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New Instruments and Methods of Measurement

METHODS AND EQUIPMENT
FOR LONG-WAVE INFRARED SPECTROSCOPY

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I. INTRODUCTION

In the present work the whole infrared* range of the optical spectrum, extending from the red limit of the visible spectrum towards the longer wavelengths and overlapping the region of millimeter radio-waves, is assumed to be divided into three regions [1, 4, 5]: a) a short-wave region bounded by the wavelengths 0.75 and 2.5 μ (13,300 - 4,000 cm^{-1}), b) a medium-wave region 2.5 - 50 μ (4,000 - 200 cm^{-1}) and c) a long-wave region covering a large range of wavelengths from 50 μ (200 cm^{-1}) to 1000 μ (10 cm^{-1}) and more.

Within the short-wave portion of the IR spectrum, i.e. in the "very near" IR region, are situated the bands corresponding to the overtones and component frequencies of the fundamental vibrations of molecules, as well as lines and bands of the electron-vibrational spectrum of atoms and molecules.

The medium-wave range (2.5 - 50 μ) contains mainly bands corresponding to the fundamental vibrational frequencies of light molecules and individual atomic groups. (This spectral region is therefore sometimes called the region of fundamental vibration frequencies.)

Methods of measurement of IR spectra in the wavelength region from 0.75 to 50 μ do not present much difficulty at the present time and they find wide practical application in research and factory laboratories. For studies in the short-wave IR region, which is most accessible to experiment, spectrometers

* For brevity the word "infrared" will henceforth be replaced by the abbreviation IR.

with glass or quartz prisms, are usually employed along with standard tungsten incandescent lamps in glass bulbs as sources and photocells or photoresistors as detectors.* Spectrometers designed for work in the medium-wave IR region make use of prisms made from crystals of alkali halide salts, including the cesium iodide crystal which is transparent up to $50 - 55\mu$, and have as sources Nernst or Globar filaments (IKR-1 filaments, silicon carbide rods) heated by an electric current; heat detectors are employed, metallic and semi-conducting thermoelements and bolometers, as well as optico-acoustic (pneumatic) receivers. For obtaining high resolution with these instruments, as also with spectrometers for the short-wave IR region, the prisms are replaced by diffraction gratings - echelettes with a large number of lines.

Techniques and instruments for producing and recording IR spectra in the $0.75 - 50\mu$ region have been well developed and are described fully enough in home and foreign surveys in the literature [1-5].

In the long-wave IR region, i.e. in the wavelength range from 50 to 1000μ and more, are located absorption and transmission bands corresponding to the variation of the rotational energy of gas and vapor molecules, as well as low-frequency vibrational bands of heavy molecules, radicals and molecular complexes. In addition this region contains various component (difference) frequencies of fundamental vibrations of various molecules, and also inter-molecular vibration frequencies.

Investigation of the long-wave IR spectra of different gaseous substances opens up the possibility of a direct study of their molecular structure (determination of molecular moments of inertia, interatomic distances and other molecular constants).

Investigation of the low frequencies of intra- and inter-molecular vibrations in solid and liquid bodies is essential to the study of crystal structure, the nature of the liquid state and molecular interactions. There are also other fields of application for long-wave infrared spectroscopy and this technique is now being used to study the optical and electrical properties of semiconductors and dielectrics in the region of longer waves [40, 42].

The application of the method of long-wave spectroscopy is apparently also of great value in the study of light-scattering by dispersed bodies (powders) and its dependence on the size of the scattering particles, their form and spatial distribution. The purpose of this investigation might be to establish the laws governing scattering of radiation by artificially modelled

* Hence the short-wave IR region is sometimes named the "photoelectric" region.

dispersed media with accurately predetermined geometrical parameters, comparable with the wavelength.

Finally, the recently established bands in the terrestrial atmosphere, transparent for electromagnetic vibrations with wavelengths of about 1500μ (1.5 mm) give us grounds for believing that long-wave IR spectroscopy will find an application also in astronomical spectral investigations, for example, in determining the temperature of planets [6].

In spite of the fact that long-wave infrared ("heat") radiation was discovered exactly 60 years ago [11], it was a long time before it was applied in molecular spectroscopy. This was due to the great experimental difficulties connected mainly with the very low energy in the long-wave IR spectrum, and also with the lack of high-sensitivity recording and detecting devices. It is only in recent times, thanks to the progress in techniques for detecting weak radiation and methods of amplifying weak currents, as well as to the development of new large-aperture diffraction gratings (echelettes) and aspherical reflecting optics of large size, that the long-wave IR region has begun to be applied in increasing degree to the solution of various problems of physics and chemistry. Nevertheless, the number of works devoted to studies in this spectral region is still very small.

In the present survey, which makes no claim to completeness, an attempt has been made to systematize the information relating to methods of long-wave IR spectroscopy and the equipment developed in recent times both at home and abroad for producing and recording spectra in the wavelength region up to 1600μ .

II. METHODS OF ISOLATING LONG-WAVE INFRARED RADIATION

The following methods may be used for obtaining long-wave infrared monochromatic radiation: 1) the method of focal isolation using quartz lenses, 2) the method based on total internal reflection, 3) selective reflection from crystals (method of "residual rays") and 4) monochromatization by means of diffraction gratings.

The first three methods possess low resolving power, yet they have definite advantages over the fourth in view of their simplicity and the great energy of long-wave radiation obtained. On the other hand, these methods are

unsuitable in cases where high resolution is required, e.g., in studying the rotational spectra of molecules. In these cases it is essential to monochromatize the radiation by using diffraction gratings.

1. Method of quartz lenses

The method of focal isolation of long-wave IR emission using quartz lenses was first carried out by Rubens and Wood [7] in 1910.* The method is based on the fact that quartz which is transparent in the long-wave region possesses a higher refractive index (of the order of 2.5) in the region of

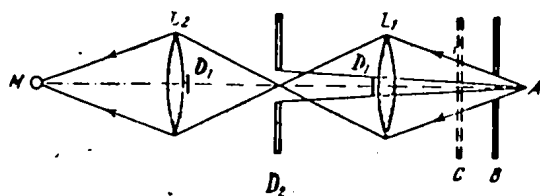


Fig. 1. Method of quartz lenses [7].

wavelengths greater than 50μ , while in the short-wave and visible spectral region its refractive index is approximately equal to 1.5.

Fig. 1. depicts the main scheme of an assembly for isolating long-wave emission by the method of quartz lenses. The quartz lens L_1 refracts the long-wave emission from the radiation source A more strongly than the short-wave emission. The diaphragms of black paper D_1 and the metal screen D_2 with aperture ensure that only the long-wave emission falls into the space behind D_2 . For further increasing the homogeneity of the radiation, a second lens L_2 repeats the action of the first lens. This is necessary to remove the short-wave radiation scattered at the surface of the lens L_1 and to focus the long-wave radiation on the detector M.

The dimensions of the apparatus of Rubens and Wood were as follows: the diameters of the effective aperture of both quartz lenses was equal to 7.5 cm, their thickness at the edges was 0.3 cm, and in the middle, 0.8 cm;

* Before Rubens and Wood this method was used for achieving monochromatic ultraviolet emission by Lenard [8] who should be considered as the inventor of the method of quartz lenses. The so-called focal monochromators for the ultraviolet region which are still in use at the present time [9], are based on this method.

the focal length of the lenses for visible rays was 27.3 cm, and for long-wave IR radiation, approximately 12 cm. The diameters of diaphragms B and D₂ were equal to 15 mm, and diaphragm D₁ - 5 mm.

With the total thickness of quartz used in the apparatus there is no transmission at all up to 80 μ , while at 95 μ the transmission is only 20% of the incident long-wave radiation and with increase of wavelength the transmission increases. In view of this the curve of spectral distribution of energy falls rather steeply towards the shorter wavelengths, and considerably more slowly in the long-wave direction.

For measurement of the wavelengths isolated by the apparatus, which depend on the relative positions of lenses, source and detector, an interferometer consisting of two quartz plates is placed in the path of the rays at D₂. A glass plate C, opaque to long-wave radiation, serves as a shutter during measurement.

The method of quartz lenses, as well as the method of "residual rays" described below, were widely applied in early studies on the transmission and reflective power of various materials in the region of longer wave-lengths [14, 15]. On account of the very low resolution, however, it cannot be used for investigating the rotational spectra of molecules.

