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THE EVAPOROGRAPHIC METHOD OF INFRARED PHOTOGRAPHY

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An article entitled "Possibilities of Astronomical Spectroscopy in the Infrared," which appeared in the preceding (December) issue of these *Publications,*[1] described in general terms various methods for exploring astronomical spectra in the infrared. Of these methods, evaporography seems to be the most promising. The present paper, a sequel to the first article, describes in detail the evaporographic method, its difficulties, possibilities, and limitations.

THE BASIC PRINCIPLE OF THE EVAPOROGRAPHIC METHOD

In the ideal method of infrared photography, the receiver should be cumulative and sufficiently sensitive. Moreover, before and after exposure, the receiver should be in thermal equilibrium with its surroundings. In principle these conditions can be met by exposing to the infrared spectrum a thin layer of substance which vaporizes or sublimes easily. Part of the substance is vaporized or sublimed away from the regions exposed to infrared radiation and deposited on the cooler unexposed regions. If the changes in thickness of the layer can be observed, they will reveal the distribution of intensity in the infrared spectrum.

To avoid the perturbing effect of dark-space radiation and collisions, the layer to be vaporized should be in an enclosed space filled with saturated vapor of the substance used. When the exposure to radiation is interrupted, the heated regions return to room temperature, and under ideal conditions, the changes in thickness should cease, since the substance is then in equilibrium with its vapor, the number of molecules released by evaporation or sublimation at any point being equal to the number of molecules deposited at that point. Thus, although dark-space radiation and collisions cannot be avoided, their disturbing effect can be avoided, at least theoretically.

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[1] P. Swings, *Pub. A.S.P.*, **56**, 220, 1944.

In its essentials this method, which is now usually called evaporography, dates back to 1840. In that year Sir John Herschel prepared a heat-absorbing surface by coating a sheet of very thin filter paper with lamp black. He then applied alcohol to the back of the paper by means of a brush and exposed the sheet thus prepared to the spectrum of the sun. The alcohol evaporated more quickly from the part of the paper exposed to the heat spectrum than from the unexposed part. The dry part could easily be seen against the undried background. The infrared spectrogram obtained in this way revealed three or four moist patches left in the dried area; these moist regions corresponded to groups of absorption lines in the infrared solar spectrum.

Such records were naturally transient, although they lasted long enough for Herschel to make certain measurements. He tried to obtain a more permanent impression, a "fixed thermograph" as he called it, by the ingenious device of dissolving coloring matter in the alcohol and then accumulating the effect by successive washes of alcohol, hence revealing the intensity distribution of the infrared radiation by changes in color on the paper.

Approximately ninety years passed before Herschel's idea was developed further; but since 1929 considerable progress in its use has been made in Czerny's laboratory.[2]

In Herschel's experiment, the alcohol evaporates from the filter paper even when no radiation reaches it. This drawback can theoretically be avoided if the paper is placed in an enclosure that is already saturated with alcohol vapor. A further improvement would be to evacuate the enclosure to the pressure corresponding to the saturation pressure, since air slows down the evaporation from the warmer to the colder regions. Other improvements can readily be imagined in the type of evaporating material (to replace the alcohol), in the nature and thickness of the membrane (to replace the filter paper), in the heat absorbent

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[2] M. Czerny, *Zs. f. Phys.*, **53**, 1, 1929; H. Willenberg, *ibid.*, **74**, 663, 1932; G. Mönch and H. Willenberg, *ibid.*, **77**, 170, 1932; M. Czerny and P. Mollet, *ibid.*, **108**, 85, 1937, and *Phys. Zs.*, **38**, 1008, 1937.

(to replace the lamp black), and in the method of observing changes in thickness.

Czerny and his collaborators, after extensive experiments, developed a method which employs a thin celluloid membrane a little less than 0.1 micron thick (1 micron, μ, $= 0.001$ mm). One side of the membrane is coated with paraffin oil, a few tenths of a micron thick, the other with a uniformly absorbing material such as bismuth black or a thin metallic layer. The saturation pressure of the paraffin oil being of the order of 0.01 mm of mercury, the enclosure must be evacuated to that pressure. Before being coated with oil, the celluloid membrane does not show any characteristic interference color in reflected light, but is neutral gray. After the paraffin oil has been deposited, bright interference colors appear in reflected light; these colors can be made perfectly constant over fairly large surfaces. A change of thickness of 0.01 μ due to evaporation of paraffin oil by local heating can easily be observed.

