rectangles cut through metal plates or cut into metal films on glass or quartz slides. Several of these slits of various widths may be cut into one plate thus giving some degree of slit width adjustment by changing the position of the plate or slide.

The adjustable type of slit is preferable to the fixed type as they can be continuously adjusted for best results. The adjustment can be made by separating or closing jams with a micrometer screw or one jaw can be fixed with the second one adjustable. The latter are known as unilateral and the former as bilateral slits. The bilateral type is preferable since they leave the centers of the spectral lines fixed in one position.

A third type of slit system combines some of the features of both of the above types. In it the two jaws (usually razor blades) can be clamped into a fixed position or they can be loosened and adjusted to any desired width. This method is tedious and may lead to inaccurate slit width setting and/or nonparallel jaws. It is the least expensive of the three and when used with a little care is usually satisfactory.

No matter which system is used the slit jaws should have sharp, straight edges and be adjusted parallel. If these conditions are not met broad, fuzzy spectral lines may result.

Collimating and Focusing Elements:

The function of the collimating lens is to render parallel the diverging beam of light between the slit and the prism. Thus the light reaching the prism has the appearance of coming from a source at an infinite distance. If the lens functions ideally and the light beam reaching the prism is strictly parallel, each point of the slit will be imaged as a point in the spectral line as the prism introduces no astigmatism under ideal conditions. This is a limit to be approached rather than an actual possibility as no lens will render the light strictly parallel. The degree to which this limit is reached depends on the degree to which the design and material composition of the lens correct for the three main image defects - chromatic aberration, spherical aberration and coma.

Chromatic aberration is the focusing of the different wave lengths passing through the lens at different rather than the same point. Therefore, the components of polychromatic light will not be rendered parallel; some will be slightly divergent, some slightly convergent and one parallel. As this defect is caused by a lens material having different refractive indices for different wave lengths and these refractive indices change for different lens materials,this defect can be partially corrected by replacing the single lens with a compound one. This compound lens, called an achromat if corrected for two wave lengths and an apochromat if corrected for three wave lengths, is made by cementing together positive and negative lenses of different lens materials. Even after these corrections, the remaining wave lengths will still not be rendered parallel but their variance will be smaller than for the uncorrected lens. This correction is simple in the visible region where glass can be used but is much more difficult in the other regions due to lack of large quantities of transparent materials.

Spherical aberration is due to the failure of the lens to bring to the same focus light which passes through it at different distances from the center. Thus a point from a distant source is focused as a blur circle on a screen placed at the best focus. This can be corrected by changing the design of the lens from simply spherical so that the light passing through all zones will be rendered parallel. This can be done with both compound and simple lenses. Such a lens is an aspherical lens.

Coma is caused by the failure of the lens to form sharp images of off axis objects resulting in blurred images. Fortunately, a lens of one type of curvature completely reverses the coma caused by a lens of the opposite type of curvature, so if the curvature of the second surface is the reverse of the first surface the effects of coma will cancel. This correction can be made on either simple or compound lenses. Thus one compound lens can be made to correct, or nearly so, for all three defects.

The camera lens focuses the dispersed rays as slit images on the recorder - either the film or the exit slit if photoelectric recording is used. This lens introduces several new image defects; astigmatism, image curvature and optical flare.

Astigmatism results in the horizontal and vertical components of the line being focused at different distances from the lens. It is due to rays passing through the lens at large oblique angles and is found in lenses corrected for spherical aberration and coma. Image curvature is caused in part by astigmatism but is still present when the astigmatism is removed.

Optical flare is due to scattered light reaching the film. It is caused by light which is reflected several times from the optical surfaces and can never be completely eliminated. This causes fogging and is especially bad when long time exposures must be made. It can be minimized by proper lens surface design elimination of air spaces between the elements of compound lenses and by baffles.

The ideal camera lens should be corrected for spherical and chromatic aberration, astigmatism, coma and field curvature. This is impossible so the best compromise must be selected. Fortunately, chromatic aberration and astigmatism cause the same effect but in opposite directions and thus can be made to cancel each other. Field curvature can be taken care of by tilting and/or curving the film. Spherical aberration and coma as well as optical flare must be reduced to the absolute minimum by proper design.

These lenses can be replaced in a spectrograph by parabolic mirrors with great advantage in many cases. This is especially true in the extreme infra red and ultraviolet for which no transparent optical material exists. Mirrors are usually cheaper than lenses especially in the larger diameters. To be effective the mirrors must be properly designed and are first surface.

Since all wave lengths are reflected alike by a mirror, chromatic aberration is eliminated. The same is true for spherical aberration if the mirror is an off center section of a parabola. Unfortunately, astigmatism, coma and field curvature are unavoidable although their effects can be reduced by forming the images on the side of the axis opposite from the slit. Pfund reduced astigmatism by placing a plane mirror, with a hole in its center, directly behind the slit thereby allowing the parabolic mirror to be used on its axis.

The number of elements can be further reduced by use of a Littrow system. Here a plane mirror placed directly behind the prism reflects the beam back along the same path. Thus the collimating and camera lenses become one element and decrease the cost of the optics by about half and the space required for the instrument by nearly half. The same saving also applies to the prism or the same prism as used in a straight spectrograph will double the dispersion.

This system gives good dispersion with moderate illumination but subjects the recorder to more reflected light. It is especially useful if the optics are made of quartz. Quartz is found in two crystal modifications known as right handed and left handed. The two types must be used as compound lenses and prisms in the regular spectrograph arrangement to eliminate polarization defects. In the Littrow system where the beam is returned through the same optics this compounding may be eliminated.

Prisms:

The prism breaks up a beam of polychromatic light passing through it into its component wave lengths. This sorting out process is possible because the refractive index of transparent materials varies with wave length; thus the various wave lengths are deviated from their original path in varying degrees.

As the light from the collimating lens is never strictly parallel the prism introduces the image defect known as astigmatism. This defect results in a point on the slit being imaged as two perpendicular lines at different distances from the optical system. As the spectrograms are line images this defect can readily be tolerated in spectrograph. It can be shown, however, that the astigmatism is at a minimum under the following conditions:

1. The prism is traversed by parallel light.
2. The slit and prism edge are parallel.
3. The light beam is parallel to a prism section perpendicular to a prism edge.

4. The rays traverse the prism at minimum deviation (i.e., equal refraction at each face).

In discussing prisms two points are of utmost importance. The first of these is its dispersion which tells how great a separation of the wave lengths can be obtained, the second is its resolving power which is a measure of the differentiation of two adjacent lines on the spectrogram.

The dispersion is stated in two ways – $d\theta/d\lambda$ the angular dispersion measured in radions per angstrom or $dx/d\lambda$ the linear dispersion measured in mm. per angstrom. The latter is dependent on the focal length of the instrument optics as well as on the prism. The two are related by the formula

$$dx/d\lambda = F\, d\theta/d\lambda$$

where F is the focal length.

The theoretical angular dispersion at minimum deviation can be calculated by

$$d\theta/d\lambda = \frac{2 \sin \alpha/2}{\sqrt{1 - n^2 \sin^2 \alpha/2}} \cdot \frac{C}{(\lambda - \lambda_0)^2}$$

where α is the dispersing angle of the prism, n the refractive index at the wave length under consideration and c and λ_0 are constants. These constants are evaluated by means of the Hartmann interpolation formula

$$\lambda = \lambda_0 + \frac{C}{n - n_0}$$

If several prisms are used the total dispersion is the algebraic sum of all of them. A good spectrograph will usually attain the theoretical dispersion.

The theoretical resolving power (R) can be calculated by the formula

$$R = t\, dn/d\lambda$$

where t is the effective thickness of the prism base and $dn/d\lambda$ the rate of change of refractive index to wave length. It is the differentiated form of the Hartmann formula. This theoretical resolving power is approached only in the best of instruments and may vary from several hundred to a million. In actuality the resolving power is a function of slit width, the relative intensities of the two adjacent lines, the mode of slit illumination, the perfection and adjustment of the optics and the characteristics of the film as well as of the dispersion and base of the prism.