2. Method of total internal reflection

In 1928 Ientzsch and Laski [10] suggested a simple method of isolating any spectral portion in the region of wavelengths 80 - 100 μ . As is known, total internal reflection of radiation does not occur exactly at the boundary between the two media, but in some region of the second medium, having a depth of the order of the wavelength. If another plate made from the material of the first medium is placed in the second medium close to the reflecting surface, then part of the radiation penetrating into the second medium passes into this plate and is not returned in the reflected beam. The limiting width of the air gap for which radiation of a given wavelength still reaches the second plate depends on the wavelength and increases with the latter. By using this fact it is possible to construct an instrument, a diagram of which is shown in Figure 2. A cube I, made from material transparent to long-wave radiation, stops the short-wave radiation, deflecting it in the direction 1; the remaining longer-wave radiation is again divided at cube II, which has a greater air gap,

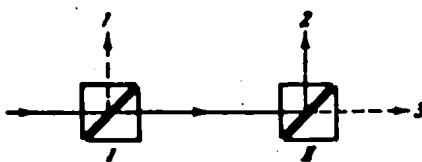


Fig. 2. Method of total internal reflection [10].

into two portions, the long waves being transmitted in the direction 3, while the shorter are deflected in direction 2, where we obtain an approximately monochromatic beam, the degree of monochromatization and mean wavelength of which depends on the thickness of the air gaps of cubes I and II.

This method for producing monochromatic long-wave emission, however, did not find wide application because of the small aperture, lack of sufficiently transparent materials for the long-wave IR region and the necessity for mechanical adjustment of the prisms of both cubes so that the small air gap between them is accurately fixed.

3. Method of "residual rays."

The most commonly used method of isolating sufficiently narrow regions of long-wave emission is the method of "residual rays," which is based on the property of crystals to selectively reflect (and absorb) radiation in the regions of anomalous dispersion, i.e. close to the characteristic vibration frequencies of the crystalline lattices, where the so-called "metallic" reflection is observed. This method, proposed as early as 1897 by Rubens and Nichols [11], is still applied in various investigations at the present time [12].

The principle of the "residual rays" method is the following. Let r be the reflecting power of a given substance in the region of "metallic" reflection. Then

$$r = \frac{(n-1)^2 + n^2 x^2}{(n+1)^2 + n^2 x^2}$$

r differing little from unity, since in the region of anomalous dispersion $2n$ is small in comparison with $n^2 x^2 + n^2 + 1$. Further, let ρ be the reflecting power of a substance in the region of normal dispersion, in which Fresnel's formulae still hold, i.e.

$$\rho = \frac{(n-1)^2}{(n+1)^2}$$

We will denote by i the ratio of intensities in two portions of the continuous spectrum, one of which lies in the region of anomalous, the other in the region of normal dispersion. After k -fold reflection from the surface of the given substance this ratio becomes equal to $i_k = i(r/\rho)^k$. If, for example, $i = 1$, $r = 0.9$ and $\rho = 0.45$, then after fourfold reflection $i_k = 2^4 = 16$, whereas after a single reflection i_k is equal to only two. Thus, by means of multiple reflections it is possible to isolate from the spectrum a fixed interval of wavelengths, namely that lying close to the characteristic vibration frequency of the crystal lattice of the substance. This explains the term "residual rays," applied to radiation isolated by this method.

For obtaining "residual rays," only the greatest reflection maxima of crystals can be used, since otherwise the intensity of long-wave radiation, of which r^k serves as a measure, is too small. The degree of homogeneity of the residual rays depends not only on the number of reflective surfaces, but also on the intensity distribution in the spectrum of the incident radiation. The wavelength, corresponding to the maximum of the isolated radiation, also depends on these circumstances, since i differs from unity.

A comparison of the behavior of the reflecting power for the series of crystals usually employed at the present time as reflectors in the described method* is given in Figure 3, which is taken from work [13].

To the data of the Figure, which represents a selection of crystals suitable for the "residual rays" method, we should add some information on the reflective power of crystalline InSb [17] and KRS = 5 [44] (a mixed crystal of TlI + TlBr). The first of these has a sharp maximum with 90% reflection at 54.6μ the second a flatter peak (75%) at 200μ . Suitable crystals for the longer-wave region have not yet been found.

In instruments designed for isolation of long-wave radiation by the "residual rays" method (diagrams of which are shown in Fig. 4), use is usually made

* Information on the reflecting power of other crystals, and also data on the properties of various materials in the region of longer wavelengths may be found in a survey of early works on long-wave IR spectroscopy, carried out by Weniger [14] in 1923, and also in the monographs of Shaefer and Matossi [15] and Parodi [16].

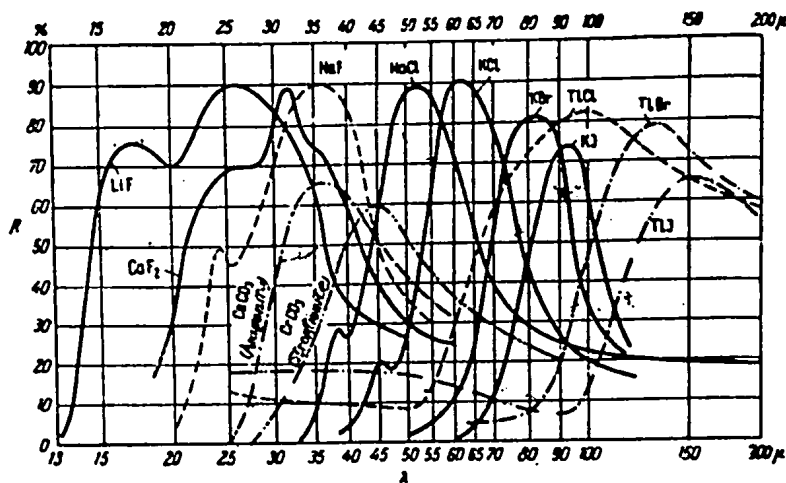


Fig. 3. Reflection from surfaces of crystals [13].

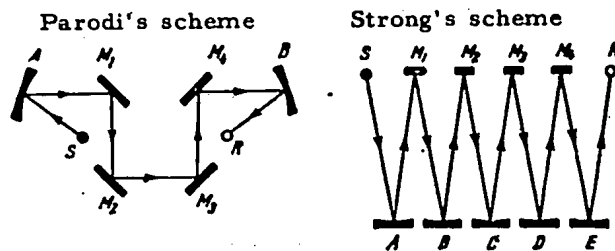


Fig. 4. Method of residual rays [16]; M_1, M_2, M_3, M_4 — crystals, A, B, C, D, E — spherical mirrors, R and S — receiver and source of radiation,

of three or four reflections from plane crystal surfaces. Here the half-width of the spectral portions isolated, e.g. for the case of crystals of NaCl (reflection peak at 52μ), KCl (62μ) and KBr (83μ) is equal to 43, 39 and 24 cm^{-1} respectively [12].

It is possible to design a scheme which would permit a much greater number of reflections to be produced from the surface of the same crystal and thus to increase several times the degree of monochromatization (purity) of the isolated radiation. Such schemes could be based on the methods of multiple reflections proposed by White [18], and also by Bernstein and Herzberg [19] for obtaining long optical paths in gas cells of relatively small size.

A diagram of an instrument constructed in accordance with White's method is shown in Figure 5. Two identical concave spherical mirrors A_1 and A_2 and a rectangular crystalline plate with a concave spherical surface B , having the same radii of curvature, are placed so that the center of curvature b of the plate lies between the mirrors A_1 and A_2 , the centers of curvature a_1 and a_2 of which must in turn lie symmetrically, at a certain distance from each other, on the spherical surface of plate B . Then the radiation entering the instrument through the entrance slit S_1 , will be reflected several times and will be focused on the surface of the crystalline plate B before it leaves through the exit slit S_2 of the instrument.

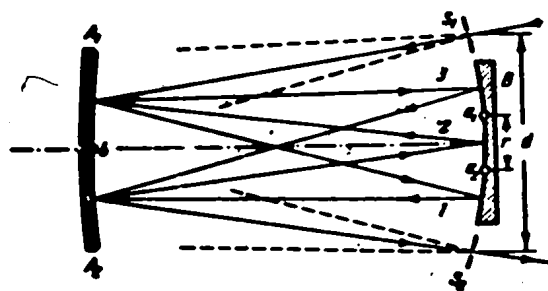


Fig. 5. Obtaining multiple reflections from a crystal.

It is easy to see from Figure 5 that the number of reflections from the crystal (or the number of intermediate images of the entrance slit S_1 on its surface) is always odd and is equal to

$$n = \frac{d}{r} - 1,$$

where d is the distance between the entrance and exit slits and r is the distance between the centers of curvature of the mirrors A_1 and A_2 .

Thus for a fixed d the number of reflections, and hence also the degree of isochromatization of the isolated radiation will depend only on the angle of rotation of the mirrors A_1 and A_2 round their common center b . With r sufficiently small ($< 5\text{mm}$) and the actual dimensions of the crystalline plate ($55 \times 10 \times 8\text{mm}$) we can apparently obtain with this arrangement more than 10 reflections. A change to other wavelengths can easily be accomplished by

substituting plates made from different crystals (according to the data of Fig. 3) which are fixed to the common movable stage.*

The advantage of the "residual rays" method lies in the fact that by comparatively simple means it enables the production of long-wave radiation of high intensity and of relatively high homogeneity. Drawbacks of the method are that the limit of its application in the long-wave region lies at 200μ , and the fact that it is impossible to isolate a desired wavelength from a continuous spectrum. Nonetheless this method is used at the present time not only for obtaining information about the transmittance and reflecting power of various materials in the long-wave IR region [15], but also for studying the fundamental vibration frequencies of certain organic and inorganic substances, e.g. cis- and trans-dichloroethylene, 1,2-dichloroethane, methyl and propyl alcohol, acetaldehyde, n-hexane, n-pentane and carbon suboxide (C_3O_2) [12].

