FINAL TECHNICAL REPORT

A LABORATORY STUDY OF THE DIFFUSE REFLECTANCE SPECTRA OF FROSTS OCCURRING ON ASTRONOMICAL OBJECTS

by

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ABSTRACT

The apparaus to be used in this investigation is described in detail. Its mechanical, optical and operating properties are examined and a possible sample contamination difficulty is explained. In general, the mechanical and operational characteristics of this apparatus are well suited for the study of the reflectance spectra of frosts.

Although some difficulty has been encountered in the infrared detection system, the optical characteristics of the system appear to be satisfactory. The infrared energy available at the detector is low and steps to increase the energy and the responsivity of the detector are being taken. The problem of a standard diffuse reflector which is useful in the far ultraviolet region is considered and it is suggested that bright gold be used as the standard.

Instrument Design Criteria

The objective of the instrument design was to provide as versatile an experiment chamber as possible without becoming totally unwieldy. The primary emphasis was placed on sample preparation, sample environment control, and the ability to make measurements over a wide spectral region. Data acquisition techniques were to be made straight forward and automated if practical. Physical size and ease of operation played secondary roles in the design selection process. An over-riding requirement was that the custom construction work must utilize conventional machining and welding techniques so that the required work could be done by the machine shop in the Physical Science Department. Material and component cost constraints were applied whenever possible.

Instrument Design, Fabrication and Operating Characteristics

Figure 1 shows a horizontal section of the sample preparation chamber and the projection of the base. This drawing, to scale indicates the positions of the beam entrance and beam exit ports as well as ports for photographing the sample and the residual gas analyzer probe. The base has two sample gas inlets, a thermocouple gauge opening and a rotary shaft vacuum seal for the standard reflector. The sample is formed on the cooled substrate directly above the center of the pumping outlet shown in the base. The front face of the substrate is 1¼ inches behind the vertical axis of the chamber. The standard reflector can be moved into position just in front of the sample; the separation is approximately ½ inch. This slight difference in geometry is corrected in the data analysis by comparing the reflectance of the standard when it is positioned in front of the sample and when it is placed at the sample position. There is a false bottom in the

experiment chamber which allows the mirrors and apertures to be positioned to provide the best focus without interfering with the gas flow, line of sight, etc. Figure 2 is a vertical section showing the relative positions of the ancillary apparatus. The configuration shown will be the usual operating form where the sample is illuminated with monochromatic radiation and the amount reflected measured. Provision has been made to mate the lamp directly to the entrance port and then scan the reflected radiation as a function of wavelength. When the frosts and substrates containing sodium are irradiated with short wavelength light, this will be the configuration used. The purpose of these experiments is to search for sodium D emission and to determine the nature of material ejected from the sample surface.

The entire apparatus is constructed from type 304 stainless steel except for the entrance window extension and its separate pumping line which are fabricated from copper and brass tubing. The steel parts are welded together making inside welds where mechanically possible. These welds were made using the ordinary DC arc method and appropriate stainless rod. The preferred fluxless welding techniques are not available in the physics shop, so rather than ship the job to Houston for MIG welding, the ordinary arc method was used. The flux from the inside welds was thoroughly removed by grinding the area to a bright finish. After considerable trials suitable vacuum tight welds were achieved using this method. Those assemblies which required outside welds were provided internal relief by counterboring slightly oversize from the inside. Trapped flux may be in these welds yielding a slow evolution of gas; the low pressure behavior of the system does indicate that outgassing is the major limitation to the ultimate pressure attainable.

The entrance window extension is mated to the main chamber through a vacuum tight slide valve. This type valve does not obstruct the

optical beam. This extension tube, fabricated some time ago for another purpose, is made of brass and has two vacuum valves along a diameter. One is a small let-up-to-atmosphere type and the other is used in the by-pass pumping line. This line includes a brass bellows to relieve any misalignment in these parts. All joints in this assembly were made using hard solders.

The flanges are designed to use o-rings to provide the seal instead of soft copper gaskets. Several factors influenced the decision to use o-rings instead of copper seals; namely, the system is not primarily an ultrahigh vacuum chamber, costs, and fluxless welding should be used to attach the flanges. In retrospect, if another similar chamber should be constructed, the fabrication should be done using fluxless welding techniques and copper gasket sealing flanges. These techniques provide vacuum tight assemblies with a minimum of problems.