Prisms are made of various materials depending on their intended use. These materials should be transparent over a wide wave length range, be isotropic, be available in large optically perfect pieces, have surfaces capable of taking a good optical polish, be resistant to corrosion by components of the laboratory atmosphere, have a large angular dispersion and have a small temperature coefficient of refractive index. As no such material exists the best one available must be selected for each purpose. This selection varies in difficulty from the visible region with its large variety of optical glasses to the far ultraviolet where all materials absorb. Prisms are also made by sealing liquids between transparent plates.

Prism systems of various types are to be found. These vary from a single prism to several prisms used in a train. They also can be made by cementing various size prisms together to get a special size or shape. The refracting angle is usually either 30 or 60 degrees.

Recorders:

Until recently all recorders used photographic plates or films. Here the photographic plate is placed at the focal point of the camera lens or mirror. One plate may record the entire spectrum in small instruments while several may be needed for this purpose in large ones. This type of recorder is the only one that can be used in spectrographs giving spectra of very low intensity or those where the spectrum intensity varies with time such as arc or spark spectra.

In using this type of recorder the proper choice of plate as to speed, contrast and grain size must be made. This last factor is especially important when the plates or films must be microphotometered. Where the spectra are very strong this method is quite rapid for qualitative work but has the disadvantage of having to be microphotometered for quantitative work.

The other type of recorder is the photoelectric type where a current is set up in a photoelectric tube or cell or a balometer or thermopile. This current is then amplified and used to drive the pen of a strip chart recorder. The strip chart gives a record of where the spectral lines show up as well as of their intensity. This type is generally preferred to the photographic type whenever it can be used. In some cases it is the only method usable.

Chapter III

Design and Construction of a New Type Raman Spectrograph

In the building of a new instrument there are two factors which must be taken into consideration before its design and construction can be started: First, for what purpose, how and where is the instrument to be used; and, second, what materials or money for them and space are available for its construction. As stated in an earlier chapter of the thesis, the spectrograph is to be used in an analytical spectroscopy laboratory for quantitative analysis and is to utilize a double beam principle so that the spectrogram of a sample can be compared with that of a standard; both being taken at the same time under the same conditions. Thus it must be able to handle and record the spectra of two samples at the same time.

The second of these factors can be subdivided into several parts and each applied to the various sections of the spectrograph, i.e., source, condensing system, monochrometer and recorder. The first section to be considered is the source as the materials for the remainder of the sections are based upon the type of radiation used here. The usual Raman spectroscopy source is one or more mercury vapor arcs as radiation from them can readily be made to meet the requirements of monochromatic illumination. There are three common types of these lamps available - the H type manufactured by the General Electric Company and the helix and Alpine Burner types made by the Hanovia Chemical and Manufacturing Company. The H lamps were considered unsatisfactory for our purposes and of the other two the Hanovia helix lamp was originally chosen. This is a low pressure lamp emitting 90+% of its radiation at 2537 Å. This wave length is well suited for Raman work, provided the sample materials are capable of standing up under it, as it produces lines of higher intensity per unit of its own intensity than does any other feasible wave length. Also in a prism instrument the shorter the wave length the greater is the resultant linear dispersion.

Unfortunately, it was later found that many of the samples for which it was hoped to use this spectrograph tended to either fluoresce or decompose when illuminated by this wave length so it was abandoned in favor of illumination of 4358 Å. This line is quite strong in the Alpine burner type lamp so it was decided to utilize four 400 watt lamps of this type. As a result of this change the optical parts of the instrument could be made of glass instead of quartz as would have been the case had the 2537 Å been used. The sample tubes, however, had been purchased prior to this change and are made of quartz in the standard design.

These lamps emit all mercury lines from the ultraviolet to the infra red inclusive and provision must be made in the unit for filtering the radiation. This can easily be accomplished by the use of a saturated solution of sodium nitrite which absorbs everything below 4358 Å. Above 4358 Å the mercury spectrum has a void for a region large enough to permit photographing the Raman spectrum with no complications so that it is not necessary to use a second filter here.

The condensing system offered a choice between lenses and mirrors. Due to available space and flexibility considerations lenses were selected. These could be either cylindrical or spherical and both were tried in various focal lengths and diameters.

Space requirements were also a factor in deciding to make the spectrograph of the Littrow type. This reduced the over all length of the instrument by about 1/3. Also, had the 2537 Å illumination been used a Littrow system would have obviated the necessity of using a compound quartz prism.

In selecting the optics a big factor to be considered is cost and delivery time. In this connection it was decided to build a prism rather than a grating instrument as prisms are less expensive and more readily available than gratings. Prisms are also more conservative of light and easier to construct. These advantages were believed to outweigh those of a grating, i.e., linear dispersion over all wave lengths as well as a larger dispersion and resolution.

For the collimating and focusing element of the monochrometer, a parabolic first surface mirror was chosen as superior to a lens.

This type of mirror eliminates chromatic and spherical aberrations which would prove troublesome in a lens. Also, it was believed that as neither a mirror nor lens of the desired focal length and diameter were available it would be easier and less expensive to make a mirror in the laboratory than to try and obtain a compound lens. Construction of the latter was beyond the capabilities of the laboratory. The mirror reflecting surface was to be made of aluminum. All other mirrors to be used in the instrument were to be first surface rhodium plated flats.

The type of slit to be used was not decided upon at this time. It was considered highly desirable to obtain a bilateral slit but as these are expensive items, a search was to be made for a substitute.

The choice of a recorder was also delayed until a later date. Of the two possibilities, most Raman spectrographs in use at this time used the photographic method. Recently, however, newer instruments are appearing making use of photoelectronic recording. The latter require a spectrum of greater intensity than the former, are more complex and more expensive. While the photoelectronic is the more desirable, if it can be used, no decision could be reached until the intensity of the resultant spectra was known. However, the instrument was to be designed and built so that either system could be used without extensive reconstruction.

The instrument was to be installed and used on an 18' x 2' laboratory bench one end of which was occupied by a hood. This latter was a convenient place to install the source unit. This is necessary so that the operator can evacuate any vapors given off by the samples as well as the large amounts of ozone generated by the source lamps during operation. As finally built the spectrograph occupied the entire width and, together with its accessories, about 4/5 of the length of the allotted space. Water and electrical outlets were easily available for cooling purposes and to furnish power for pump and blower motors. Power to operate the lamps was obtained by installing a breaker box containing four 15 A breakers on the wall next to the hood.

Design:

After deciding on the type of instrument to be built and on the types of elements it was to contain, a rough design for it was laid out. The design included a source unit, a condensing lens system and a monochrometer (the recorder was not included at this time). From calculations based on using 2537 Å illumination, quartz optics and the desired focal length, it appeared that the parabolic mirror focal length should be about six feet. This focal length was not changed when the source was later changed to 4358 Å. After the mirror was made, the above design was altered to accommodate it and the changes made necessary by the switch in illuminating wave length.

The source unit and housing were designed and drawn to scale. The drawings were sent to the Chemical Engineering Department Machine Shop for construction of the unit. The original design and construction of the unit was based on using the helix lamp and had to be modified later, to accommodate the Alpine Burner.

A prism - 60° refracting angle and 7 cm. edge - was obtained and a mount designed for it that will allow the prism to be rotated about any or all of three mutually perpendicular axes. The design utilized a war surplus astro compass as the rotating mechanism, and included a base for the Littrow mirror mount.

The monochrometer was set up on a bread board and using a razor blade slit and a bull's eye lamp as a source, tested. From these tests designs for the monochrometer base and housing were made and drawn to scale. The drawings were sent to the Bethlehem Steel Corporation Research Department Machine Shop for construction of the unit. A drawing for construction of the source unit housing base was sent to them at the same time.

Mounts for the parabolic, Littrow and Pfund mirrors and for the condenser lenses were next designed. This was done with the idea of building them in the laboratory, and making use of the Chemical Engineering Machine Shop for machine work. Also plans were made for obtaining and adding to the instrument parts for the circulating and cooling system for the light filter, a cooling system for the source unit and a power supply for the lamps.