4. Monochromatization by means of diffraction gratings.

Great successes in the analysis of infrared radiation have been achieved with the help of diffraction gratings, the application of which alone permits the attainment of high resolution in the long-wave region of the spectrum.

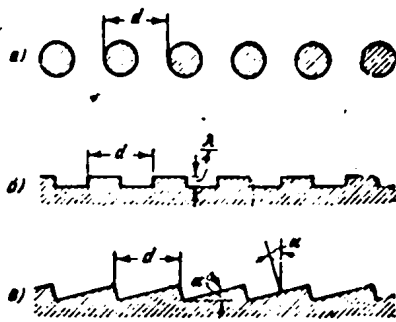


Fig. 6. Profiles of diffraction gratings: a) wire, b) laminar, c) echelette.

*Note that when using crystalline plates in the longer wavelength region there is no necessity to prepare them with an accurately polished spherical surface since a mat surface scatters short-wave radiation and is a good reflector for long waves; besides this, such plates can apparently be prepared by pressing or by deposition of crystalline layers on a spherical glass surface by evaporation of the substance in vacuo or by precipitation from solutions.

Prisms cannot be used since at present there are no materials which in thick layers are sufficiently transparent in the wavelength region $> 50\mu$ and which are suitable for making prisms.*

In early investigations of long-wave IR spectra transmission wire [21] and reflection laminar (plate) [22] gratings were employed (Fig. 6, a and b). In recent years and at the present time exclusive use is made of reflection stepped echelette gratings [23] which, because of the specially chosen groove profile (Fig. 6, c) are capable of concentrating the greater part of the incident energy in a narrow region of diffraction angles, for example, in the region of one of the first orders. In the most favorable conditions the intensities of long-wave radiation isolated by using wire, laminar and stepped (echelette) gratings are in the ratio 1:4:10. [13].

The wavelength distribution of the spectrum given by reflection gratings is described by the known equation

$$m\lambda = d(\sin\phi \pm \sin\psi),$$

where m - spectral order, d - grating constant, and ϕ and ψ - angles of incidence and diffraction, **

If the spectrum is scanned by rotating the grating at fixed angles of incidence and reflection, which is the usual procedure in spectrometry, the wavelength will be

$$m\lambda = 2d \cos \frac{\theta}{2} \sin \beta$$

or $m\lambda = K \sin \beta$, where θ - angle between the directions of incidence and diffraction, β - angle of rotation of grating (Fig. 7) and K - instrument constant.

The relative intensity distribution, for example in the first order spectrum of the echelette, which depends on the wavelength and the groove form of the echelette surface, is determined from the expression

*As early as 1898 Rubens and Aschkinass [20] made an attempt to isolate long-wave radiation by using acute-angled quartz prisms. Yet the result was unsatisfactory, since they did not succeed in removing the short-wave radiation to the desired extent.

**In this formula the (+) sign corresponds to the case where the incident and diffracted rays lie on one side of the normal to the grating, and the (-) sign when these rays lie on different sides of it.

$$J_{\text{rel.}} = \left(\frac{\sin \frac{\pi \Delta}{\lambda}}{\frac{\pi \Delta}{\lambda}} \right)^2$$

where in the case of small values of the angle between the directions of incidence and diffraction ($\theta = 0$) Δ has the value

$$\Delta = 2d \sin(\beta - \alpha),$$

where d — echelette constant, β — angle of its rotation and α — angle of inclination of step (see Fig. 6, c).

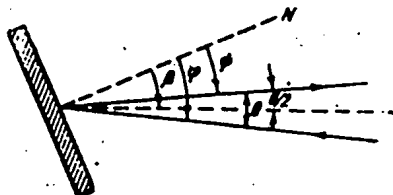


Fig. 7. Reflection from echelette.

It is easy to see that the maximal intensity will be possessed by radiation diffracted in the direction of specular (geometric) reflection from the working surfaces of the echelette steps. This direction is sometimes called the "blaze" of the echelette and the angle between this direction and the normal to the echelette surface is called the "blaze" angle.

The application of diffraction gratings requires the exclusion of higher order spectra which overlap the fundamental spectrum in the form of an unwanted background. A preliminary monochromatization by means of a low-dispersion prism is usually employed for separating the orders in spectrometers with diffraction gratings designed for work in the near and medium IR regions. In spectrometers for the long-wave region such a method is inapplicable and the exclusion of the rich energies of higher order spectra, as well as the removal of scattered short-wave radiation, is realized by employing the described methods of quartz lenses and "residual rays" and by the use of various transmission and reflection filters, and also by the application of the method of selective modulation which will be discussed below.

The ratio of the energies of the interfering (short-wave) to the isolated (long-wave) radiation is particularly high in working at the "blaze" angles of

echelettes. Outside the "blaze" angles this ratio is much lower. Nevertheless the elimination of interfering radiation, the energy of which is many times that of the wanted radiation, presents great difficulties.

We will consider one other method of isolation of long-wave radiation, first proposed by Walsh in 1952 [24].

The method is based on the application of reflection zone plates, the profile of which is similar to the echelette profile. The action of such plates is analogous to the focusing action of the transmission zone plates of Fresnel, but because of the specially selected profile of the reflecting ring zones there results a considerable gain in the energy of the IR radiation isolated in a fixed direction.

Consider a parallel beam of radiation falling on an echelette zone plate, the radial section of which is depicted in Figure 8. Then radiation of wavelength λ diffracted by the plate will be focused at a point O situated at a distance f from the center of the plate subject to the condition

$$r_n = [n\lambda(2f + n\lambda)]^{1/2},$$

where n - number of zones, r_n - their radius.

The profile of the reflecting ring zones can be chosen in such a way that the direction of a diffracted beam of a given wavelength coincides with the

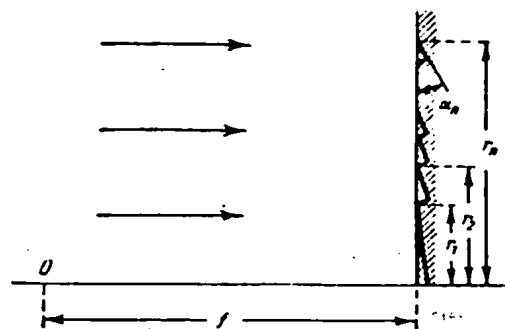


Fig. 8. Radial section of an echelette zone plate.

direction of specular reflection from the surface of each zone, as occurs in the echelette. Then the angles of the zone steps, dependent on their radius, to a first approximation must be equal to:

$$\alpha_n = \frac{1}{2} \arctg \left(\frac{r_n}{f} \right).$$

If by means of a specially constructed lathe, echelettes can be cut, the ring zones of which satisfy the two given conditions, then these echelettes, according to Walsh, may be effectively used in a large-aperture (with relative aperture less than $f/2$) spectrometer for isolation of long-wave radiation in the region 50 to 500 μ . One of the possible schemes of such a spectrometer is depicted in Figure 9. Radiation of a given wavelength from source S is collimated by the zone plate Z_1 and then is focused on the detector D by a similar

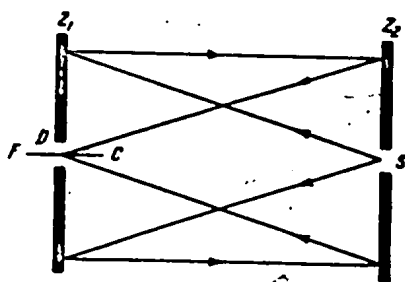


Fig. 9. Schematic diagram of long-wave IR spectrometer with echelette zone plates [24].

plate Z_2 . Radiation of other wavelengths will be focused at other points lying on the focal curve FC. It may be focused on the detector by varying the distance between the plates Z_1 and Z_2 .

For covering the whole spectral region from 50 to 500 μ several pairs of such zone plates will be required, since one pair of plates isolates only a limited region of wavelengths.

The author of the method thinks that by using the method he proposes, along with the multiple monochromator principle [25] described by him earlier, it will be possible to attain high resolving power in the long-wave IR region.

III. SPECTROMETERS FOR THE LONG-WAVE IR REGION AND THEIR APPLICATIONS

1. Short historical survey

One of the first spectrometers with a wire diffraction grating was the instrument constructed by Czerny [26] in Germany in 1925. In spite of the fact that the instrument possessed low resolution on account of its small aperture, Czerny succeeded in resolving the rotational structure in the vapor spectra of hydrogen halides in the 40 to 100 μ region [27].