The vacuum pumping equipment consists of a two inch oil diffusion pump backed by a mechanical pump with a rated speed of ten cubic feet per minute. Backstreaming from the diffusion pump is prevented by a water cooled baffle and a trap cooled with liquid nitrogen. The calculated pumping speed at the chamber is 37 l/sec and according to the manufacturer's literature the pump maintains its rated speed to 5×10^{-7} Torr using DC-704 fluid before decreasing to zero at pressures on the order of 5×10^{-8} Torr. The lowest pressure achieved thus far has been about 3×10^{-6} Torr after long pumping. This pressure is reached after about eight hours of pumping, but is not lowered even after seven to ten days of pumping and warming the system to about 75°C. The system has been thoroughly checked for leaks using acetone spray with the changing response of the ionization gauge to indicate the presence of a leak. This method is not capable of detecing small leaks but no other leak detection apparatus is available at present. However, using the above

pressure and pumping speed data, the estimated leak rate is 2.3×10^{-4} std cc/sec. The simple acetone spray method should be capable of detecting leaks of this size. Further, when the sample chamber is isolated from the pump the pressure quickly rises to the 10^{-4} Torr range and then continues to increase more slowly. Such behavior indicates that the source of this gas is internal to the system. Several possible sources are: unremoved welding flux, the nitrile rubber o-rings, backstreaming from the mechanical pump, gases from the high vacuum grade epoxy resin used to seal the windows, and possibly other sources. A number of steps are being taken to eliminate these sources of extraneous material. A reasonably clean environment must be maintained for the frost samples. When the residual gas analyzer is put into operation the composition of this material will be further clarified.

The frost sample is formed on a cold surface by deposition from the vapor state. The crystal structure of the frozen material is determined in part by the temperature of the substrate. The morphology of the frost is also dependant on the deposition rate and the age of the frost. The substrate is cooled by a commerical refrigeration unit using liquid nitrogen as the cryogenic fluid. The unit selected is an Air Products and Chemical Heli-Trans, Model LT-3-110 whose rated capacity is about 20 watts at $77^{o}K$. The temperature is controlled by regulating the flow of cryogen and a heater; the temperature can be varied from $77^{o}K$ to $300^{o}K$ within $0.1^{o}K$ by an automatic control unit. The refrigeration capacity of the unit can easily be exceeded during sample preparation if a high deposition rate is allowed. This is particularly true for materials such as water which have a large heat of sublimation and specific heat. A rough calculation shows that a maximum rate of 37 mg/sec may deposited without exceeding the cooling

power of the cold end. Rates much less than this are used in practice. The gas flow into the system is controlled by a variable leak valve and the system is pumped continuously but throttled to keep the pressure in range so that the heat load does not exceed the cold tip capacity. The proper adjustments are made by observing the tip temperature and reacting accordingly.

There are two gas inlets in the base of the chamber, so that two materials can be introduced simultaneously by separate external gas handling systems. Each line consists of a cut-off valve adjacent to the chamber, thermocouple pressure gauge, metering valve, and the pressure regulator. The procedure for sample preparation consists of evacuating these lines to the gas cylinder valve and then purging with the sample gas several times. Neither line shows any detectable leak. It is judged that no appreciable contamination will be introduced along these gas lines. The addition of the residual gas analyzer will be invaluable in determining whether this procedure is adequate.

After a frost sample has been formed a photographic record of it is made. Initially no attempt to determine grain size will be made but at some future time such an investigation may be desirable. These photographs are primarily for qualitative frost morphology evaluation. The sample is oriented at approximately 45^{o} to the entrance port placing the substrate normal along the view-photograph port. A full face view of the sample is presented to the camera and the photograph is made using the light from a tungsten illuminator. No photographs have been made yet but visual inspection of several frost samples indicate that a very fine grained frost is formed on the flat portions of the cooled substrate. The frost tends to build up with a somewhat coarse structure on "sharp" portions of the substrate, such as screw heads. These frosted structures will not be presented to the optical beam but only

the reflectance of the uniform fine grained portion will be observed. These considerations only hold when the substrate consists of a disk of OFHC copper approximately one inch in diameter. It is planned that powdered rock samples will also form the base for the frosts. The coarse grained morphology will probably be formed on the rock grains and then the reflectance may be altered considerably.

The sample preparation chamber has two parallel beam exit ports. One port is provided with a window which transmits well in the ultraviolet and the other with an infrared transmitting window. At present LiF and KBr are used as the window materials although quartz and CaF_2 windows are also available. The windows provide an aperture of approximately 16mm in diameter which accomodates the 14mm beam very nicely. Inside the chamber the reflected light is gathered by a concave spherical mirror, directed out the window, and brought to focus on the active portion of the detector. The inner surfaces of the chamber will be covered with a material to reduce the scattered light to a minimum. This will be postponed until the vacuum problems are resolved.