In the process of building and adjusting the spectrograph for best results some of the original design was modified. The design of the instrument as it was finally set up and operated is described below. Drawings of the instrument and some of its component parts and all required calculations appear in the appendix. The description is based on the drawings and the parts referred to are shown by letters in the drawings. Those parts which were bought as a unit or which can be described in a few words are not shown in separate drawings, but only described. None of these drawings are exactly to scale.

Figure 1 shows the spectrometer in plan and elevation and the optical system (top). In the optical system the sample tubes "A" are illuminated by lamps "B" (shown in the plan only) and send light through condenser lenses "C" and slit "D" to the collimator (the parabolic mirror) "E". The parallel light beam is sent to prism "F" where it is dispersed and then impinges on Littrow mirror "G". Here it is reversed and returned via the prism to the parabolic mirror. The mirror now acts as the camera mirror and focuses the beam on camera "H".

In the spectrograph the source unit housing at "I" contains in addition to the source unit "J", lead ins "K" which conduct the power for the lamps into the housing. Not shown are the filter circulating and cooling system, the lamp transformers, the blower used to cool the source unit and housing and the sample cooling system. These are located either in the hood or in the cabinet under the hood. The source unit and its housing are shown in detail in Figure 2. At "L" is the external beam separator plate, used to keep the upper and lower beams from interfering with each other. It is 5" wide and 44" long and runs from the source housing to the slit. "M" are legs supporting the plate and a superstructure which serves to hold a cloth cover over the source housing to slit area. The condenser lenses are again shown at "E". "N" is the source housing base, consisting of a 12" x 21" x 1/4" steel plate welded to two 21" lengths of 4" channel.

"O" is the monochrometer base and housing. The base was made by welding 1/4" steel plate to appropriate lengths of 4" channel. It is 93" long, 24" wide from the slit end to a point 48" from this end. The other 45" length (i.e., the mirror end) is 12" wide. The housing is made of 1/16" steel sheet. It is welded to the base along the back wall and the two left-hand ends; the front walls and right hand (slit) end are bolted to the base and the other parts of the housing. All bolted joints overlap 1 1/2" as does the cover. The cover is also equipped with a light gate on the inside to insure a light tight seal between it and the sides. The walls rise 15" above the top of the base. The monochrometer contains the parabolic mirror "E", the prism "F", the Littrow mirror "G" and a light baffle "P". On the right-hand end are located the camera "H" and the slit "D".

The center of the parabolic mirror is 8" above the base and 6" from the rear wall. The mirror is 75" from the slit. The centers of the prism, slit and Littrow are 6" above the base. The slit and camera centers are 6" from the rear wall while the prism center is 11" away. The distance between the prism center and the Littrow mirror is 2 7/8" and between the prism center and the end plate is 5 7/8". The baffle is placed 9 1/2" from the slit end.

Figure 2 shows the elevation and rear view of the source unit housing. It is an aluminum box 16" high, 9" wide and 10 1/2" long. At "A" are located the 8 power lead ins; between the two sets are two 1 3/8" diameter holes to permit exhaustion of the hot air, ozone and sample vapors; at "C" are the holes through which a furnace door blower "B" forces cool air into the box; and at "D" are the 8 porcelain connectors which are connected to the lead ins with #14 wire. The back of the box has a 6" square cut out with center 4 1/2" from the side and 6" from the floor and four holes for 1/4" bolts drilled to match those in the end plates of the source unit. It is attached to the box by #6-32 screws which fasten into a 1/4" keystock frame riveted to the rear of the box. The top and bottom are riveted to the sides and front. The front has a 4" diameter cut out with center 4 1/2" from the sides and 6" from the floor, four 1/4" holes and four 1/2" holes drilled to match those in the end plate of the source unit. The box is bolted to a stand of 1" angle iron (not shown).

The source unit, Figure 3, consists of two 1/4" x 8 1/2" aluminum end plates "A" held together by 8 threaded 1/4" steel rods "B". The distance between the plates is 9". The rods pass through holes drilled at equal distances from each other close to the periphery of the plates. Four of these rods are also used to hold the unit in place in the housing. An aluminum cylindrical reflector "C" fits snugly inside the rods and is separated from the front plate by a distance of 1" and from the rear plate by 1 1/2". The four lamps "D" are bolted to the reflector and fit into 3/4" holes drilled into the end plates so that the lamp ends fit into them easily and loosely. The light filter "E" consists of two concentric glass tubes (75 mm. and 100 mm. diameters) which end in grooves of 2 3/4" i.d., 4" o.d. and 1/8" deep cut into the end plates. Rubber gaskets in these grooves form liquid tight seals with the glass tubes. A hole was drilled and tapped for 1/4" pipe thread in the top center of the groove of the front plate and fitted with a brass elbow to serve as an outlet connection between the filter and reservoir. A hole similarly drilled, tapped and fitted in the bottom center of the groove in the rear plate serves as the inlet. An aluminum plate "F" of the same width as the Raman tubes serves as an internal beam separator and extends the entire length of the unit. Holes "G" to hold the sample tubes are bored on the vertical axis of both end plates. They are of a diameter a little larger than that of the sample tubes and their centers are 3/4" above and below the centers of the plates. Those in the front plate are bored only one-half the distance through the plate with slightly smaller diameter holes bored through the second half. This gives a shelf or stop against which the tube can be pushed.

The parabolic mirror mount is shown in Figure 4. The mirror "A" is fastened to a 1/8" x 8" x 9" steel plate "B" with aluminum brackets "C". This plate is connected to a 9" x 10" x 1/4" steel plate "D" by a spring inside of a 1 1/2" length of brass tubing "E"; this coupling permits the mirror to be rotated about its vertical and horizontal axes. The mirror can be focused by screws "F" which are threaded through plate "D" and end in depressions in plate "B". A plate "G" prevents the mirror from rotating around the axis running through the mirror to slit. Plate "D" is bolted to two 14" lengths of 1 1/2" angle iron "H" which are slotted to permit raising or lowering the mirror to any desired position. These supports are bolted to two 12" lengths of 1 1/2" angle iron "I" which are bolted to the monochrometer floor. They are also slotted to permit moving the mirror closer or further away from the slit. This is accomplished by screw "J" one end of which is fastened to a bar bolted to "G". "J" is threaded through support "K" which is bolted to the monochrometer floor.

Figure 5 shows the slit holder. It consists of an outer ring "A" and an inner disk "B". The outer periphery of one face of "A" is cut away to give groove "C" while groove "D" is cut on the inner periphery of the other face. "A" has an o.d. of 4" and an i.d. of 2 1/2"; "B" has a diameter of 3"; "C" is 1/16" deep and has an i.d. of 2 3/4"; and "D" is 7/16" deep and has an o.d. of 3". "B" has a groove "E" cut away from the outer periphery of one face. "E" has an i.d. of 2 3/4" and varies in depth from 1/8" on the outside to 1/4" on the inside. "B" is held in place in "A" by three set screws "F". A 1 1/4" x 1/8" slot is cut in the center of "B". Two razor blades are bolted to "B" with #3 screws "G". The centers of the holes for these screws are 3/8" from the vertical and horizontal axes of the disk. Both "A" and "B" are made of stainless steel. The upper section shows "B" with razor blades bolted into place.

The prism is held on a triangular base by a "C" clamp which utilizes the base as one of its arms. A screw in the other arm bears on the top of the prism and holds it securely in place. This base is bolted to the top of an astro compass. The legs of the compass were removed and it was fastened to a 6" x 6" x 1/8" steel plate in such a manner that one side of it can be raised or lowered. A 1/2" x 2" x 8" steel bar is bolted to one side of this plate to serve as part of the base of the Littrow mirror mount.

The Littrow mirror is held in an aluminum frame which is fastened to a steel disk so that the mirror is perpendicular to the disk. A shaft of 1/4" drill rod connects the disk to a worm gear and ends in a thrust bearing in the bar fastened to the prism mount. This bar forms the bottom arm of a "C" clamp the top arm of which lies between the disk and worm gear. A thrust bearing in this arm holds the shaft in position so that the mirror face is parallel to a plane passing perpendicularly through the center of the prism. The worm gear can be locked in place for photographic recording or rotated to enable the scanning of the spectrum for photoelectronic recording. The mirror itself is a first surface rhodium plated 4" square.