In 1929 Badger and Cartwright [28] in America constructed an instrument with a reflection laminar grating and recorded the long-wave IR spectrum of ammonia.

The best of the wire diffraction grating instruments was the Barnes spectrometer [29] constructed in 1934.* This instrument was used to obtain the long-wave IR spectra of water [30], ammonia and heavy ammonia [31], and also benzene in the vapor and liquid states [32]. On a similar instrument Cartwright investigated the spectra of water vapor [33] and the spectra of liquid (ordinary and heavy) water [34].

Spectrometers with wire and laminar gratings, however, did not have sufficient resolution and were not suitable for examining the fine structure of the rotational spectra of molecules. For instance, using the Barnes instrument, in which the slit-widths were 4.42 cm^{-1} at 50 μ , 1.67 cm^{-1} at 100 μ and 1.14 cm^{-1} at 150 μ , it was impossible to resolve the doublets in the ammonia spectrum, the distance between the components of which is equal to 1.33 cm^{-1} .

The first long-wave IR spectrometer of large aperture and high resolving power was developed by Randall [35] in 1932 and was built in Michigan University. As a result of the employment of large-size echelette gratings (250 x 550 mm), high-quality parabolic and elliptical mirrors, as well as sensitive thermoelements, the author succeeded in the 18 to 140 μ region in obtaining under a resolution of 0.5 - 1.0 cm^{-1} the spectra of gaseous NH_3 and PH_3 [36], as well as the water vapor spectrum [37] which is still used at the

*The Czerny-type spectrometer with wire diffraction gratings [29a] constructed by Barnes [26] in 1932, had very poor characteristics. Nevertheless the data obtained on it in the wavelength region from 20 to 135 μ for the transmittance of fused and crystalline quartz of different thicknesses, and also of rhombic sulfur, mica, cellophane, celluloid, black paper and various soot coatings, was of definite interest.

present time for the testing and calibration of instruments designed for work in the long-wave IR region.

In 1938 Randall's instrument was improved [38] by enclosing it in vacuum chambers and employing continuous recording (photo-trace) of spectra by making use of a Firestone resonance galvanometric amplifier. On this apparatus the absorption spectra of heavy water at different vapor pressures have been recorded under a resolution of 0.5 cm^{-1} [39].

In 1939 in Germany, Maar [40] made a diffraction grating with constant 4 mm and used it in the construction of a spectrometer for work in the 200 to 500μ region. As a source of long-wave radiation a high pressure quartz mercury lamp was used while a radiometer specially designed for the long-wave region served as detector. This instrument was used to study the spectra of water vapor [41] and the transmission of some solid dielectrics with the aim of determining their dielectric constants in the long-wave region 0.2 - 0.5 mm.*

Further investigations in the long-wave IR region were renewed only after the war.

In 1950 McCubbin and Sinton [43], using an instrument built by them and which was equipped with echelettes of small size ($73 \times 100 \text{ mm}$) and quartz optics, pneumatic detector and high-pressure quartz mercury lamp attained a resolution of $3 - 5 \text{ cm}^{-1}$ in the study of atmospheric transmission in the 100 to 600μ region, and also obtained the transmission curves in this region for certain gaseous (NCl , NH_3) and solid substances (crystalline and fused quartz, glass, magnesium oxide, polyethylene, polystyrene, paraffin, teflon, mica and crystals of LiF , NaCl , KBr).

In 1952 the same authors [44] produced a large aperture instrument with relative aperture $f/1$, constructed according to Pfund's self-collimation scheme (echelette with hole, parabolic mirror), on which spectra of water vapor in the 100 to 700μ region were obtained under a resolution of $1 - 2 \text{ cm}^{-1}$. In addition, measurements were made of the spectral reflection of crystalline TlCl , TlBr , TlI , PbS , PbCl_2 , ZnS , CsBr , as well as KRS-5 and KRS-6 [45]. In

*A similar instrument with laminar gratings and echelette working in the double Pfund scheme was built later by Meier [42]. This instrument was used in the 150 to 500μ region to obtain the spectra of atmospheric water vapor and to determine the dielectric constants of certain insulators according to their reflecting power in the long-wave IR region.

the same year Oetjen et. al [46] constructed a vacuum recording spectrometer with an echelette having 7 lines per mm, working in the wavelength region 40 to 150 μ . As a radiation source they used a thorium-oxide-coated platinum ribbon heated by an electric current, and as receiver employed a Golay pneumatic detector tuned to the modulation frequency of the light beam at 10 cps. Testing the instrument by obtaining the spectra of water vapor and ammonia at different pressures showed that its maximum resolving power was equal to 0.5 cm^{-1} . Later this instrument was used in the 40 - 150 μ region to measure the rotational spectra of gaseous molecules of HCl, DCl, HBr and NH₃ [47], ND₃ [48], PH₂D and PHD₂ [49], and also the spectra of PH₃, PD₃, AsH₃ and AsD₃ [50] from which the rotational constants of the molecules of these compounds were determined. Recently this instrument was applied in the 20 - 200 μ region to investigate the optical constants of crystalline InSb [17], the transmission of ZnS powder suspended in paraffin and polyethylene [51], as well as the rotational spectra of the molecules HI, DI, DBr, H₂Se, NH₂D and NHD₂ [52] and the spectra of the molecules CO, NO, N₂O in the 100 to 600 μ region [65].

In 1952 in Japan, Yoshinaga and Yamada [53] also built a long-wave IR spectrometer with echelette gratings which they had designed for work in the spectral region 25 μ and beyond. The radiation source in their instrument was a carborundum rod ("Globar"), and the detector was a compensated thermoelement connected directly to a galvanometer. Because of the absence of an amplifying system, and the inadequacy of the echelette, the authors did not succeed in recording radiation of wavelengths greater than 35 μ .

In 1953 Bohn et al. [54] in America and Hadni in France produced recording vacuum instruments for the 20 to 80 μ region. In the Bohn spectrometer two echelettes were used in the first order: one (for the region 22 - 40 μ) had 24 lines per mm, the other (for the 40 - 70 μ range) had 15 lines per mm; the resolution in this case was 1 - 2 cm^{-1} . The Hadni instrument had a relative aperture $f/2.5$ and employed one echelette with 14 lines per mm, which in the second order in the 20 to 60 μ region made it possible to attain a resolution of 0.74 cm^{-1} . In both instruments, fast thermoelements with ac amplifiers were used as detectors. These instruments were used to improve the accuracy of thermodynamic functions by studying the spectra of cis- and trans- dichloroethane [56], ammonia [57] and methyl alcohol [58].

In 1956 Hadni reported on a small spectrometer which he had developed for the long-wave region [59], in which the collimator mirror of focal length 10 cm had dimensions 4×4 cm, and the width of the 16 mm high slits was varied between 0.5 and 1 mm. This spectrometer employed two echelettes with 8 and 4 lines per mm and a Schwarz element with modulation. Interfering radiation was removed by Christiansen filters, and also by selective reflection and selective modulation. The results obtained with this instrument, however, have not yet been published.

An instrument for investigating the region of longest IR waves is the vacuum spectrometer built recently in Western Germany by Genzel and Eckhardt [60].

By using in an Ebert-Fastl apparatus, a set of echelettes with constants 315.5; 625.0; 833.3 and 1250.0μ , a quartz mercury lamp as source and fast metal bolometers with an electronic amplifier and recorder, the authors succeeded in recording with sufficiently good resolution the rotational spectra of water vapor, and also the spectra of gaseous HCN, NH_3 , and H_2S in the region of 300 to 1600μ (1.6 mm). In this case the components of the fine structure of the rotational lines (inversion doubling) in the ammonia spectrum were distinctly resolved and a study was made of their pressure dependence.

Thus, the intermediate region between the optical and electrical (micro-wave) ranges of the electromagnetic spectrum* has now been covered, and the recording of the optical spectrum in this region is being carried out under a resolution, not inferior to that which is usually attained in work in the short-wave and medium wave IR regions.

In concluding the present brief summary of the literature we note that, along with the development of new instruments designed exclusively for studies in the long-wave region of the IR spectrum, attempts are being made at present to use the usual standard prism spectrometers for such investigations. For instance, Plyler and Acquista [62], by removing the prism in a Perkin-Elmer spectrometer and replacing the plane Littrow mirror by echelettes of 57×76 mm with 13 or 7 lines per mm, and also by substituting a window of cesium

* We note that with the application of purely radio techniques it is now possible to obtain spectra in the region of wavelengths below 1 mm. For instance, the rotational spectrum of the OCS molecule in the 0.7 mm (700μ) region has been recorded [61].

iodide (for work in region up to 56μ) or quartz for the window on the thermo-element, have found it possible by applying appropriate reflection filters instead of mirrors to register the absorption spectra of water vapor and certain substituted ethylenes and ethanes in the region 50 to 125μ [63].