If an infrared spectrum is projected on the absorbing side of a membrane prepared in this way, the formation of the spectral image can be followed visually on the other side of the membrane where the interference colors change at the heated, evaporating spots. When an image of the desired clearness is obtained, the layer can be desensitized by reintroducing air into the instrument. The image, which remains for some time, can be photographed with an ordinary camera. Excellent sensitivity can be reached. To prepare for a new exposure, the membrane is simply illuminated for a short time by an electric lamp, so that the remaining paraffin oil is evaporated.

ESSENTIAL PARTS OF AN EVAPOROGRAPHIC RECEIVER[3]

An evaporographic plate consists of three parts: the membrane, the absorbing layer, and the subliming or evaporating layer. These parts will be discussed in succession.

The membrane.—In all the experiments by Czerny and his collaborators, the celluloid membrane is prepared by pouring a

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[3] This subject is discussed in detail at the request of several colleagues who base great hopes on the astronomical applications of evaporography, especially in the field of solar spectroscopy.

few drops of lacquer[4] on a large surface of dust-free distilled water (area of the order of 50×50 cm^2). The lacquer spreads out, forming a very thin film over about half the area of the water surface. The solvent evaporates, leaving a thin film of celluloid that can be taken off the water on a metal frame. The thickness of the film is controlled by varying the dilution of the lacquer; thicknesses of approximately $0.05\ \mu$ are easily obtainable. Czerny designed a frame which made it possible to prepare a double film, each layer adhering to the other on the wet side so that no drop of water remained on the surface of the film. Such drops cause spots on single films in the process of drying, even when distilled water is used. In the preparation and preservation of the membranes, dust must be avoided as much as possible.

The preparation of thin membranes has recently become of great technical importance on account of the applications of such films to problems of electron diffraction and of electron microscopy.[5] Schaefer and Harker use a polyvinal formal (known by the trade name of Formvar) dissolved in dioxane or ethylene dichloride, from which excellent membranes as thin as $0.01\ \mu$ can be obtained. Other electron microscopists use polystyrene or a benzene solution of Resoglaz.

It appears safe to state that no serious difficulty will be encountered in the preparation of membranes of moderate size (a few square inches) such as would be needed in infrared astronomical work of low dispersion. On the other hand, the preparation of membranes eight or ten inches across (comparable in size to a high-dispersion stellar spectrogram) may present serious problems.

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[4] The lacquer used by Czerny consisted of pyroxylin and amyl acetate. Other solutions have also been used. For example, L. Harris and E. A. Johnson, *Rev. Sci. Instr.*, **4**, 454, 1933, prepared thin films, using methyl and ethyl acetate solvent for two parts cellulose acetate and one part glyptal lacquer at 0° C.

[5] H. Mahl, *Zs. f. tech. Physik*, **21**, 17, 1940, and *Metallwirtschaft*, **19**, 488, 1940; L. H. Germer, *Phys. Rev.*, **56**, 58, 1939; V. J. Schaefer, *Jour. Phys. Chem.*, **45**, 681, 1941; V. K. Zworykin and E. G. Ramberg, *Jour. of App. Phys.*, **12**, 692, 1941; V. J. Schaefer and D. Harker, *ibid.*, **13**, 427, 1942; R. D. Heidenreich and V. G. Peck, *Phys. Rev.*, **62**, 495, 1942; *Jour. of App. Phys.*, **14**, 23, 1943; R. D. Heidenreich, *ibid.*, **14**, 312, 1943.

The absorbing layer.—Since the membranes are too thin to absorb a sufficient portion of radiation, they must be covered on one side by an absorbing substance. A layer absorbing more or less uniformly in the infrared is desirable.