The camera is a regular cut film holder capable of holding two 4" x 5" films. It is held in place by a wooden frame mounted on the monochrometer end plate above the slit holder. The frame is similar to those holding the plate holders in commercial cameras.

The baffle in the monochrometer is a steel plate with a 1" x 2" cut out in front of the slit; a 2 5/8" x 3 1/8" cut out in front of the prism and a 5 1/4" x 1 3/4" cut out which allows light from the parabolic mirror to reach the camera.

Construction:

After the rough design had been made construction of the various elements was begun. The first of these was the source unit and its housing. As stated above they were made in the Chemical Engineering Machine Shop. After they were built the source unit was assembled using the helix lamp but no filter unit. (As this lamp emitted essentially monochromatic light no filter was necessary.) In this unit the end plates were made of steel and had a diameter of only 8". After the illuminating wave length was changed the end plates were remade, this time as described above. The new end plates were made by the Bethlehem Steel Corporation Shop. The new lamps and the filter were installed in the unit, and it was fitted into the housing which had been altered to fit the larger unit and new lamps. The blower had previously been installed on the rear wall of the housing.

The next element to be constructed was the parabolic mirror. Glass blanks, 8" x 1 1/4", were purchased from the Pittsburgh Plate Glass Company and ground, polished, and figured according to instructions given in "Amateur Telescope Making" by Albert Ingalls. The progress of the grinding was checked with a spherometer and of the polishing and figuring process by the Focoult Shadow test. After it had been polished and figured to the desired form it was aluminized in a high vacuum metal evaporating rig. This coating was unsatisfactory and was replaced. A layer of chromium was added as an undercoating before the mirror was realuminized. When it was finished the mirror had a focal length of 75".

The prism was taken to the Physics Department where its refractive indices were determined for several wave lengths on a spectrometer table. The results were as follows:

n	λ in Å
1.56779	4078
1.56468	4358
1.55668	5461

The prism mounting and base for the Littrow mirror holder were made in the Chemical Engineering Shop. The mirror holder itself was made in the laboratory.

The parabolic mirror and the prism plus a temporary slit and Pfund mirror were set up as a bread board monochrometer and tried out. Originally it was hoped to eliminate the Littrow mirror by aluminizing one face of the prism. This was found to be unworkable and the Littrow mirror was restored. While the monochrometer base and housing were being built, from designs based on the results of these experiments, the parabolic mirror mount, Pfund mirror mount and condenser lens holder were built here in the laboratory.

When all parts had been built and delivered the monochrometer was assembled on a temporary basis and tested. These tests indicated the need for several changes. First, the line images were fuzzy due to excessive vibration in the parabolic mirror mount. It was redesigned and rebuilt in its present form eliminating this difficulty. Next it was found that the Pfund mirror was unnecessary and was eliminated. The prism position was changed to one close to the slit. These changes helped eliminate a lot of stray light and simplified focusing the monochrometer. The stray light was reduced further by the addition of the baffle.

During the assembly of the spectrograph the various auxiliary elements, such as the filter circulating and cooling system, mentioned previously were added. The filter system as originally built used copper tubing for the connections and a steel can for the reservoir. These were changed to glass for reasons given in the following chapter.

The final spectrograph is shown in Figure 1 of the Appendix. Its design was settled only after completion of much of the experimental work described in the next chapter.

Chapter IV

Experimental Results and Conclusions

After assembly of the spectrograph and its accessories had been completed, experimental work to prove that it would perform as desired was begun. During the course of these experiments several changes in its design and construction were made - especially in the condensing lens and light filter systems.

The instrument was adjusted to give the desired spectra on the recorder and test runs made. When the adjustments and/or changes gave usable spectrograms several compounds were run as samples to see if constant ratios were obtainable. When this was shown to be true a known sample was run. The results of all these runs are given in a later section of this chapter.

Experimental:

Before starting any experimental runs a check on the light tightness of the monochrometer was made. The slit was sealed, the outside of the monochrometer housing illuminated and a film was exposed in the camera for three hours. This and several subsequent tests showed that there was no light leak into the monochrometer.

The optical system was aligned using light from a small mercury vapor lamp placed in back of the source unit housing as a source. All light reaching the optics had to travel the same paths as those later traversed by the light from the sample tubes. This focusing produced two mercury spectra on a card held in front of the camera. The spectra were well separated and one was directly above the other. Each could be extinguished separately by blocking off one or the other of the sample radiation outlets in the source unit. This showed that each sample tube should image its spectrum in the desired position.

The sample tubes were filled, put into their proper places, and illuminated, and the resultant spectra photographed. The developed film showed two spectra but the intensities were so weak that only the mercury spectra (from Rayleigh scattering) appeared. Slight adjustments in the focus of the instrument failed to change the results as did going to longer exposure times. A 16" cylindrical condensing lens was being used at this time. It was changed to one with 20" focal length with no better results. Subsequently other focal length lenses were introduced either singly or in combination and with appropriate source to slit distance changes but none gave as good results. The slit width was changed, during the above experiments, from 100 μ to 400 μ.

Various exposure times had been used with each change in the condensing lens. Comparison between the different lengths of exposure for the same lens and between those of the same length of time for different lenses showed that the Rayleigh scattering intensity was decreasing with each exposure. The source unit was overhauled and it was found that the outer filter tube was covered with such a heavy layer of dirt that the intensity of the sample illumination was cut about 75 per cent. The filter solution, a saturated solution of sodium nitrite plus 1 part in 50000 of a rhodamine dye, was suspected as the source of the dirt film; the dye having plated out under the influence of the ultraviolet radiation.

The filter was cleaned and reassembled and the experimental runs continued. This time the filter solution did not contain the dye but again deposited dirt on the tube. It was finally determined that the deposit was copper and iron leached from the solution lines and reservoir. As a result the copper tubing was replaced with glass tubing and the reservoir can with a pyrex battery jar. These changes plus the addition of an air trap to the solution lines eliminated these troubles.

The experimental runs were again continued and now produced films with two spectra containing weak Raman lines. However, with increasing focal length of the condensing lens the spectra, while becoming more intense, began to overlap. With complete overlap the Raman line intensities were still too weak to use. As a result it was decided to completely revamp the condensing lens system.

The idea of using a cylindrical condensing lens or lenses was abandoned and spherical lenses were substituted. Also the lens system was designed to conform to the ideas advanced by

J. R. Nielsen in his article in the Journal of the American Optical Society, Volume 20, 1930, Page 701, entitled, "The Filling of a Spectrograph with Light Considered as a Geometrical Radiation Problem". It discussed the best location for a condensing lens as well as the optimum slit to lens distance for maximum intensity of Raman spectra. This places the lens so that its focal point is the rear section of the Raman tube and it is z inches from the slit. z is calculated by

$$z = \frac{h + s}{h} f$$

where 2h is the source height, 2s is the slit height and f is the focal length of the lens.

Lenses of 9 1/2" and 12" focal length were tried. While two spectra with Raman lines in each appeared on the films the intensities were still very weak. These spectra were well separated as the external separator plate mentioned in the previous chapter had been installed and effectively prevented interference of the two beams with each other.

The intensity of the Raman lines was finally increased to a usable level by inserting two 20" focal length lenses, one for each tube, in the system. This reduced the illuminated area in the monochrometer and concentrated the light where it would do the most good. Films made with this system were tested on the densitometer and found to have readable intensities. The exposure time needed was approximately three hours.

When this stage was reached the specteograph was adjusted to give the greatest spectral line intensity, the cleanest lines free of scattered light and the best focus. Test runs on several compounds were made.

Data and Results:

To prove that the spectrograph would give the desired constant intensity ratio between the chosen lines, various compounds were run as samples vs. carbon tetrachloride as a standard. These runs were - four with benzene, two with cyclohexane, three with toluene and two with n-heptane.