The characteristic features of long-wave IR spectrometers and their individual components (sources and detectors of radiation, filters, etc.) will be discussed below and descriptions will be given of the design and construction of certain laboratory instruments, including the prototype of the long-wave infrared spectrometer (DKS-1) constructed in the Soviet Union in 1956 [64]. When this instrument had been completed by enclosing the whole optical system in a vacuum and by employing more sensitive detecting and recording devices it was used to obtain the rotational spectra of water vapor at different pressures in the 20 to 500μ region with a maximal resolution of 0.3 cm^{-1} and accuracy of 0.05 cm^{-1} .

2. Characteristic features of spectrometers and their components

As we noted above, the first and main difficulty in carrying out spectral investigations in the long-wave IR region is the extremely small quantity of energy in the long-wave spectrum of heat radiation sources. Calculation shows that in the case of using a blackbody at temperature 2000°K as source, the value of the energy at wavelength, say, 100μ amounts to one millionth part of the energy at the maximum (at 1.44μ), while the value of the energy at 200μ , according to Table 1 is less than a tenth of that. For actual heat sources the situation is worse still.

Therefore a spectral instrument designed for isolation of long-wave monochromatic radiation must have as large an aperture as possible and at the same time also possess high resolving power.

These requirements can be met by a spectrometer which has an echelette of large size, a short focus collimator mirror and slits of large angular dimensions.

The use of echelettes in such a large-aperture instrument, especially when high-temperature heat radiation sources are employed, requires the surmounting of the second great difficulty in conducting spectral studies in the long-wave region, namely, the necessity to eliminate the energy-rich

TABLE 1

Relative Energy Distribution in the Spectrum of a Blackbody at Temperature 2000°K.

Wavelength in μ	Frequency in cm^{-1}	Relative energy
1.44	6950	1
2	5000	$8 \cdot 10^{-1}$
5	2000	$9 \cdot 10^{-2}$
10	1000	$9 \cdot 10^{-3}$
50	200	$2 \cdot 10^{-5}$
100	100	$1 \cdot 10^{-6}$
200	50	$8 \cdot 10^{-8}$

spectra of higher orders, overlapping the main spectrum, as well as the short-wave radiation scattered in the instrument.

In order to have some idea of the relation of the energies of useful and interfering (short-wave) radiation we will consider Table 2 which gives the relative intensities of different spectral regions diffracted in the "blaze" direction of an ideally reflecting echelette having, say, 7.5 lines per mm and concentrating radiation at $\lambda = 100\mu$ into a spectrum of the first order. The data of the third column of the Table are calculated for a radiation source having a temperature 1300°K and obeying Planck's Law.

We see from the Table that if, for instance, investigations are being conducted in the spectral region at 100μ , i.e. in the "blaze" region of the given echelette, then the ratio of the total interfering (short-wave) radiation to the useful radiation is approximately $1.75 \cdot 10^5$.* Outside the "blaze" angles this ratio is greatly reduced; nevertheless the exclusion of short-wave radiation remains a serious problem.

Hence, in long-wave IR spectrometers effective measures must be taken to eliminate short-wave radiation and, on the other hand, use must be made

*In fact this ratio is somewhat smaller, since the echelette's surface scatters short-wave radiation. Moreover, in the calculation the entrance and exit slits are assumed to be infinitely narrow; with the employment of wide slits the ratio must be still further reduced.

TABLE 2

Relative Intensities of Different Spectral Regions Obtained by Using an Ideal Echelette at the "Blake" Angle and a Blackbody at 1300°K [46].

Spectral Region in μ	Order of Spectrum	Relative Intensity
100	1	1
50	2	8
33.3	3	24
25	4	54
20	5	99
16- $\frac{2}{3}$	6	161
14- $\frac{2}{3}$	7	241
10-13	8-10	1 371
7-10	11-14	3 870
4-7	15-25	~ 25 100
1-4	26-100	~145 000
1-100 μ	1-100	~ 175 000

of radiation sources in which the energies of long-wave and short-wave radiation are in the best possible proportions. Naturally, the detecting and recording systems of such spectrometers must possess the highest sensitivity.

The fact that atmospheric water vapor strongly absorbs long waves out to a wavelength of 1500 μ imposes one other condition on the construction of long-wave IR spectrometers; their optical system must be isolated from the room air and must permit evacuation to pressures of 0.1 - 0.2 mm Hg, at which the absorption bands due to water vapor in air of normal relative humidity (50%) disappear from the long-wave spectrum. We note that no other means (drying of instrument, flushing and filling it with dry nitrogen, etc.) are effective in removing the unwanted absorption of water vapor and hence all modern long-wave IR spectrometers are constructed as vacuum instruments.

A. Radiation Sources

For work in the wavelength region 100 - 150 μ the usual heat emitters are suitable. These include the silicon carbide rod ("Globar"), the Auer-Welsbach mantle which was widely used in early spectroscopic studies, and the positive crater of the carbon arc. The exclusion of short-wave radiation, however, is more complicated when the last method is used.

The silicon carbide rod, employed in works [54] and [64] is only suitable in the region up to 100 μ , since in the longer-wave region its emission is small.

By testing various heat sources in work [46] it was found that the most effective emitter in the 40 to 150 μ spectral region was a thorium-oxide-coated platinum strip heated by an electric current. The dimensions of the strip were 100 \times 7.6 \times 0.13 mm and it was heated to a temperature of 1300°K by a current of about 100 amps. It is believed that this source has a better ratio of short-wave and long-wave intensities than a blackbody at that temperature.

It is quite possible that other high-melting oxides possess the same properties but the appropriate investigations have not yet been carried out.

In the wavelength region from 100 to 1000 μ and beyond, the only radiation source available at present is the high-pressure quartz mercury lamp which gives, as Rubens showed in 1911 [66], a weak continuous emission in the long-wave part of the spectrum.

The continuous long-wave emission of mercury vapor excited in the discharge and its dependence on voltage, current density, vapor pressure, dimensions of the lamp envelope and so on, have been the subject of many investigations since 1938 [67]. Yet even up to the present day there is no unanimity on the nature of this radiation. On one hand it is considered as the result of vibration-rotation transitions in excited quasi-molecules of mercury. According to another hypothesis it arises as a result of braking of electrons in the field of positive ions. The first point of view is supported by the presence of long-wave emission in discharges of zinc and cadmium (in the same column of Mendeleev's table and with molecules having potential curves similar to mercury) and the absence of such emission in discharges of sulfur and thallium, which is inexplicable from the standpoint of the second hypothesis [68].

Whatever might be the nature of the emission from the mercury lamp, this point requiring further study, it is suitable for conducting spectral measurements in the wavelength region 100 to 1600 μ [60].

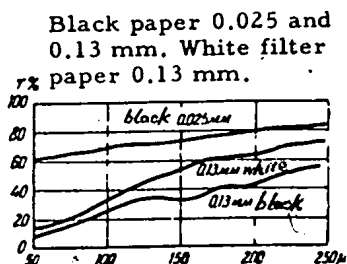
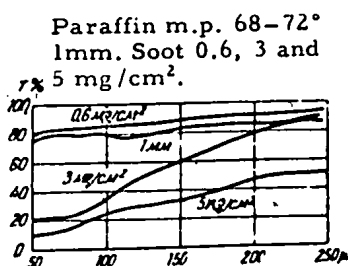
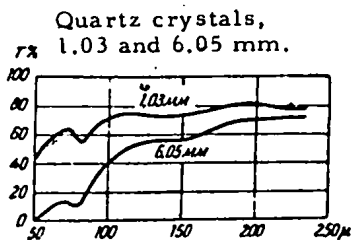


Fig. 10. Transmission of quartz, paraffin, soot and paper in the 50 - 250 μ region [69, 13].

A layer of crystal quartz 35-40 mm thick completely absorbs in the 4 to 100 μ region and transmits up to 75% at 500 μ . Fused quartz gives much poorer transmission.

A 1 mm thick plate prepared from paraffin of high melting point (68 - 72°C) or from ceresine transmits long-wave radiation well, but strongly absorbs and

B. Methods of excluding short-wave radiation.

The exclusion of scattered radiation of smaller wavelengths in spectrometers designed for studies in the long-wave IR region is achieved by using various selectively transmitting and selectively reflecting filters, and also by employing the above-discussed methods of isolating long-wave radiation (methods of quartz lenses and "residual rays") and by selective modulation of the light source.

1. Transmission filters. The following substances may be used as filters to hold back the short-wave radiation and transmit the long-wave: crystal quartz, paraffin, turpentine soot, black (photographic) paper, ground polyethylene and certain other materials. The transmission of these materials in the regions 100 to 240 μ and up to 600 μ is shown in Figures 10 and 11.

A crystal quartz plate 4-5 mm thick absorbs all short-wave infrared radiation, beginning at 5 μ ; in the long-wave region its transmission increases, reaching 80% at 400 μ .