The chamber contains two identical mirrors each of focal length 55mm and diameter 25mm. The mirrors are used in an off-axis configuration but the distortion due to the astigmatism is not very large. The apparent increase in the focal length is on the order of ten percent for reflected rays lying in the vertical plane when the mirror is used 15^{o} off-axis. The focal length for the rays in the horizontal plane is decreased by nearly the same amount. Since the active area of all of the radiation detectors is large compared to the slit image only a small amount of light may be lost due to imperfect focusing of the mirrors. The field of view is limited by an aperture stop so that only the central portion of the sample is viewed by the detector. This amounts to a sample area approximately 14mm in diameter, the same as

the slit height.

When the infrared region is being investigated an important consideration is the effect of the radiation from surrounding objects that reaches the detector. Assume the sample chamber acts as a cavity emitting blackbody radiation corresponding to an equilibrium temperature of 300°K. The detector senses the radiant flux which strikes the active area of dimension 2mm by 0.2mm. Estimating the field of view of the detector, it receives 140 μW of power on the active area; this power is that associated with radiation in the wavelength region extending from 2 μ to 20 μ. The detector further senses the radiant energy in this region which is brought to focus by the mirror; the mirror acts to extend the field of view of the detector. As mentioned above the mirror has a 14 mm diameter circular field of view at the sample. The sample temperature will lie in the range from 80°K to 150°K. The detector now receives an addition background power amounting to 30 μW to 1300 μW from radiation gathered by the mirror. This energy is contained in the same spectral region. Thus, the detector responds to a steady background power amounting to 170 μW to 1,440 μW. Since the detector has a responsivity of approximately 20 V/W the corresponding output will be a DC voltage in the range 3.4 mV to 29 mV. A simple test of the radiation thermocouple showed that the output was 20 μV when measured using only the copper substrate as the sample. The cause of this low output value is being investigated but it appears as if the responsivity of the detector is not as great as the manufacturer claims.

To this point the emphasis has been on details of operating in the infrared region. There are two beam exit ports and a distinct mirror for each spectral region. A gold coated mirror is used in the near and intermediate infrared, .7μ to 20μ while an aluminized mir-

ror with a MgF_2 overcoat optimized for 1216A is used in the far ultraviolet through the visible spectrum. No special efforts are required when the ultraviolet and visible beams are brought to the detector; the contribution to the energy incident on the detector from a blackbody source is negligible. A photomultiplier tube, EMI type 9783B with a spectrosil window is used in the visible region down to about 1600 A. To detect shorter wavelength radiation, a thin glass slide coated with sodium salicylate is placed in front of the photomultiplier window. Sodium salicylate has a high and nearly uniform flourescent efficiency for radiation in the region from 3400 Å to 400 Å. The EMI photomultiplier is used to observe the flourescent emission of the sodium salicylate and, thus, acquire the reflectance data in the far UV region. The near infrared radiation is detected using a dry-ice cooled PMT with an S-1 response. The thermocouple detector is used to measure radiation with wavelength greater than 1.2 μ .

The purpose of two beam exit ports fitted with different windows is to permit the sample to be studied over a wide spectral range. The sample is prepared, photographed and rotated into the incident beam making the desired observation angle relative to the mirror. Once the sample is prepared it can be studied throughout the region from 1000 Å to 20μ without disturbing it. This technique has the advantage of sample integrity; that is, data is obtained under the same conditions of frost morphology, temperature, history, composition, etc. rather than having different samples for study in different spectral regions. The purpose of the entrance window extension is to permit changing windows when going from the ultraviolet and visible spectrum into the infrared. This portion of the system can be let up to air, the window and external optical apparatus changed, and then re-evacuated without disturbing the sample. These alterations together with the requisite changes in

detector configurations are accomplished in a reasonably short time. The time required might be as short as thirty minutes to as long as two hours which is about the same time required to scan the reflectance spectra. However, there is a possible difficulty which could be important and will be investigated thoroughly before any data analysis is done. This is the problem of sample contamination. The sample chamber is evacuated to as high a vacuum as possible with moderate heating to remove as much absorbed material as feasible. Although an initial pressure in the range of 10^{-8} Torr may be attained the system will continue to outgas. The equilibrium vapor pressure of various sample gases dictate that once the sample frost is formed pumping on the chamber must be stopped otherwise the frost sample will be pumped off the substrate. The table shows the equilibrium vapor pressure for some sample gases at two temperatures expected to be used for frost formation and study. It