In his first experiments, Czerny deposited lampblack on one side of his membranes by simply passing the moist membrane through an open petroleum flame. It is evident that such a coating will rarely be of uniform thickness. In his later work, he deposited bismuth black following the technique described by A. H. Pfund.[6] When bismuth is evaporated at pressures of the order of 0.25 mm mercury, it forms perfect jet-black layers. A small specimen of bismuth (about 5 mm in diameter) is placed on a tungsten ribbon which is electrically heated. The membrane is placed about 10 cm from the evaporating bismuth. In Czerny's experiments, the gas pressure is controlled with a small discharge tube: the best results are obtained at pressures corresponding to a stratified discharge. When the pressure is too high, the layers are ash gray instead of jet black; when the pressure is too low, the coating gives rather a metallic reflection. The evaporation requires from 4 to 10 minutes. If the bismuth is overheated, black clouds which form in the evacuated jar cause the membranes to be less homogeneous. The bismuth black is deposited more easily if the membrane is cooled from the back; Czerny does this by placing a brass plate 10 mm thick 0.5 mm behind the membrane.

Unfortunately, the transmission curve of bismuth black in the infrared varies considerably with wave length. A very thin layer may absorb 90 per cent of the radiation at 1 μ, but only 20 per cent at 5 μ. By increasing the thickness of the coating, it is possible to have high absorption all through the infrared, but a coating of such thickness would diffuse the heat rays so much on either side of the heated spot that the resolution would be lost. Membranes of different thicknesses should preferably be used in different spectral regions.

Pfund has studied a wide variety of metallic blacks in addition to that of bismuth. In 1933 he published some of his re-

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[6] *Phys. Rev.*, **35**, 1434, 1930; *Rev. Sci. Instr.*, **1**, 397, 1930.

sults[7] on the metallic blacks obtained by distilling gold, silver, nickel, copper, zinc, cadmium, lead, antimony, selenium, and tellurium. The distillation which must proceed at a pressure of 3 to 5 mm, is more satisfactory in an atmosphere of hydrogen. Thin membranes can be coated very well when they float on a clean surface of mercury. In his classical paper of 1937 on radiation thermopiles,[8] Pfund recommends blackening the receiving area with a metallic black of zinc.[9] A coating of zinc black, of such thickness that it transmits a barely recognizable visual image of a tungsten lamp filament, transmits less than one per cent between 1 and 14 μ. I do not know of any attempt to apply these recently developed black coatings to the evaporographic method. I understand, however, that in making thermopiles, some physicists prefer to use a metallic black of gold distilled in hydrogen. The only requirement for thermopiles is high infrared absorption; whereas an evaporographic plate requires a layer so thin that little diffusion takes place on either side of the irradiated spot.

For progress in the evaporographic method, it would be of great interest to make a systematic laboratory investigation of the spectral distribution in the infrared of the transmission and scattering of films of various metallic blacks at different thicknesses. Thicknesses of a few tenths of a micron or more can be measured interferometrically.

Another approach to the problem of thin absorbing layers may be found in the metallic reflecting coatings. Such thin layers can now be produced easily with silver, aluminum, platinum, rhodium, etc., by vacuum distillation. Theoretical and experimental investigations[10] show that these thin layers have a nearly constant absorption coefficient for all wave lengths in the infrared. Experiments have been made in Czerny's laboratory on membranes coated thinly with aluminum in high vacuum.

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[7] *Jour. Opt. Soc. Amer.*, **23**, 375, 1933.

[8] *Rev. Sci. Instr.*, **8**, 417, 1937.

[9] Metallic zinc, when heated on a tungsten spiral, tends to explode. Use an alloy of four parts of zinc to one part of antimony.

[10] For example, W. Woltersdorff, *Zs. f. Phys.*, **91**, 230, 1934.

Such aluminized membranes were found to be usable, especially in the longer wave-length region where the bismuth black used by Czerny is relatively transparent. But the sharpness of the images obtained with aluminized membranes was definitely less than that given by blackened membranes, because a metallic layer possesses an appreciable thermal conductivity even when very thin. Czerny's published experiments concern the aluminum coatings only; further laboratory work is highly desirable.