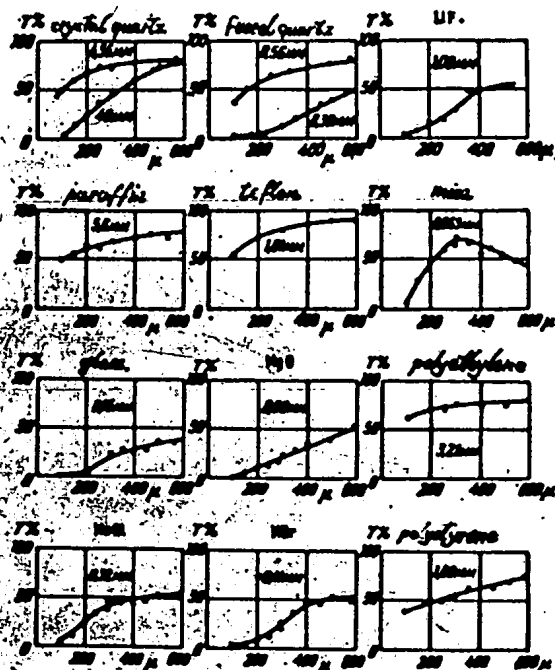


Fig. 11. Transmission of certain materials in the 100-600 μ region [44].

scatters short-wave radiation. A thick plate of paraffin (5-6mm) transmits 50% at 100 μ and more than 75% at 600 μ .

Turpentine soot completely absorbs all the visible and near region of the IR spectrum; its transmission greatly increases in the long-wave region and depends to a considerable extent on the thickness and density of the layer. For instance, a layer obtained by uniform deposition of 0.6 mg of soot on 1 cm² of the surface of a plate of paraffin, quartz or polyethylene, transmits more than 95% of radiation of wavelength 250 μ , while a layer of density 5 mg/cm² transmits in this region only 50% (Fig. 10). Black cigarette and photographic paper also possess good transmittance.

Organic plastics: polyethylene, polytetrafluoroethylene (teflon), polystyrene, polyvinyl chloride (vinidur) and polyurethane in layers 1 mm thick and more, which strongly absorb medium-wave radiation, become "transparent" to long-wave (Fig. 11, 12). Sometimes the surfaces of strips prepared from these materials are roughened with emery paper which further reduces the short-

wave radiation by scattering. Usually polyethylene and quartz are used in the making of spectrometer windows and cells, while vinidur and polyurethane are used as filters for work in the longest-wave region of the spectrum.

2. Reflection filters. The property of selectively reflecting long-wave IR radiation, as in crystals ("residual rays"), is also possessed by diffraction echelettes used in zero order, and also by mat metal surfaces.

According to White [70], an echelette grating with constant d a little smaller than the wavelength λ of the radiation being isolated acts like a plane mirror towards radiation of that and longer wavelength, i.e. such an echelette reflects radiation with $\lambda > d$ and $\lambda \gg d$ in zero order. The echelette reflects radiation of smaller wavelengths ($\lambda < d$ and $\lambda \ll d$) in other orders, which are diffracted to the side and do not reach the optical system of the instrument. Hence in the given case the echelette fulfills the role of a one-

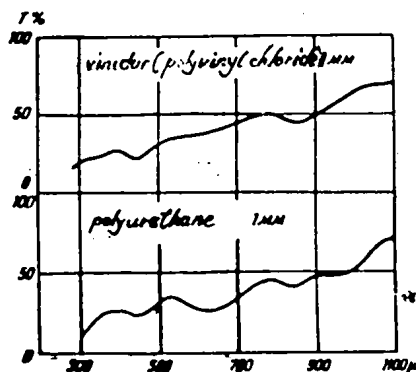


Fig. 12. Transmission of vinidur and polyurethane in the 300 - 1100 μ region [60].

way filter, specularly reflecting long-wave radiation and scattering the short-wave. When working in a wide long-wave range of the spectrum it is necessary to employ several such echelettes. For instance, in studying the 100 to 1600 μ region in work [60] along with the transmission filters (quartz, paraffin, soot, vinidur, polyurethane) two echelette-filters, with constants 0.411 mm for the 100 - 700 μ region and 0.625 mm for the 700 - 1600 μ region, were used.

The reflection of radiation from plane aluminum or silver mirrors roughened with emery paper, also results in scattering of the short-wave

radiation with a relatively high reflection of the long-wave. For work in different spectral regions the mirror should be ground in such a way that its surface structure contains grains which differ little in size from the wavelength of the IR radiation to be isolated. In practice this amounts to the choice of an abrasive of appropriate grain size [64].

3. Method of selective modulation. The removal of scattered short-wave radiation when fast detectors are employed may be accomplished by using the method of selective modulation of the light beam [46]. In this method the modulator is a rotating sector disk constructed of materials transparent in the region up to 25 - 50 μ and which absorb the longer waves (for instance, KBr or CsI crystals). On rotating such a disk in the path of a beam of light, the greatest depth of modulation will be applied to those spectral regions which are not transmitted by the crystal sectors of the modulator. The visible, near and middle regions of the IR spectrum, which are not absorbed by the crystal, will not be modulated and the constant detector signal will not be passed by the ac amplifier. Thus, the crystal modulator acts as a filter, holding back radiation of short wavelengths and transmitting the long-wave up to the wavelength at which the particular crystal again becomes transparent.

On passing through the modulator sector the short-wave radiation transmitted by the crystal will be weakened by partial absorption and twofold reflection from the air-crystal interfaces, hence it will be partially modulated and on the output of the amplifier device it will give a signal, the magnitude of which, on account of the great energy in the short-wave region, may exceed the desired signal. For removing this unwanted background metal diaphragms, which compensate the energy loss due to reflection, are inserted into the intermediate openings of the modulator.

For obtaining the purest long-wave spectra, free from the superposition of short-wave radiation, modern spectrometers employ a combination of the methods described above.

B. Radiation detectors

At the present time the spectral resolving power and operating accuracy of infrared spectrometers is limited by the sensitivity of the detecting-amplifying and recording devices and in the first place — by the sensitivity of detectors of IR radiation.

In long-wave IR spectrometers designed for the recording of extremely small energies of monochromatic radiation (of the order of $10^{-8} - 10^{-10}$ w), the threshold sensitivity of the detector plays a very important, if not a decisive role [71].

Other important characteristics of a detector are its time constant, which determines its applicability when modulated light is used, and its specific sensitivity and receiver surface area which, because of the large apertures of long-wave spectrometers and the difficulties arising from the concentration of energy in a small volume, must not be too small.

The demands of a high specific (S_0) and threshold (Q_{\min}) sensitivity, a low time constant (τ) which will allow a modulation frequency of the order of 10 cps, and a sufficiently large receiver surface (F) are satisfied by Golay pneumatic detectors [72] which have characteristics: $Q_{\min} = 7.6 \cdot 10^{-11}$ w, $\tau = 0.02$ sec., $F = 4 - 7$ mm², and by Schwarz thermocouples [73] ($Q_{\min} = 4.2 \cdot 10^{-11}$ w, $\tau = 0.03$ sec., $S_0 = 24$ v/w, $F = 0.4$ mm²), and by Baird metallic bolometers [74] ($Q_{\min} = 1.10^{-10}$ w, $\tau = 0.0041$ sec, $F = 0.2$ mm²) which have, however, small receiver surfaces. These detectors, as well as bolometers and thermoelements of other firms, are employed at present in foreign spectrometers designed for the medium-wave and long-wave regions of the IR spectrum.

In the USSR we have also developed sensitive metallic bolometers [75] with parameters: $Q_{\min} = 6.10^{-11}$ w, $\tau = 0.02$ sec, $S_0 = 28$ v/w, $F = 1.0$ mm²),* as well as high-sensitivity thermoelements [77]. In comparison with bolometers the latter possess a rather lower threshold sensitivity (up to 2.10^{-10} w), but have larger receiver surfaces (2.5 mm² and more). The large time constants of these thermoelements (0.2 - 0.3 sec) do not allow their application when interrupted illumination is used. Nevertheless, with suitable amplifiers they may be employed in long-wave IR spectrometers [64]:

An important factor in the development of new efficient devices intended exclusively for detection of long-wave IR radiation is the choice of absorbing coatings for their receiving elements, since the coatings employed in the

*The parameters of foreign and home detectors are taken from N. M. Markov's paper [76] in which he compares fast detectors of IR radiation; the value of the threshold sensitivity Q_{\min} is determined for a time constant 1 sec.

usual detectors (soot, metal black, etc.) become more transparent as the wavelength increases. The conduction of further special investigations in this direction is required.

3. Spectrometers of laboratory type

As we noted above, between 1938 and the present there have been built several laboratory spectral instruments designed for high-resolution study of long-wave IR spectra. Yet so far no industrial instrument of such type has been developed. This can be explained by the fact that the long-wave IR region has not yet found such wide application as the medium-wave and short-wave IR regions.

We will examine briefly the schemes of certain laboratory instruments constructed in recent times.