	140°K	90°K
CH_4		10^2 Torr
CO_2	1	10^{-5}
H_2S	1	10^{-5}
H_2O	10^{-9}	10^{-13}
NH_3	10^{-2}	10^{-8}

is clear that except for water and ammonia at 90°K frosts of these gases cannot exist long at pressures much lower than their equilibrium vapor pressure. The cold frost will then accumulate the condensible outgassed material; oxygen and nitrogen will not condense at these temperatures and pressures but water, carbon dioxide, and most organic compounds do. These materials, particularly organic compounds, may interfer with the determination of the reflectance spectra when they form a layer on the frost sample. If the partial pressure of these

materials is very low, on the order of 10^{-9}Torr, then approximately 20 minutes pass before a monolayer of material accumulates on a freshly formed surface. Only one minute passes before a monolayer is formed if the partial pressure is 5×10^{-8} Torr. The expected data acquisition time suggested above is longer than the surface coverage time. The sample frost may be several hours old before data is taken if the entrance window and the external optical apparatus are changed to accommodate the shift in spectral region.

The molecular weight of the oils and greases which may form the bulk of outgassed organic material are above the range of the residual gas analyzer whose range is 1 to 100 amu. Hence, this technique will not be available to assist in determining the amount of contamination to be expected. There are two approaches to study the effects of possible contamination which are available and both will be utilized. As the sample ages outgassed material presumably accumulates and its interference becomes more appreciable. A study of the reflectance as a function of time should reveal such an effect if the time required to accumulate a detectable amount is less than the data acquisiton time. The effects of accumulated organics are most pronounced in the far ultraviolet region where a thin film of oil on optical components renders them useless. Thus, the sample frost can be observed using Lyman Radiation (1216 A) during formation and for some period afterwards. An observation time of several hours would seem appropriate. If times longer than this are necessary to accumulate a detectable level of contamination, then the effects of such impurities will be negligible. This approach takes into account the dynamic processes which occur at the solid-vapor interface of a material coming to equilibrium with its vapor. Further, on the basis of the microscopic view of reversibility, such processes continue even though macroscopic equilibrium is established.

The effect of the condensation of outgassed materials can also be established by observing the reflectance of the substrate alone. Data taken when the substrate is at ambient temperature and presumed clean can be compared with that taken when the substrate is cold and has accumulated the outgassed material. In this manner the degree of interference caused by such substances may be judged. Although a great deal of space has been devoted to this possible problem of contamination, it is not expected to be so severe as to limit the validity of these studies. However, it must be firmly established that the data gathered represent the behavior of the frost and not some impurity.

Preliminary Results and Procedures

After the frost sample is prepared and photographed the reflectance spectra of the frost is recorded. The reflectance of the frost is compared to the reflectance of a standard reflector over identical wavelength ranges. The standard reflector is a compressed powder sample of Eastmann White Reflectance Standard, a very pure form of borium sulfate. This material has a reflectance of better than 90% from .2μ to 2.5μ and will be used as the standard in this spectral region, although, at least one study has used this material down to 1600 A. There is no accepted standard of reflectance for radiation with wavelength longer than 2.5μ. The reason for this is simply because diffuse reflectance spectroscopy has been confined mainly to the study of dyestuffs and pigments where only the visible region is of importance. The sulfate in the Eastman White standard will probably show strong absorption in the 10μ region and perhaps at other wavelengths as well. Magnesium oxide and other materials will be tried as the standard if the borium sulfate is unsuited in certain regions.

The response of the thermocouple detector appears to be independent of wavelength from the visible to the near infrared. The detector was checked against a standard of spectral radiance lamp supplied by Instrumentation Specialties Company. The power emitted by this lamp is known in the region from 0.4μ to 2.0μ. The thermocouple detector's D.C. response has been measured as a function of wavelength and compared with the calibrated output of the lamp. As noted previously this detector does not seem to have the sensitivity that the manufacturer claims so that this comparison may not be especially meaningful and thus the detailed results are omitted. However, the output does appear to follow the spectral intensity of the lamp, but small signal

voltage, <.1 μ V, drift and noise make for a poor quantitative comparison. When the system can be used in the A.C. mode many of these difficulties should be eliminated and a meaningful comparison made. The response is expected to be linear over the entire infrared region and will be assumed so for the region beyond 2.0 μ unless the data below 2.0μ show significant deviations.