The sublimating or evaporating layer.—In his first experiments, Czerny used solid materials such as camphor or naphthalene which sublime easily or, expressed otherwise, have a high vapor pressure at room temperature. The sublimation away from an illuminated (heated) spot toward a cooler unexposed region should proceed as rapidly as possible. At atmospheric pressure, camphor, which has a saturation pressure of 0.50 mm, is more effective and faster than naphthalene, which has a saturation pressure of only 0.054 mm. But the speed of the process of sublimation is affected strongly by the ease with which the sublimating molecules diffuse away from the exposed surface. As a result, the speed increases considerably at reduced pressure. Actually, it reaches its theoretical maximum when the free path of the gas molecules is of the order of the dimensions of the enclosure, that is, at a pressure of the order of 0.001 mm mercury. Obviously, it is not possible to lower the pressure within an enclosure containing camphor or naphthalene below the saturation pressure of the compound, that is, below 0.5 mm for camphor and below 0.05 mm for naphthalene. Consequently, the sublimation of naphthalene can be speeded up by a factor of about 1000 by lowering the pressure, while the sublimation of camphor can be speeded up only by a factor of about 100. At the lowest attainable pressures, camphor and naphthalene should thus sublime at speeds which are of the same order. Under such conditions, naphthalene is better adapted to the work since desensitization by reintroduction of air at normal pressure is then more effective.

The changes in thickness produced by sublimation of a naphthalene or camphor layer irradiated by infrared are very small, as is apparent from the following considerations. Let s be the

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heat of sublimation and d the density of the material considered. If we expose the layer to the radiation of a Hefner candle placed at a distance of one meter, 7.7×10^{-2} calories will fall per hour on each square centimeter of the exposed layer. Under the most favorable conditions (no loss of energy), one calory sublimes $\frac{1}{sd}$ cm^3 of the material. Hence, under the best conditions, the Hefner candle would cause the sublimation of a thickness $7.7 \times 10^{-2} \times \frac{1}{sd}$ cm of the material per hour. If we adopt the value $s = 100$ cal./gm and $d = 1$, which are certainly of the correct order of magnitude, we find for the thickness sublimated in one hour the value 7.7×10^{-4} cm or $7.7\ \mu$. This figure is based on the assumption that the radiation received by the layer is not dissipated by heat conductivity, radiation, or any other process except sublimation. Experiments show that this is actually the case, and a similar conclusion is reached by a theoretical discussion of the problem.[11] The sublimation process has an excellent efficiency.

Czerny obtained fairly satisfactory experimental results with layers of naphthalene. If the membrane covered on one side with naphthalene is not coated on the other side with absorbing black while exposed to unabsorbed radiation of an infrared source, the sublimation occurs only in the regions corresponding to the infrared absorption bands of naphthalene. Czerny obtained in this way the naphthalene absorption bands of wave length as long as $6\ \mu$. The enclosure was evacuated to about 0.2 mm pressure. To photograph the bands, Czerny placed a sheet of black paper behind the membrane and illuminated the membrane from the front. To obtain the infrared absorption spectrum of a substance other than naphthalene itself, the membrane must be blackened.

Czerny and his collaborators soon recognized the disadvantages of coating the membrane with a solid substance when extremely small changes in thickness have to be observed. A solid substance such as naphthalene can be reduced to a fine crystal-

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[11] M. Czerny, *Zs. f. Phys.*, **53**, 1, 1929 (see pages 8, 9, and 10).

line powder which gives a fine-grained, dull coating. But such layers tend to recrystallize. The smallest crystals have a higher vapor pressure than the larger ones; hence the small crystals sublime away toward the larger ones. As a result, the graininess of the layer increases, which renders accurate work difficult. At the exposed places, the crystals become smaller on the average, hence have a slightly higher vapor pressure, so that the sublimation process continues when the irradiation is interrupted. The corresponding increase in contrast, after exposure to radiation, seems at first sight a rather attractive feature, but it actually turns out to be quite impractical since accidental contrasts, as well as systematic ones, are enhanced. The result is that the distribution of material on the plate soon becomes irregular.