In making these runs no attempt was made to use rigidly standardized conditions. Exposure times were kept with in only ± 15 minutes. The films used came from two different batches of Eastman Kodak Super Panchro Press Type B. The power to the lamps was not regulated in any way and experience with the building power supply shows that it is quite variable. One of the benzene vs. carbon tetrachloride runs was made with the sample (benzene) in lower and the standard in the upper tube; in the other three runs this was reversed. Before making the third toluene run one of the mercury lamps burned out so this run was made using only three lamps in the source unit.

In addition to these test runs another run was made using carbon tetrachloride in both tubes to test the intensity balance of both beams. Another run having both tubes filled with carbon tetrachloride was made to secure a film with sufficiently sharp and narrow Rayleigh lines to get accurate measurements of the line to line distances. From these distances were calculated the constants in the Hartmann interpolation formula which was then used to calculate the wave length of the spectral lines. The distances were measured with a General Electric Company slide rule.

Using the formula

$$\lambda = \lambda_0 + \frac{c}{d_0 - d}$$

and the lines 4358.4 Å; 4916.0 Å; and 5460.7 Å appearing at points 18.565 cm.; 21.340 cm.; and 23.260 cm. respectively, the values of the constants were calculated to be:

$c = 43072$

$\lambda_0 = 1682.1$ Å

$d_0 = 16.094$ cm.

In calculating the wave lengths of the Raman lines d_0 was replaced with $\bar{d}_0$ where

$$\bar{d}_0 = d_0 + d_1 = 34.659 \text{ cm.}$$

The wave lengths calculated were then converted to wave numbers. Subtraction of the wave number of the 4358.4 Å line gave the wave number of the Raman shift.

As a final check on the instrument a run was made using a sample of 50 per cent benzene in carbon tetrachloride. Again only three lamps in the source were working so the exposure time was increased to compensate for the decreased intensity as well as for the decrease in the number of sample molecules present.

All films were evaluated for line density on a General Electric Company photometer. The ratios of the intensities of the chosen lines vs. carbon tetrachloride were calculated using the carbon tetrachloride line intensity as 1.

The results of these runs, the exposure times and the $\Delta\tilde{\nu}$ of the lines used are given in Table II.

Table II

	CCl_4		Sample			Exposure time
$\Delta\tilde{\nu}$	I	Compound	$\Delta\tilde{\nu}$	I	Ratio	in hr. ± 15 min.
465	223	C_6H_6	998	260	1.18	3
465	225	C_6H_6	998	262	1.16	3
465	171	C_6H_6	998	204	1.19	3
465	206	C_6H_6	998	246	1.19	3
465	233	C_6H_{12}	809	203	.871	3 1/2
465	202	C_6H_{12}	809	173	.856	3 1/2
465	206	$C_6H_5CH_3$	787	184	.893	3
465	216	$C_6H_5CH_3$	787	196	.907	3 1/2
465	212	$C_6H_5CH_3$	787	188	.887	5
465	156	CCl_4	465	158	1.01	3
465	304	CCl_4	465	154	.503	8
		C_6H_6	998	184	.601	

The sample mixture results showed it to contain 49.8 per cent carbon tetrachloride and 50.9 per cent benzene. They were calculated as follows:

Average $C_6H_6 - CCl_4$ ratio = 1.18

Sample $C_6H_6 - CCl_4$ ratio = .601

$CCl_4 - CCl_4$ ratio = 1.01

Sample $CCl_4 - CCl_4$ ratio = .503

$$x = \% \ CCl_4 \qquad\qquad y = \% \ C_6H_6$$

$$\frac{x}{100} = \frac{.503}{1.01} \qquad\qquad \frac{y}{100} = \frac{.601}{1.18}$$

$$x = 49.8\% \qquad\qquad y = 50.9\%$$

As can readily be seen the calculations are very simple and easily done. All that need be determined from the sample spectrogram is the carbon tetrachloride - unknown intensity ratio. This ratio is converted directly to per cent.

Conclusions:

The results show that the fundamental idea, the use of a double beam principle to get constant intensity ratios, upon which the spectrograph is built is practically as well as theoretically sound. The ratios were nearly constant for the samples shown. This should apply to other types of samples as well. Also the ratios should become more constant as new improvements are made in design and construction.

A new instrument of any type is never perfect but has parts which need to be perfected. Absolute perfection is a limit which is never reached as there are always new ideas for improvements. Several new ideas for improving the performance of the spectrometer were formulated during the experimental runs.

One of these is to increase the sample illumination intensity by eliminating the air gap between the filter and the sample tubes. This will eliminate two glass air interfaces and should cut down on the amount of light wasted by reflection at the interfaces. This elimination could be accomplished by placing the sample tubes directly in the filter solution with the added advantage of eliminating a glass cylinder. This method of construction should also supply more efficient sample cooling as pumping cold filter solution around the sample tubes should be better than circulating room temperature air. An intensity increase here would also allow a decrease in exposure time.

Background on the films is a very troublesome factor when low intensity lines are encountered. This was illustrated by the case of n-heptane where the lines were barely visible above this background. The line to background ratio was so low that it was impossible to get results on the densitometer for these films. Further work should be done to find methods to either eliminate the background entirely or to get a line density evaluation system which will differentiate between line and background intensity. Probably a combination of these two ideas would be the most practical. Until this is accomplished the samples that the instrument can handle are limited to those where a high line to background intensity is obtained.

Further improvements would be along lines to increase the intensity of the Raman lines, to reduce the intensity of or completely eliminate the Rayleigh lines of longer wave length than 4358, to coat the prism and lenses with magnesium fluoride, and finally to get an instrument which can use a photoelectric recorder.

APPENDIX

Calculation of dispersion and resolving power

Dispersion:

Substitution of the refractive index vs. wave length values of:

n	λ
1.56779	4078
1.56468	4358
1.55668	5461

in the Hartmann formula $\lambda = \lambda_0 + \frac{c}{n - n_0}$ gave the following values for the constants:

$C = 82.80$

$\lambda_0 = 1486\ \text{Å}$

$n_0 = 1.53586$

Substituting these values, the refractive index of the prism at 4358 Å, and 60° for the refracting angle in

$$d\theta/d\lambda = \frac{2 \sin e/2}{\sqrt{1 - n^2 \sin^2 e/2}} \cdot \frac{C}{(\lambda - \lambda_0)^2}$$

an angular dispersion of 3.22×10^{-5} rad./Å was found for the Littrow system.

Using this value and the focal length of the parabolic mirror as 1875 mm. (75") the linear dispersion of the instrument was calculated by

$$dx/d\lambda = F\ d\theta/d\lambda$$

to be 6.05×10^{-2} mm./Å or 16.5 Å/mm.

Resolving Power:

The theoretical resolving power (R) was calculated by means of (again for the Littrow system)

$$R = t\, dn/d\lambda$$

as 1406 indicating a possible separation at 4358 Å of

$$d\lambda = \lambda/R \simeq 3\ \mathring{A}$$

Actually it was found possible to separate lines differing by at least 8 Å at this wave length.

Reproducibility:

Table III shows the reproducibility of the wave number shifts for four lines of the carbon tetrachloride spectrum. Values are in cm^{-1}.