The response of the detectors used in the near infrared and in the visible will be directly determinable during each run by comparison with the known reflectance of the white standard. The calibration of the detector used in the far ultraviolet is not so straight forward. Most materials are very poor reflectors of far ultraviolet radiation so that an efficient diffuse reflector is unlikely to be found. The borium sulfate standard has been used for radiation as short as 1600 A, but its usefulness at shorter wavelengths is unknown. Therefore, if the borium sulfate is not suitable, then the standard reflector in the region below 1600 A will be a bright gold coated flat. Rather than using no standard, the measurements will be taken relative to the specular reflectance of gold. The measurements can be correlated by using the thermocouple detector and the fluorescence of sodium salicylate at the Hg 2537 A line. The fluorescent efficiency of freshly prepared salicylate films has a constant value of about 65 percent for exciting radiation between 400 A and 3400 A. Assuming this to be true then the source output can be monitored using the reflected radiation from the gold film.

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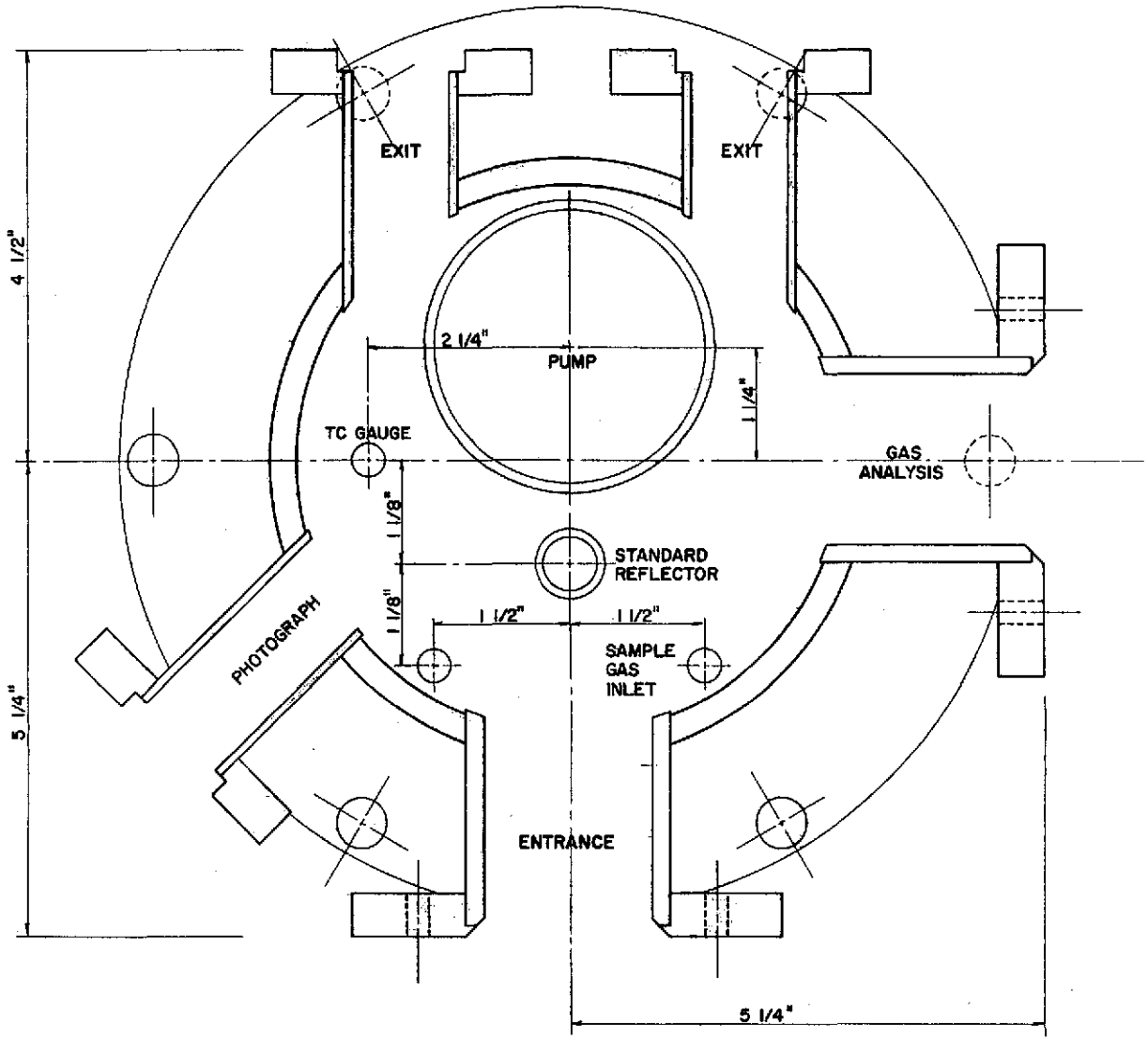