It may seem advantageous to replace the dull coating by a clear crystalline layer or by a vitreous coating such as may be obtained by vacuum sublimation of clear naphthalene. The technical difficulties encountered during the corresponding experiments led Czerny and his collaborators to use liquid instead of solid coatings. Yet it would seem worth while at present to repeat similar experiments, profiting from the experience gained in vacuum distillation in recent years.

In vacuum distillation, a layer of a specific liquid, for example some kind of oil, may be formed. Liquids may behave in two ways. Some may condense on the membrane as small droplets distributed in a haphazard fashion, hence forming a liquid equivalent to the previously described dull coating of crystalline powder. Other liquids may adhere completely, forming a layer of perfectly smooth surface. Since a thickness of a few tenths of a micron suffices for the layer, the internal friction prevents the flowing of the liquid.

Very small changes in thickness of the liquid layer can easily be observed in two ways. The layer may be formed on a dull surface presenting microscopic irregularities which are filled by the liquid, the outer surface of which is perfectly smooth and clear; at evaporated spots, the surface again becomes dull. This is a sensitive method, but the equilibrium of the liquid with its vapor is not perfect, since the vapor pressure at any given point will depend on the local thickness, or rather on the local curvature, caused by the irregularities of the rough underlying surface. If the layer is deposited on a clear underlying surface, small variations in thickness can be made apparent and measurable by interference colors.[12] According to Czerny and his collaborators, this is by far the most satisfactory method.

Measurement of small changes in thickness by observation of the interference colors.—Let m (Figure 1) be the thickness

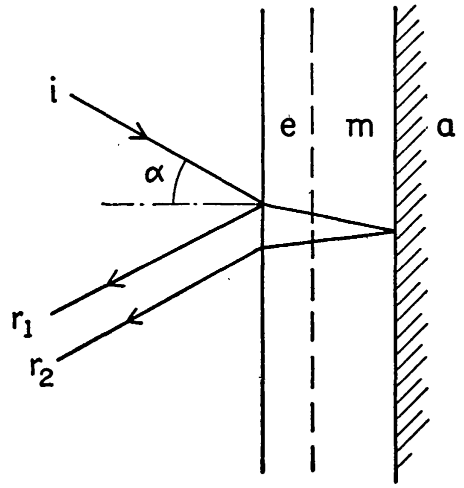

FIG. 1.—Diagram illustrating how small changes in the thickness of the evaporating or subliming layer, e, of an evaporographic receiver can be determined from the colors produced by the interference of the reflected rays r_1 and r_2. The radiation falls on the absorbing layer, a.

of the membrane; e, the thickness of the evaporating or subliming layer; a, the absorbing layer; i, an incident ray; r_1 and r_2, the rays reflected at the front surface of the evaporating layer and the back surface of the membrane; and α, the angle of incidence. If the refractive indices of the evaporating layer and membrane are not very different, $e + m$ may be considered as a single layer of index n. The reflected light will be colored as a result of the interference of the rays r_1 and r_2. Intense interference colors will be observed if n is large and if low orders of interference (1st to 3d order) are obtained. The difference Δ in light-path between r_1 and r_2 should thus, if possible, be smaller

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[12] Dyes of sufficient volatility do not exist.

than 3λ, where λ is the mean wave length of the light used in the experiment ($\lambda \simeq 0.6\,\mu$). We have

$$\Delta = 2\,(m+e)\sqrt{n^2 - \sin^2\alpha} + \frac{\lambda}{2}$$

or in normal incidence

$$\Delta = 2\,(m+e)\,n + \frac{\lambda}{2}.$$

The condition $\Delta < 3\lambda$ leads, in the case of normal incidence, to

$$m + e < \frac{5\lambda}{4n},$$

or approximately (for $n \simeq 1.5$)

$$m + e < 0.5.$$

This condition is easily fulfilled since properly prepared membranes $0.05\,\mu$ thick have sufficient strength for surfaces of a few square inches.

The initial thickness $m + e$ which gives the violet interference color is the most favorable for visual observations, since that color varies most for a small change in thickness. This thickness is $m + e = \frac{0.56}{n}\,\mu$ or $\frac{0.28}{n}\,\mu$, for which a change in thickness of as little as $0.005\,\mu$ produces a perceptible change in color. For a liquid layer deposited on the membrane by evaporation in vacuum, the optimum thickness is easily obtained by watching the formation of the deposit on the membrane and interrupting it when the violet interference color is reached.