1. Randall's spectrometer (1932 - 1938). The optical scheme of the monochromator (Fig. 13) is very simple and at the same time free from aberrations, which are eliminated by the use of an off-axis parabolic mirror M_1 with relative aperture $f/1.5$ and an on-axis elliptical mirror M_2 with focal lengths 89 and 445 mm (diminution 1:5). The entrance and exit slits S_1 and S_2 of height 5 cm are located above the echelette G , the grooved surface of which has dimensions 250×550 mm. Two echelettes are employed, these having 14 and 5 lines per mm, covering the spectral region from 18 to 200μ and operating in the first order within a 6-degree angle. The radiation source is a thorium-oxide coated platinum ribbon heated by a current. Short-wave radiation is eliminated by using "residual reflectors" of KBr and KI and filters of paraffin and crystal quartz. The detector is formed of vacuum thermoelements

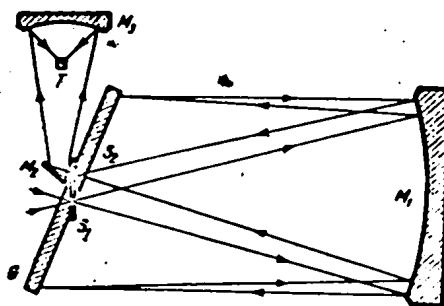


Fig. 13. Scheme of Randall's spectrometer [35].

with windows of potassium bromide or paraffin and is continuously evacuated by using liquid air. Absorbing coatings for the receiver surfaces of the thermoelements are chosen with regard to the wavelength of the spectral region under investigation.

The amplification of the thermocurrent is accomplished by means of a Firestone resonance amplifier with amplification factor 100 or more. The spectra are recorded by photographic registration of the galvanometer vibrations and takes from 3 to 8 hours dependent on the resolution required. The whole optical system of the instrument is enclosed in a vacuum.

2. The spectrometer of McCubbin and Sinton (1952) is an instrument of very large aperture. Its relative aperture is $f/1$ with diameter of parabolic collimating mirror 440 mm and echelette dimensions 300 x 300 mm.

The spectrometer is constructed on the self-collimation scheme of Pfund (Fig. 14) without the additional plane mirror; the entrance and exit beams pass through a hole in the center of the echelette. The exit slit is the circular, 3 mm in diameter, receiver area of the detector - a Golay pneumatic type.

It employs two echelettes with "blaze" angle 10° in the first order; one 2.6 lines per mm for the 100 - 300 μ region, the other 1 line per mm for the 300 - 700 μ range.

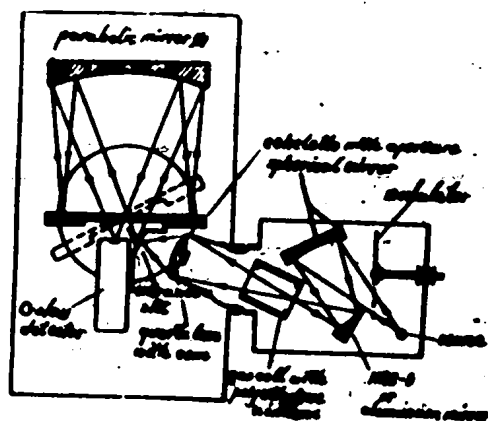


Fig. 14. Scheme of spectrometer of McCubbin and Sinton [44].

The sources employed are quartz high-pressure mercury lamps; lamp

H-3 (for the 100 - 300 μ region) and a powerful lamp with liquid cathode of "Hanovia" type (300 - 700 μ).

Removal of short-wave radiation was achieved by focal isolation using a quartz lens, selective reflection from a KRS-5 crystal, and also by smoking with turpentine soot the surfaces of the quartz lens, echelette and the quartz plate situated in front of the detector.

Water vapor absorption was partially eliminated by filling the monochromator and illuminator with dry nitrogen.

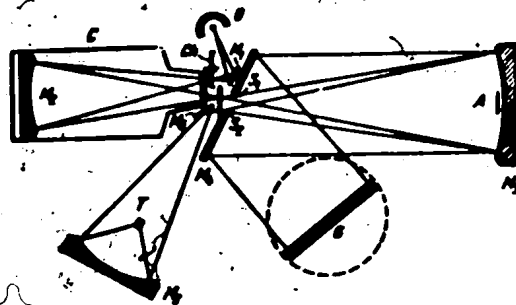


Fig. 15. Scheme of Bohn's spectrometer [54].

3. Bohn's spectrometer (1953) is also built according to a self-collimating scheme consisting of a plane mirror M_4 with a hole in the center, a parabolic mirror M_2 of diameter 250 mm and an echelette G , dimensions 185 X 200 mm (Fig. 15).

Radiation from the source O (a silicon carbide rod), focused by a cylindrical "residual reflector" M_1 onto the plane of the intermediate image, where the crystal (selective) modulator (chopper) Ch is located, enters the gas cell C through a polyethylene window and is focused by the spherical mirror M_2 on the entrance slit of the monochromator S . Radiation leaving the exit slit is concentrated by means of a plane M_3 and elliptical M_4 mirror on the detector — a thermoelement (bismuth-antimony, resistance 20 ohm) connected to the input transformer of an ac amplifier (amplification factor 10^7 , band pass width 2 to 20 cps). The amplified signal is mechanically rectified and falls on an RC-filter, the maximal time constant of which was 60 sec. with band width 0.003 cps. The spectrum was recorded on a 10 mv Brown recorder.

For the 22 to 77 μ spectral region two echelettes, having 15 and 24 lines per mm, are used. The crystal chopper was made from sodium chloride (for 22 - 40 μ region) and potassium bromide (40 - 77 μ) and the cylindrical reflector from fluorite, and also from sodium chloride and sodium bromide.

4. Meier's spectrometer (1953). The principle of this instrument, designed for obtaining spectra in the 150 to 600 μ region, is the double Pfund scheme, comprising two spherical mirrors H_2 , H_3 (diameter 250 mm, focal length 600 mm), plane mirror R_2 and echelette G with hole (Fig. 16). The source Q is a high pressure mercury lamp (PRK-2 or PRK-4), the detector

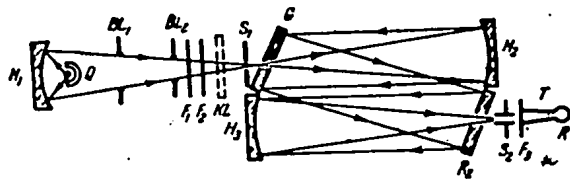


Fig. 16. Scheme of Meier spectrometer 42].

R - a radiometer with 2 mm thick quartz window and conical light guide T ;
 F_1 , F_2 and F_3 - filters of black paper 0.13 mm thick, KL - plate of rock salt.
Point measurements of spectra are obtained.

5. Spectrometer of Genzel and Eckhardt (1955 - 56) is designed for recording IR spectra in the longest wave region, 100 to 1600 μ .

The monochromator of the instrument, constructed according to the Ebert-Fasti scheme (Fig. 17) consists of two spherical mirrors of diameter 200 mm, with aperture ratio $f/3$, echelette and two 60 mm high slits which can be opened to 30 mm.

Four echelettes with "blaze" angle 20° and constants 0.315; 0.625; 0.833 and 1.250 mm are used in the first order for work in the regions: 100 - 350 μ , >250 - 700 μ , 350 - 950 μ , and 500 - 160 μ .

A quartz mercury lamp of type PRK-2 is focused by a parabolic mirror (diameter 200 mm, relative aperture $f/0.6$) on the entrance slit with fourfold magnification.

Radiation modulated at frequency 12.5 cps, passing through the exit slit, is reflected from the echelette-filter and the plane mirror and is focused by

a concave mirror ($f/0.5$) on the receiver surface of a bismuth bolometer. For matching the size of the slits, which have a different width dependent on the isolated wavelength, with the size of the receiver surface, four bolometers are used, these having different receiver areas: $0.6 \times 6 \text{ mm}^2$, $1.5 \times 6 \text{ mm}^2$, $3 \times 10 \text{ mm}^2$ and $6 \times 12 \text{ mm}^2$ and different resistances: 2, 0.9, 0.8, 0.5 kohm respectively.

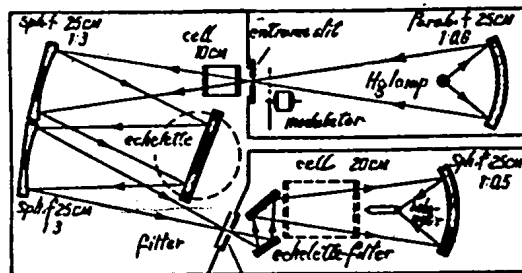


Fig. 17. Scheme of spectrometer of Genzel and Eckhardt [60].

Short-wave radiation is removed by using filters of quartz, paraffin, soot, polyurethane, vinidur, and also by means of echelettes with constants 0.211 and 0.625 mm, working in zero order.