EXPERIMENT CHAMBER

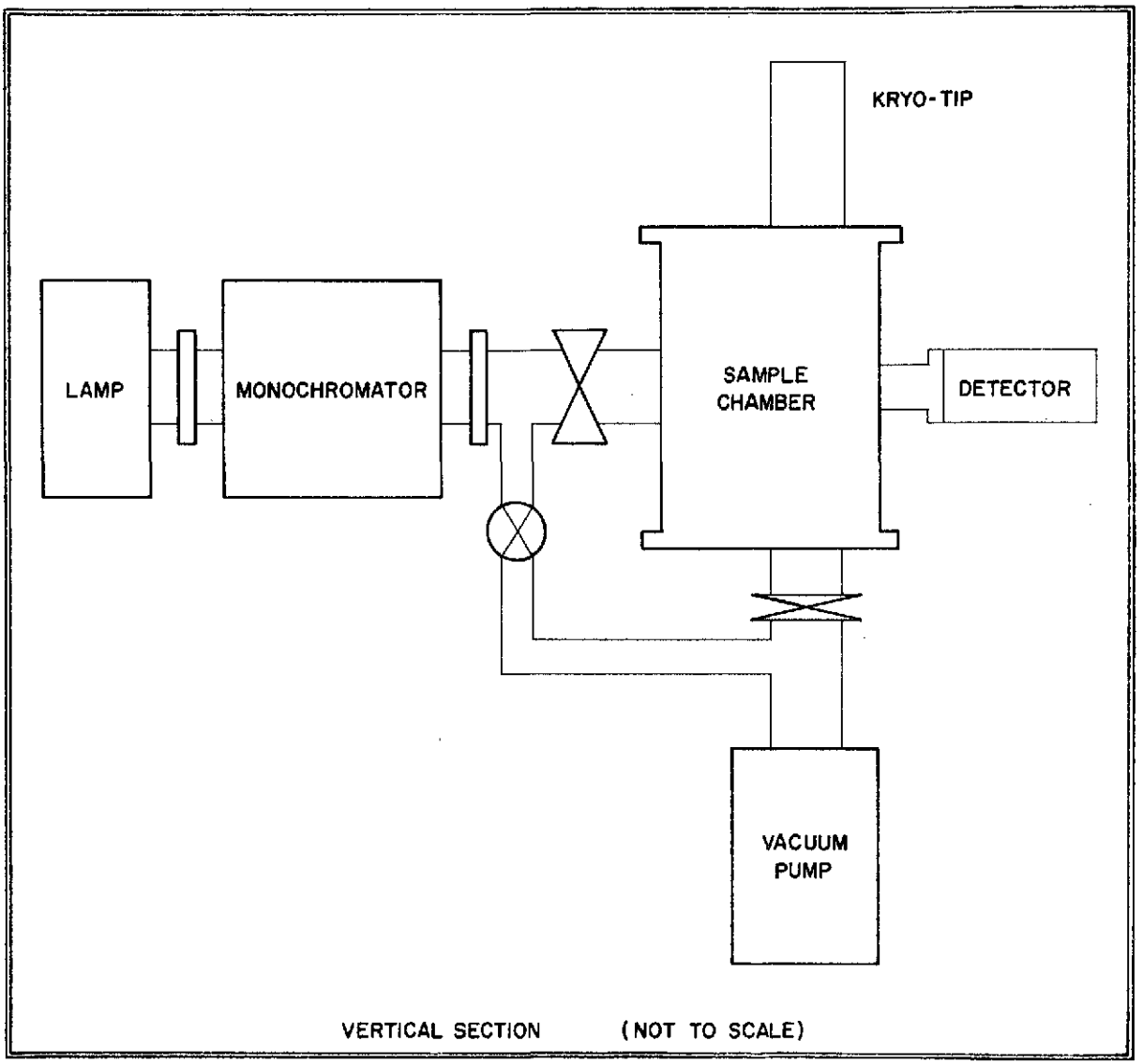

FIGURE 2