If a vertical membrane covered with liquid is used, the liquid should not flow, otherwise changes in thickness would appear, but a simple calculation shows that the flow is much too slow to become a source of trouble. For a vertical membrane, however, the barometric variation of the vapor pressure with height brings about a change in thickness which is a function of the height along the membrane as well as of the time. This variation can definitely be of practical importance, so that horizontal or inclined membranes may be preferable for fairly long exposures. Finally, surface tension reduces the contrast between neighboring regions which have been very differently evaporated. For example, if "lines" separated by 0.1 mm are formed with initial "depths" of 50 μ in a layer of tridecane,[13] the "depths" will be reduced to 25 μ after 23 minutes. This effect may be of great importance in astronomical applications.

Choice of the evaporating liquid. — The experiments by Czerny, *et al.*, were mainly with oils. A number of conditions must be fulfilled by the liquid, In order to give specific interference colors, the substance must form a uniform layer on the membrane, not a granulated agglomeration of small droplets. Paraffin oils of low refractive index have a tendency to form such droplets (diameters of the order of 100 μ), which reduce the resolution of the "plate." On the other hand, the "plate" must not be too slow; this means that paraffin oils of high refractive index which have a small saturation pressure are objectionable. A satisfactory liquid should have a vapor pressure of the order of 10^{-2} mm.[14] The substance should be as inert as possible, and should attack neither the membrane, nor any other part of the instrument (metallic parts, windows, packing, cement). Another essential requirement is that the liquid layer should have a sufficiently long life and not evaporate in a matter of seconds. Although the basic principle of the evaporographic method is to place the subliming or evaporating layer in an atmosphere where it is in equilibrium with the vapor, this primary condition of long life is at present the least satisfactorily fulfilled, and a good deal of experimental work will still be required to improve the situation.

Mixtures of liquids having different saturation pressures are excluded because in preparing a layer with such a mixture by vacuum distillation, the most volatile constituents of the heated mixture evaporate first and deposit on the membrane. The layer thus formed having a slightly higher vapor pressure than the stock mixture, and therefore not being in equilibrium with it,

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[13] One of the paraffin oils ($C_{13}H_{28}$) used by Willenberg.

[14] Glycerol is excluded because its vapor pressure is too low; decahydronaphthalene because its vapor pressure is too high; 1-bromonaphthalene because it forms droplets; ethyl benzenecarboxylate because it destroys the membrane.

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will distill away from the membrane. Various attempts have been made to obtain a layer having the same vapor pressure as the stock mixture, for example, by first covering the membrane with a layer of oil of low volatility to which an oil of higher volatility is then added. But these attempts have not met with success, especially since the "sensitivity" of the plate was then considerably reduced. Even assuming that it may be possible to deposit an oil layer having exactly the same composition as the stock mixture, difficulties will still arise when the membrane is exposed to infrared radiation, although the layer should, theoretically, have an infinitely long life when unexposed. When the layer is irradiated, its most volatile components will evaporate first; when the irradiation is interrupted, condensations take place at the evaporated spots, thus reducing the contrast.

In the first experiments on evaporography using liquid layers, Willenberg, because he could not find satisfactory pure[15] liquids, used a petroleum fraction, a complex mixture of a number of paraffin oils $C_nH_{(2n+2)}$ the boiling point of which was between 260° and 280° C. Despite the unavoidable imperfections, the corresponding evaporographic plate was about 50 times as sensitive as a membrane with a naphthalene coating.

In subsequent experiments, Mönch and Willenberg used, instead of a mixture, a synthetic saturated hydrocarbon $C_{14}H_{30}$ (tetradecane), which was supposed to have a specific vapor pressure. Yet, contrary to their expectations, the $C_{14}H_{30}$ layer disappeared without any illumination, just about as fast as did the layers of complex petroleum mixtures previously used. Mönch and Willenberg thought that this was possibly because the stock substance was not sufficiently pure.