TABLE III

Sample	Line I	Line II	Line III	Line IV
1	769	465	313	213
2	773	465	318	213
3	769	459	313	208
4	769	465	318	213
5	769	465	313	213
6	769	465	313	208
7	773	465	313	213
8	769	465	313	213
9	773	465	313	213

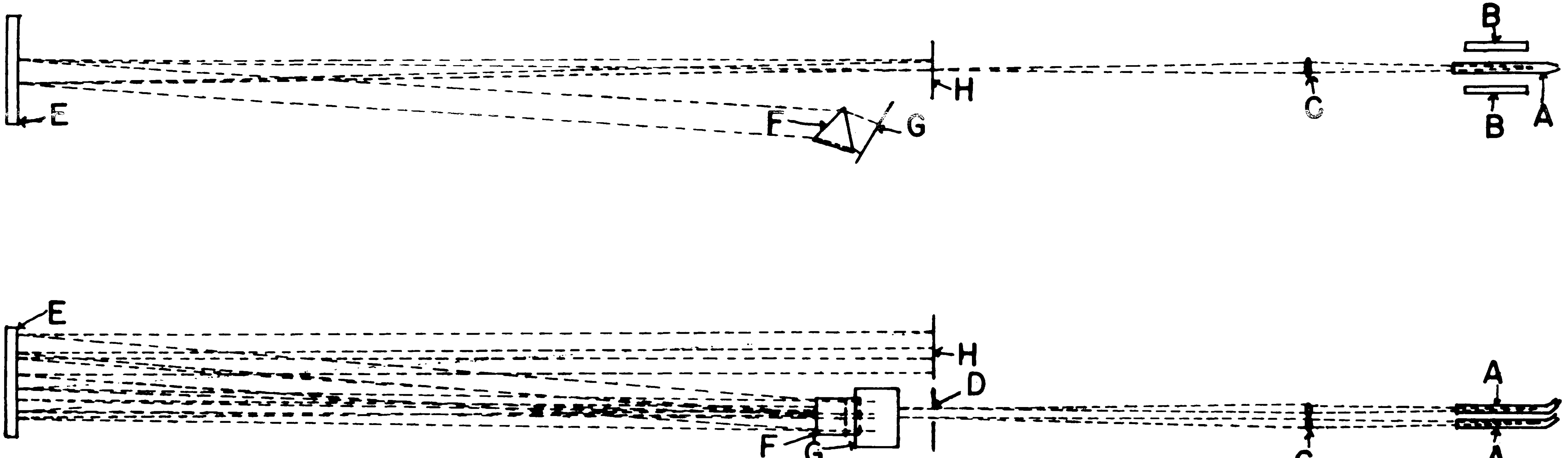
TABLE III (Continued)

Sample	Line I	Line II	Line III	Line IV
10	769	465	313	208
11	769	465	313	213
Literature values	780	459	314	217

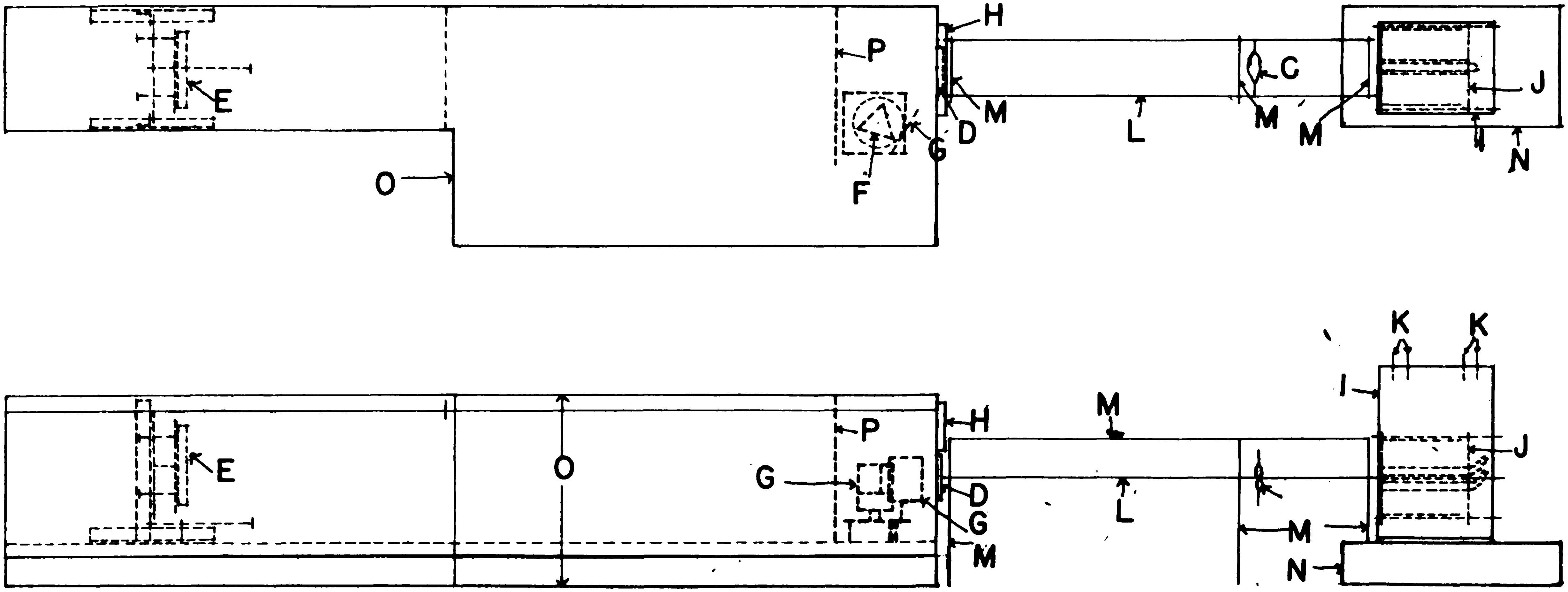
In measuring the distances between lines on the films the measurements agreed to 0.005 cm.

Focusing of condensing lens:

As stated in the text the condensing lens was placed in the position indicated as the optimum. This position was gotten from calculations based on the work of J. R. Nielson. The further criterion should also be added that it must be of such a size and so placed that it does not permit the slit to see the walls of the sample tube.