The whole optical system is enclosed in a steel tube and allows evacuation to pressures of the order 0.1 mm Hg.

6. Spectrometer DIKS-1 (1956). The main feature of this spectrometer, designed for automatic recording of IR spectra in the region from 20 to several hundred microns, is the optical scheme (Fig. 18) which in the monochromator system resembles that of the Bohn spectrometer [54] and in its illuminating system - the scheme of the instrument of Oetjen et al. [46]. The radiation beam from the source 12 (silicon carbide rod or quartz mercury lamp PRK-4), previously reflected from one of the four crystal plates fixed on a rotating stage, is focused in the plane of the intermediate image, where the crystal sector disk of the selective modulator 13 is situated. After reflection from the mat mirror and echelette-filter, the beam is focused by mirror 2 on the entrance slit of the monochromator which consists of a collimating mirror 5 (diameter 350 mm, relative aperture $f/2.2$), a plane mirror with hole 4 and an echelette 6. The plane mirrors 7 and 8, and the spherical mirror 9,

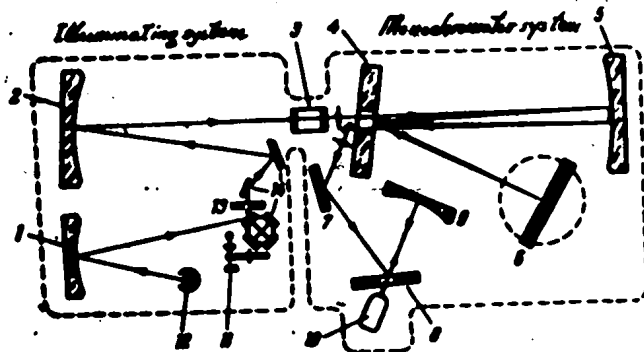


Fig. 18. Optical scheme of DIKS-1 spectrometer [64]: 1, 2, 5, 9 - spherical mirrors; 6, 7, 8 - plane mirrors; 3 - gas cell; 4 - echelette; 10 - radiation detector; 11 - device for obtaining reference voltage of synchronous detector; 12 - radiant source; 13 - crystal modulator; 14 - reflecting filters.

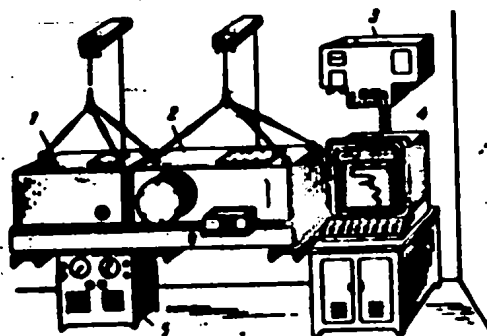


Fig. 19. General view of assembly with spectrometer DIKS-1: 1 - illuminator, 2 - monochromator, 3 - amplifier, 4 - recorder, 5 - power supply with vacuum apparatus.

situated behind the exit slit concentrate the monochromatic beam through the hole in mirror 8 onto the detector 10. An auxiliary device 11, consisting of an additional light source, lens, photocell and metal modulating disk, supplies the reference voltage required for the operation of the synchronous rectifier.

For obtaining spectra in the 20 to 500 μ region we use three echelettes 250 X 250 mm ("blaze" angle - 1 $\frac{1}{2}$ °, number of lines per mm - 12, 6 and 2), made in the laboratory of F. M. Gerasimov [78], and also various reflection and transmission filters. The illuminating system and monochromator are

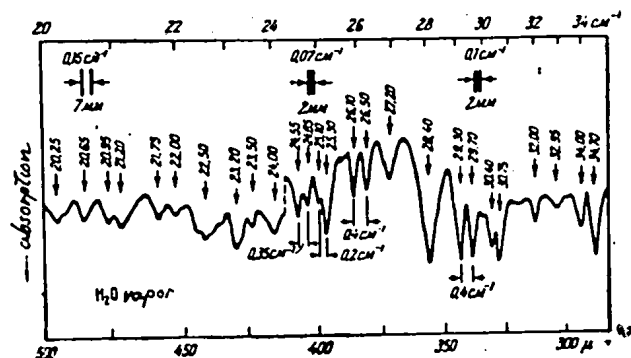


Fig. 20. Water vapor absorption in the 300 - 500 μ region.

contained in chambers united by a bellows tube and can be evacuated to a pressure of 0.1 to 0.2 mm Hg. A general view of the whole apparatus is given in Figure 19. Figure 20 shows one of the first specimens of spectrograms of atmospheric water vapor, recorded by the instrument in the 300 to 500 μ region. For recording the spectrum a mercury lamp PRK-4 was used as a source, and the detector was a six junction compensated thermoelement made by Prof. B. P. Kozyrev, which was connected with two series-connected photoelectro-optic amplifiers of type FEOU-15 and FEOU-17 [77], with an electronic potentiometer EPP-09 on the output. When this receiving-amplifying system was employed, the device 11 with modulator was disconnected. An echelette with 2 lines per mm was used; the transmission filters were a soot-coated 1 mm thick polyethylene plate and a quartz crystal.

In conclusion, Table 3 gives the principal characteristics of recently-constructed laboratory-type spectrometers designed for obtaining and recording long-wave infrared spectra.

The estimate of the spectral resolution achieved with these instruments, shown in the last column of the Table, is derived for the long-wave and short-wave limits of the spectral curves given by the authors.

TABLE 3

Laboratory Spectrometers for the Long-Wave Infrared Region.

No.	Authors, country, year	Spectral region	Principal parameters of instrument	Resolution achieved in cm^{-1}
1	Randall and Firestone, USA, 1932-8 [35, 38]	10-200 μ	Echelettes 250 x 550 mm; 14.4; 4.8 and 3.8 lines/mm; source-ThO 1300°K; det.-thermoelement with resonance amplif.; photographic record; vacuum 0.1 mm Hg.	0.5-1.0
2	Maar, Germany, 1939 [40]	200-500 μ	Lam. refl. gr. 120 x 135 mm with const. 4 mm; rel. aper. f/2; source - Hg lamp; det.-radiometer.	10-20
3	Hopf, Germany, 1940 [41]	150-400 μ	Lam. refl. gr. 200 x 200 mm; rel. aper. f/2.4; source-Hg lamp; det.-radiometer.	3-5
4	McCubbin and Sinton, USA, 1950 [43]	100-600 μ	Echelettes 73 x 100 mm.; 2.6 and 1 lines/mm; source-Hg lamp; det.-Golay amplif. 10 cps.	5-10
5	McCubbin and Sinton, USA, 1952 [44]	100-700 μ	Echelettes 300 x 300 mm; 2.6 and 1 lines/mm; rel. aper. f/1; source-Hg lamp; det.-Golay 10 cps.	1-2
6	Oetjen, Haynie et al., USA, 1952 [46]	40-150 μ	Echelettes 180 x 230 mm; 7.2 lines/mm; source-ThO 1400°K; det.-Golay 10 cps; vacuum 0.1 mm Hg; pen recorder.	0.5-1.0
7	Bohn, Freeman et al., USA, 1953 [54]	20-80 μ	Echelettes 185 x 200 mm; 24 and 15 lines/mm; source-Globar; det.-thermoelement; amplifier 5 cps; automatic recorder.	2-5
8	Meier, Germany, 1953 [42]	150-600 μ	Echelette and lam. gr. 200 x 200 mm; 2 and 0.5 lines/mm in double Pfund scheme; source-PRK-4 lamp; det.-radiometer.	8-20
9	Hadai, France, 1953 [55]	20-60 μ	Echelette 14 lines/mm in orders I and II; rel. aper. f/2.5; Randall's scheme; source-silicon carbide rod; det.-thermoel. with amplif. 5 cps.	0.7-1.0

TABLE 3 (continued)

No.	Authors, country, year	Spectral region	Principal parameters of instrument	Resolution achieved in cm^{-1}
10	Genzel and Eckhardt, West Germany, 1955-6 [60]	100-1600 μ	Echelettes 200 X 200 mm with const. 0.3; 0.6; 0.8 and 1.25 mm in Fasti scheme; rel. aper. f/3; source - Hg lamp; det. - metal bolometers; amplif. 12.5 cps; vacuum 0.1 mm.	0.3-0.5
11	Iaroslavkii, Zheludov, Stanovich, USSR, 1956 [64]	20-500 μ (DIKS-1)	Echelettes 250 X 250 mm; 12, 6 and 2 lines/mm; rel. aper. f/2.2; source - silicon carbide rod and Hg lamp PRK-4; det. - thermoel. with amplif.; pen record on EPP-09; vacuum \sim 0.1 mm.	0.3-5
12	Plyler and Acquista, USA, 1956 [63]	20-125 μ	Perkin-Elmer standard instrument with echelettes 57 X 76 mm, 12.6 and 7 lines/mm instead of prisms; thermoel. with CsI and quartz windows.	0.8-1.5

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