Czerny and Mollet made a systematic study of a large number of paraffins in the following way. They subjected a technical paraffin oil to multiple vacuum distillations and obtained a series of substances having properties varying in an almost continuous sequence. The refractive indices of the substances resulting from the distillations were measured with a sensitive Abbe-refractometer at a constant temperature. Half a dozen distillations

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[15] The expression "pure liquid" refers to a substance that is not a mixture.

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were applied, each distillation stage giving rise to four or five components, each of which could then be subdivided again into four or five components. Many components were investigated for possible use in infrared photography, the conclusion being that only a fairly narrow group of oils with refractive index near $n_D = 1.4655$ at 22° C could be used.[16] These oils gave very homogeneous layers which did not evaporate too quickly. Yet, just as Willenberg and Mönch found with tetradecane, the oil layers prepared by Czerny and Mollet had a life of only a few minutes, even when shielded carefully from infrared radiation. At the time of the last publication available to me, Czerny had not succeeded in avoiding the short lifetime of the oil layers, which, however, were sensitive enough to give good laboratory results.

This difficulty is very serious for astronomical applications, since it prevents the cumulative effect of long exposures. But since there is no theoretical reason why liquid layers of long life and high sensitivity cannot exist, one may hope that the investigations carried on during the war in organic chemistry will reveal compounds that are more satisfactory than those studied by Czerny and his collaborators. The collaboration of organic chemists, physicists, and astronomers would certainly be desirable in this connection.

General description of an evaporographic camera.—From the preceding description and discussion of the receiver, the general form of the evaporographic camera is obvious. An enclosure that can be evacuated to a pressure of about 0.01 mm has on one side a well-polished rock-salt window, and on the other side a plane-parallel glass window. The oil is vaporized on a small electrically heated coil in the enclosure itself. The membrane is placed on a ring in such a way that it is in contact as little as possible with the walls, which become covered with oil, hence contaminate easily the black coating (the latter should not extend to the edge of the membrane).

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[16] The refractive indices of n-tridecane ($C_{13}H_{28}$) and n-tetradecane ($C_{14}H_{30}$) are respectively 1.4419 (at 16.8° C) and 1.4459 (at 20° C). Pentadecane is still a liquid (refractive index not available), but hexadecane and heavier n-paraffins are solid at temperatures lower than 18° C.

The infrared spectrum under investigation is focused on the black side of the membrane, through the rock-salt window. To observe the local changes in thickness which give a picture of the infrared spectrum, a parallel beam of light which has been filtered of all its infrared, red, and orange is thrown normally on the oiled surface of the membrane after reflection by a half-reflecting plane mirror. The interferences are then viewed or photographed normally to the surface of the membrane, through the half-reflecting mirror. When the photograph has been taken, a simple exposure of the membrane to the unfiltered radiation of a lamp evaporates the remaining oil, making the membrane ready for a new oil coating.

RESOLUTION AND SENSITIVITY OF AN EVAPOROGRAPHIC PLATE

As mentioned before, the resolution attainable depends on the type (absorbing black or metallic reflector) and thickness of the absorbing layer, since the widening of the lines is mainly due to the thermal conductivity of the membrane, although other factors, such as the transverse flow of the liquid, also play a role. Numerous experiments by Willenberg and by Czerny and Mollet have shown that two lines 40 μ wide and 100 μ apart can easily be separated on a blackened membrane. Actually, the reproductions published by Czerny and Mollet indicate that lines as close as 70 μ would still be separated. This would mean that a properly prepared evaporographic plate has a resolving power comparable to that of a photographic plate of average grain size. When aluminum instead of bismuth black is used as the absorber, the resolution is lower: lines 200 μ apart are still separated, but not those 100 μ apart.

The line sharpness attainable by evaporography would probably suffice for many astronomical problems in which broad bands or lines are studied. Moreover, the spectral purity would be improved by an increase in linear dispersion, even with the slit width increased so that the speed of the instrument remained the same. Obviously, the dispersion and spectral range are limited by the size of the membranes that can be prepared having the desirable constancy of their properties.