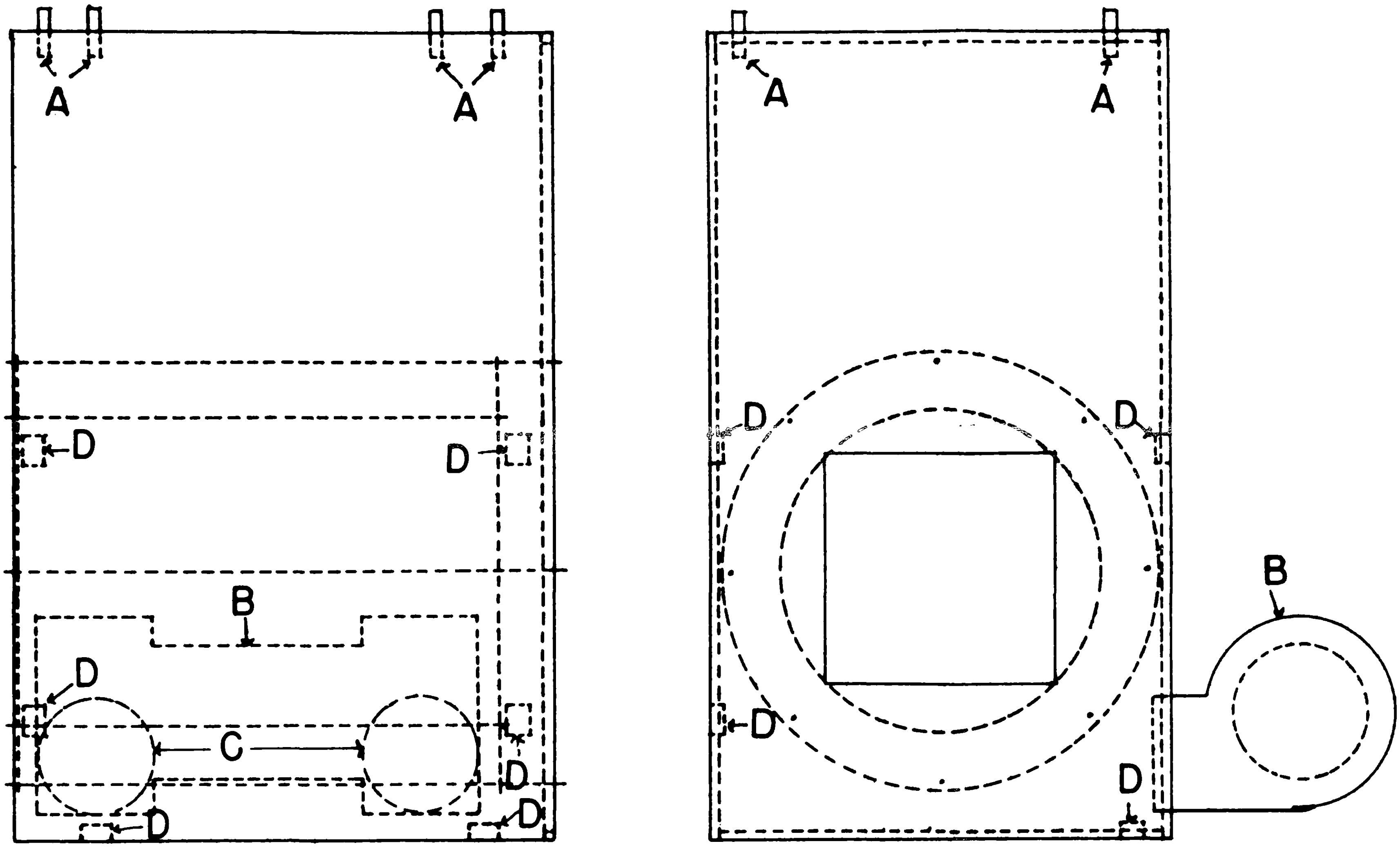


OPTICAL SYSTEM



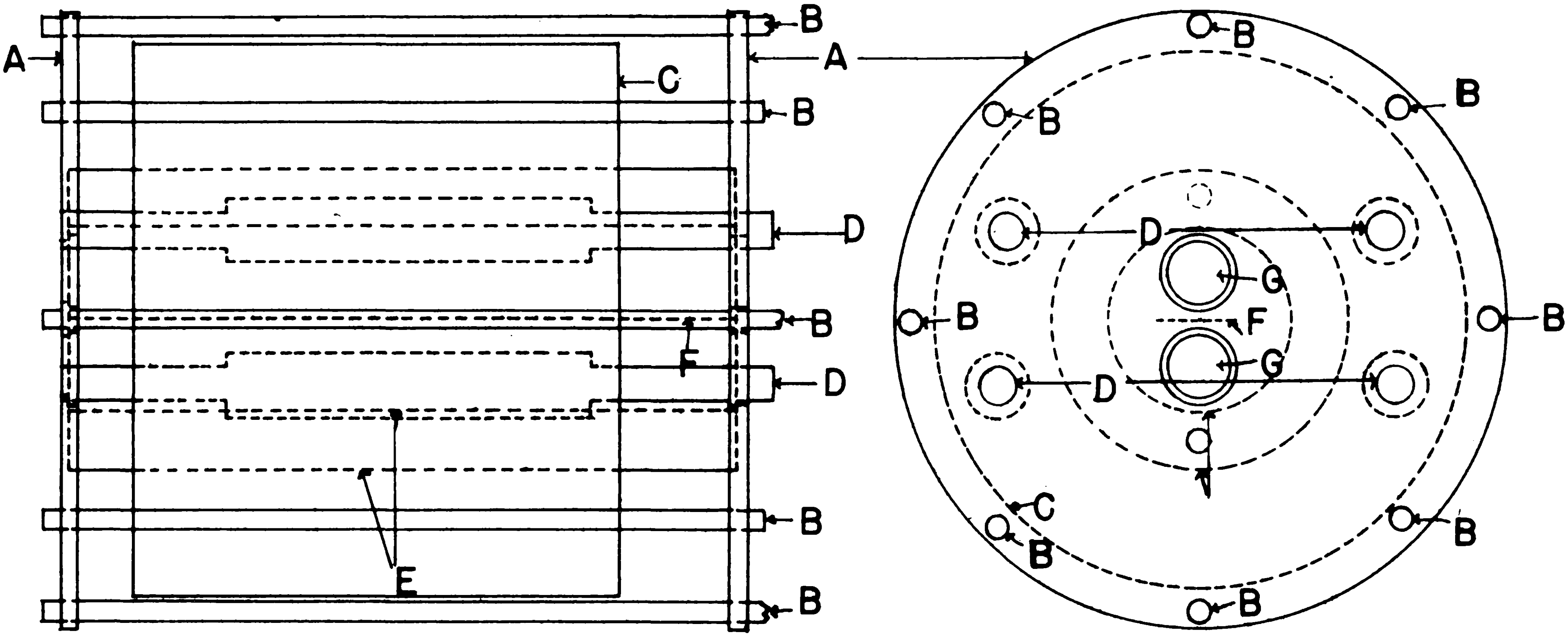
RAMAN SPECTROGRAPH

FIGURE I



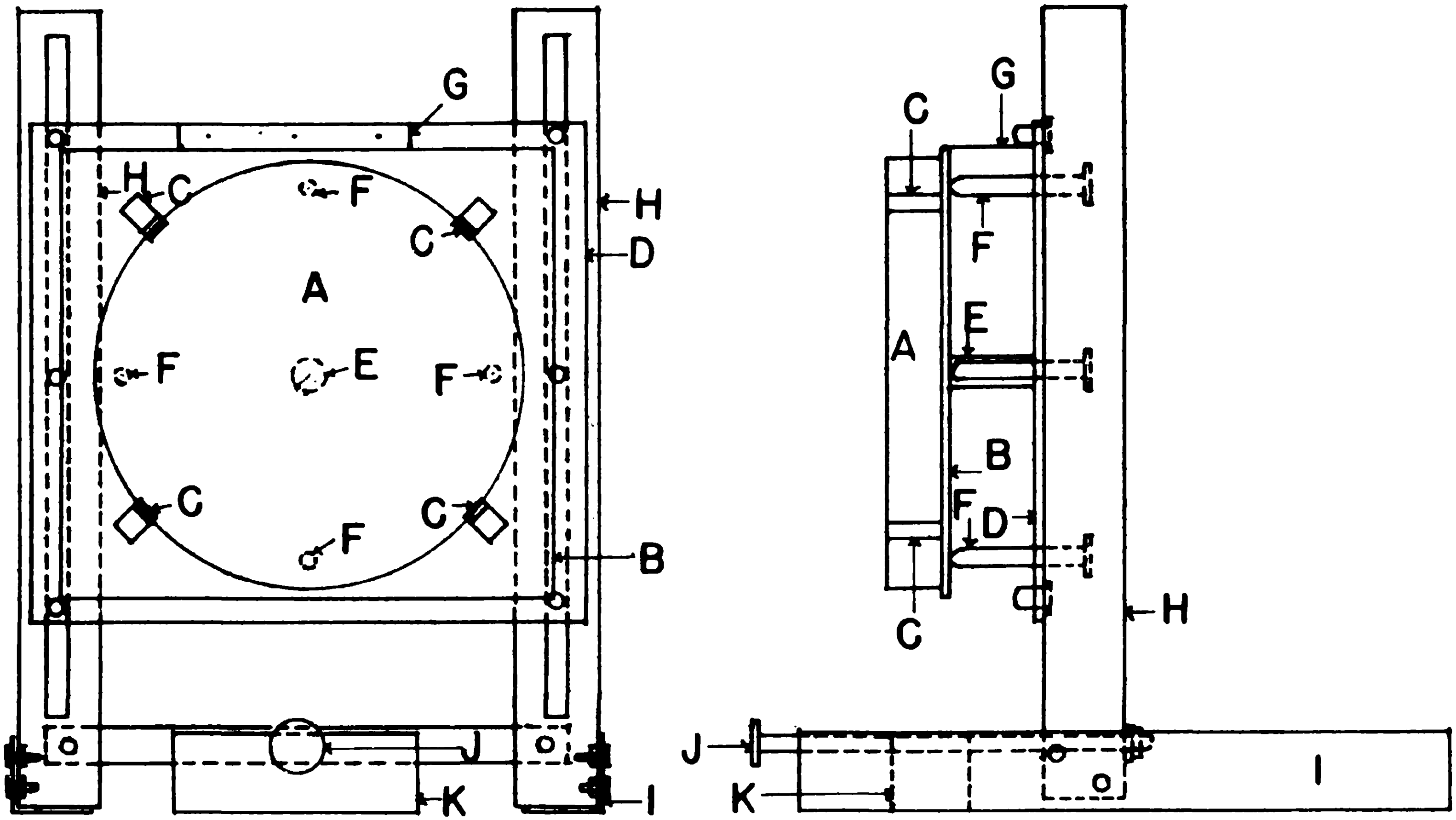
SOURCE HOUSING

FIGURE 2



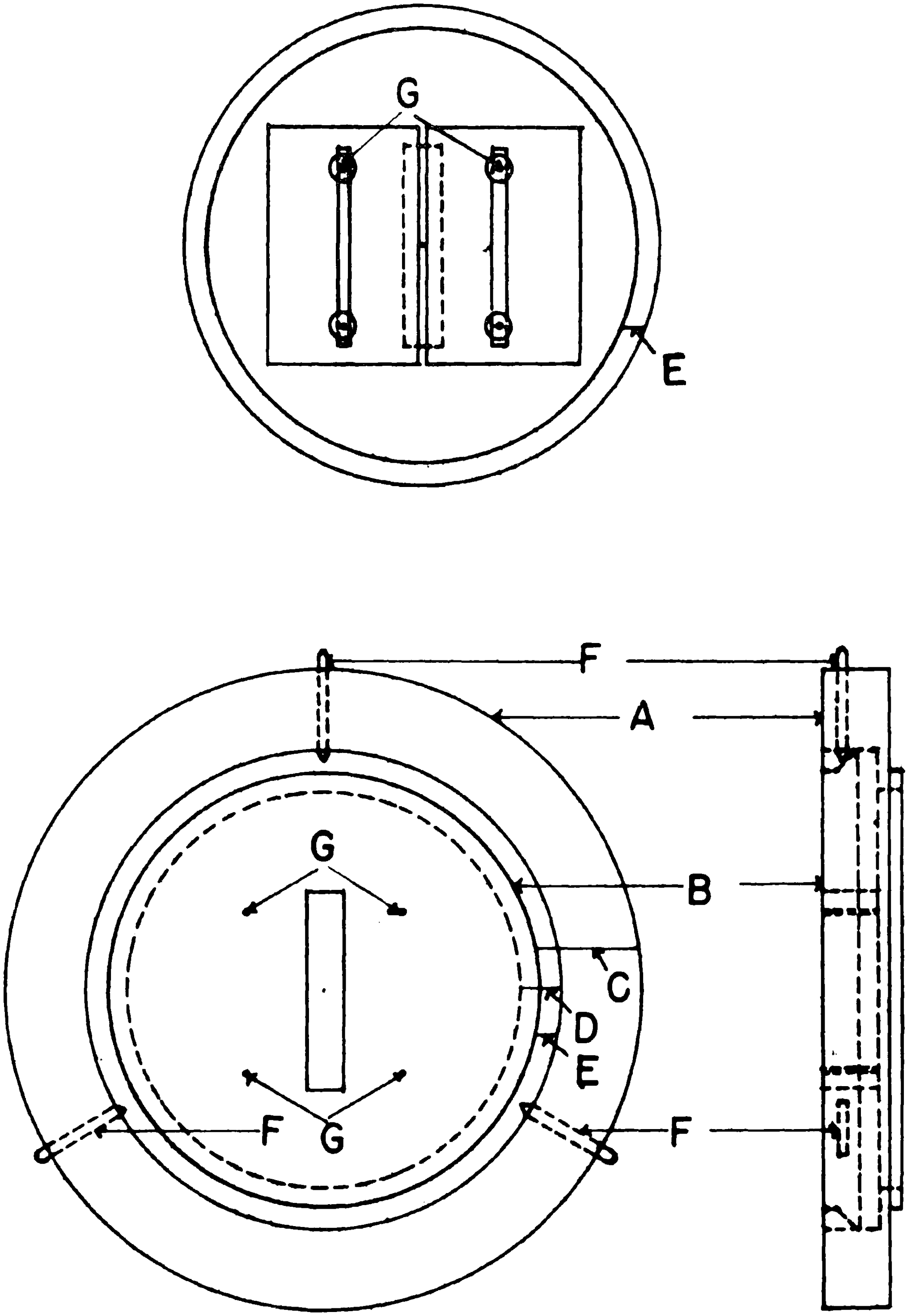
SOURCE UNIT

FIGURE 3



MIRROR MOUNT

FIGURE 4



SLIT HOLDER
FIGURE 5

BIBLIOGRAPHY

Several of the items in the bibliography contain numerous other references:

1. Bhagavantam, S.; Scattering of Light and the Raman Effect; Andhra University; India; 1940.

2. Brode, W. R.; Chemical Spectroscopy; John Wiley and Sons, Inc.; New York; 1946.

3. Gibb, T. R. P.; Optical Methods of Chemical Analysis; McGraw-Hill Book Company, Inc.; New York; 1942.

4. Glockler, G. and Haskin, J. F.; Raman Tube Filters; J. Chem. Phys.; Vol. 15; Page 759; (1947).

5. Hibben, J. H.; The Raman Effect and Its Chemical Applications; (A.C.S. Monograph); Reinhold Publishing Corp.; New York; 1939.

6. Ingalls, A. G.; Amateur Telescope Making; Scientific American Publishing Co.; 1928.

7. Nielsen, J. R.; The Filling of a Spectrograph with Light Considered as a Geometrical Radiation Problem; J. Opt. Soc. Amer.; Vol. 20; Page 701; (1930).

8. Pfund, A. H.; Apparatus for the Study of the Raman Effect; J. Opt. Soc. Amer.; Vol. 28; Page 264; (1938).

9. Rank, D. H.; Correlation of Intensity Measurements in Raman Spectra Obtained with Different Instruments; Anal. Chem.; Vol. 19; Page 766; (1947).

10. Rank, D. H.; Fenske, M. R., Braun, W. G., Weigand, R. V., Quiggle, D., and McCormick, R. H.; Raman Spectra of Hydro Carbons; Anal. Chem.; Vol. 19; Page 700; (1947).

11. Reilly, J. and Rae, W.; Physico-Chemical Methods; Vol. II; Chapter VII; D. Van Nostrand and Co., Inc.; New York; 1943.

12. Sawyer, R. A.; Experimental Spectroscopy; Prentice-Hall, Inc.; New York; 1944.

13. Weissberger, A.; Physical Methods of Organic Chemistry; Vol. II; Chapter XVII; Interscience Publishers, Inc.; New York; 1946.

VITA

William Edwin Keiser, the son of Clarence E. and Eva M. Keiser, was born at Lyons, Pennsylvania, on August 25, 1919. He received his primary and secondary education in the grade schools at Lyons; the Model School and Junior High School, sponsored by the Keystone State Normal School at Kutztown, Pennsylvania; and the Kutztown High School from which he graduated in June 1937. In September of 1937 he entered Lehigh University at Bethlehem, Pennsylvania, majoring in Chemistry and graduating in June of 1941 with the degree of B.S. in Chemistry. In June of 1943 he was admitted to the Graduate School of Arts and Sciences of the University of Pennsylvania, Philadelphia, Pennsylvania, where he majored in Physical Chemistry and from which he graduated in June of 1947 with the degree of M.S. In September of 1947 he was admitted to the Graduate School of Lehigh University for work toward a Ph.D. degree majoring in Analytical Chemistry. From June of 1941 until March of 1943 he worked for Celanese Corporation of America as a chemist at their Cumberland, Maryland, plant. This was followed by similar positions in the Research and Development Departments of Publicker Commercial Alcohol Company at Philadelphia, Pennsylvania, from March 1943 to October 1944 and of Socony-Vacuum Oil Company at Paulsboro, New Jersey, from October 1944 until June 1947. From June 1947 until the end of 1948 he held a Bethlehem Steel Company research fellowship at

Lehigh University and while working for his Ph.D. was favored with a grant for his research by the University Institute of Research. Since April 1950 he has been working in the Analytical Section of the Central Research Department of Minnesota Mining and Manufacturing Company at St. Paul, Minnesota. On April 29, 1944 he was married to Martha Ann Focht. They have one child, Martha Ann Keiser, born May 9, 1946.

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