Experiments by Czerny and Mollet have shown that the sensitivity of the evaporographic method compares favorably with that of the most sensitive thermal receivers, such as the microradiometer. Moreover, the evaporographic plate exceeds the thermoelectric receiver in speed: only a very complex thermoelectric infrared spectrometer can, at present, record in one minute a whole infrared spectrum with many details.[17]

Czerny and his collaborators have also compared the sensitivity of the evaporographic method with that of the ordinary photographic plates at wave lengths 0.9, 1.05, 1.2, and 1.3 μ. For comparison, Agfa-infrared plates 1050, not hypersensitized with ammonia, were used with suitable colored filters. At 0.9 μ the photographic plate was definitely faster than the evaporographic receiver; at 1.2 μ they had approximately the same speed; at 1.3 μ (and, of course, beyond) evaporography was definitely faster.

As long as the exposure time did not exceed four minutes in Czerny's experiments, the time required for the appearance of a trace of evaporographic image was approximately inversely proportional to the intensity of the illumination; this was tested by varying the distance of the source and by using a rotating sector. Exposures longer than four minutes gave irregular results, a phenomenon certainly related to the spontaneous disappearance of the oil layer.

Although the evaporographic method is still in its pioneering stage and doubtless can be considerably improved, the present results on the sensitivity and resolution are most gratifying.

EXAMPLES OF SPECTROSCOPIC LABORATORY APPLICATIONS

The papers published by Czerny and his collaborators describe several interesting spectrographic results obtained by evaporography. As tests for the method, the most typical examples concern the rotational structure of the 3.46 μ band of gaseous hydrochloric acid, the double structure of the 4.3 μ band of carbon dioxide, and the details of the 6.3 μ band of water vapor. With an exposure of only one minute, the separate rota-

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[17] See, for example, E. B. Baker and C. D. Robb, *Rev. Sci. Instr.*, **14**, 362, 1943.

tional lines of the band of HCl at 3.46 μ, which are approximately 0.03 μ apart, appeared very clearly on a low-dispersion spectrogram. In the CO_2 band at 4.3 μ the two components which are separated by 0.055 μ were clearly resolved: the corresponding distance on the evaporographic plate was 0.09 mm, which indicates an excellent resolving power. More than 25 separate absorption lines of H_2O were measured in the 6.3 μ band; the wave lengths obtained agreed well with those obtained with thermoelectric receivers. Liquid dichloromethane (CH_2Cl_2) showed a very detailed spectrum in the region from 1 to 2.2 μ, with an exposure of ¼ minute. All the exposures mentioned were on a membrane blackened with bismuth black. Using an aluminum absorbent instead, Czerny and his collaborators obtained with exposures of one minute, excellent spectra of liquid 2-furancarbonal ($C_4H_3O \cdot CHO$), extending beyond 9 μ. The absorption bands obtained with the metallic coating were as expected, a little less sharp and contrasty than those obtained with a black coating.

LIMITATIONS AND POSSIBILITIES OF THE METHOD

In its present state, the main drawback of the evaporographic method is the limited exposure time. Another difficulty is the occasional spottiness of the pictures, which, however, is reduced when dust and impurities are carefully avoided during the preparation of the membrane. Moreover, the lacquer used by Czerny for preparing membranes was not optically clear. These two limitations seem to be of a purely technical nature. It should be possible to overcome them, so that a cumulative method of infrared photography of high resolution and of satisfactory sensitivity would become available to the astronomer. Great care will have to be taken in the photometric reductions of an evaporographic exposure; but it will probably be possible to overcome the difficulties by proper calibration.

Obviously, all the considerations discussed in this paper apply to direct photography as well as to spectrography. Promising laboratory experiments have already been made on infrared photography, such as the photographing purely by its thermal radiation a blackened bottle containing hot water.

It may be hoped that once evaporography has been rendered more practical, its applications to astronomy will be of considerable interest both in direct photography and in spectrography. There is scarcely any field of astronomy to which applications of evaporography could not be dreamed of. The applications should start with the infrared spectrography of the sun for which high dispersion data have already been obtained with thermoelectric receivers.

December 21, 1944