# New Apparatus and Methods of Measurement

## *REAL SPECTRAL APPARATUS*

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### 1. IDEAL AND REAL APPARATUS

1. Real spectral apparatus are not, as is well known, ideal harmonic analyzers of radiation i.e., the distribution of energy over the spectrum obtained with the help of real spectral apparatus differs from the "ideal" or "true" distribution, which gives the Fourier expansion of the radiation being investigated. In any real apparatus, the differences of the observed distribution from the true (or as we shall say, the distortion) result from many very different reasons. The following classification of the distorting factors by the nature of the distortions produced by them is useful. In the first group we list distortions produced in the investigation of a spectrum of even comparatively crude structure, i.e., with slowly changing brightness, for example in the investigation of a continuous spectrum. Among such distortions are the change with the wavelength (a) of the solid angle of the exit pupil of the filter, (b) of its dispersion, (c) of the angular and linear magnification, (d) of the sensitivity of the radiation detector, etc. In the majority of cases, these factors lead to a slow change in the scale along the spectrogram or to a slow change of the coefficient of proportionality between the illumination (or current) measured and the true spectral density of the radiation. We can also include among these factors parasitic exposure of the spectrogram, brought about by scattering of radiation on parts of the apparatus and leading as a rule to an addition of some slowly changing quantity to the true distribution. It is usually comparitively easy to take these distortions into consideration and at the present time there are workable methods for such consideration (see, for example, references 1, 2). In what follows we shall not consider these factors.

In the study of the fine structure of a spectrum (singlet, doublet, etc, spectral lines, narrow bands, and so forth), over the range of which one cannot take into account distortions of the first group, there are important distortions of another type, which we shall place in a second group. These distortions are brought about by the fact that even in monochromatic radiation a real spectral apparatus gives some distribution of energy over a spectrogram of finite width. The form of this distribution and its width are determined by various factors: diffraction on the diaphragms of the optical system of the spectral apparatus, its aberrations, the finite aperture widths, the time lag of the recording instrument, scattering in the light-sensitive photographic emulsion, etc. It is important to emphasize that, independent of its nature, the finite width of the distribution in a monochromatic radiation is common to all real spectral apparatus and determines to a significant degree the possibilities of investigation of fine details or structure of a spectrum.

In addition to distortions of a systematic character, brought about by factors of the first and second groups, a difference between the "true" and "observed" distributions is also caused by factors that lead to random errors of measurement. We shall put these factors in a third group. The appearance of random errors is connected with the change of parameters of the optical system during the time of the experiment, by fluctuation phenomena in the light detector, and for similar reasons. In a number of cases, changes in the brightness of the light source and fluctuations of the liminous flux connected with the corpuscular character of light also lead to random measurement errors.

The demarcation for random and systematic distortions is expedient because they are produced by physically different causes and consequently require for their reduction different (and sometimes even contradictory) changes in the apparatus. However, the possibilities of the apparatus as a whole are limited by factors of the second and the third groups taken together; in consideration of such questions as the resolution, accuracy of measurement of the real energy distribution, etc., it is necessary to take their joint action into account.

2. Let us now consider a quantitative description of the distortions brought about by factors of the second group. Let the true energy distribution over the spectrum be described by the function $\varphi(x)$, while the distribution obtained by real apparatus for monochromatic radiation be represented

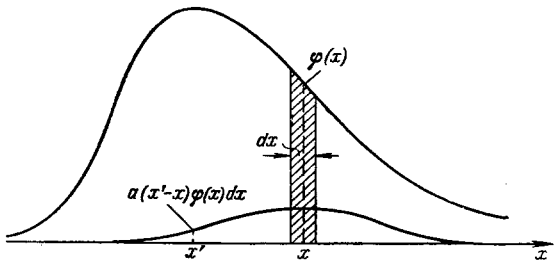


FIG. 1. For the derivation of Eq. (1).

by the function $a(x)$, which we shall call the apparatus function of the spectral equipment. The observed distribution can be plotted in the following way. Each monochromatic component $\varphi(x)\,dx$ of the true radiation is replaced by the apparatus function, as a result of which, at some arbitrary point $x'$, there is created an illumination (or current) $a(x'-x)\,\varphi(x)\,dx$ (see Fig. 1). Other monochromatic components of the true distribution also make a corresponding contribution to the illumination at the point $x'$, and as a result the observed distribution $f(x')$ will be expressed by the following integral

$$f(x') = \int_{-\infty}^{\infty} a(x'-x)\,\varphi(x)\,dx. \qquad (1)$$

The function $a(x)$, and consequently the formula (1), take into account distortions both in the optical and recording parts of the apparatus. It is easy to see that each of these parts can be characterized by its own apparatus function $a_1(x)$ and $a_2(x)$. For example, the distribution of the illumination $f_1(x')$ in the focal plane of the objective of the recorder is

$$f_1(x') = \int_{-\infty}^{\infty} a_1(x'-x)\,\varphi(x)\,dx. \qquad (2)$$

It is easy to show that the apparatus function of the spectral equipment $a(x)$ is expressed in terms of $a_1(x)$ and $a_2(x)$ in the following way:

$$a(x) = \int_{-\infty}^{\infty} a_1(x-y)\,a_2(y)\,dy. \qquad (3)$$

Applicability of Eqs. (1) – (3) can be limited by the following circumstances. In the derivation of (1) it was assumed that the apparatus function was the same at different wavelengths. It is easy to see that the condition for invariance ought to be satisfied essentially only in a comparatively small region around the point $x'$, where $a(x'-x)$ is appreciably different from 0.

This condition is satisfied in the overwhelming number of cases, although in regions of the spectrum at great distances from one another, the apparatus function will change appreciably. For example, if the apparatus function is almost completely determined by diffraction on the aperture diaphragm, then its width is proportional to the wavelength and it is doubled in the transition, say, from 5000 A to 10,000 A. However, the apparatus function is essentially different from zero only in a region with dimensions on the order of $2\lambda/R$, where R is the Rayleigh resolving power, and where it is quite clear that over the range of such a region we can neglect the change in the apparatus function. Besides, these conditions are sometimes not observed, and it is necessary at the same time to consider factors of the first and second groups (for example, see reference 3). In what follows such cases will not be considered.

It is appropriate to make some remarks of a terminological character. Several names are given in the literature for the function $a(x)$: instrumental contour, apparatus function, distortion function, etc. In English and American literature on infrared spectroscopy the term "slit function" is used. Everywhere in what follows we shall use the term "apparatus function" both for all apparatus as a whole and for the description of particular distorting factors: the apparatus function of the slit, the apparatus function of the diffraction, the apparatus function of the photo layer, etc., where by apparatus function of any factor is meant the observed distribution of illumination (current) for monochromatic radiation and for vanishingly small effects of the remaining distorting factors.

Up to now we have spoken about the true and observed energy distribution over the wavelengths, consequently identifying the arguments x, x', y with the wavelength. However, by x, y, etc., we can also understand the frequencies either of the coordinate in the density spectrum or the coordinate in the recorded spectrum, obtained by a microphotometer or by scanning of the spectrum by some recording device.

This situation is evidently connected with the fact that we are limiting ourselves to a consideration only of distortion factors of the second group, and of comparatively narrow spectral intervals, where the conversion coefficients (type of linear dispersion) from the wavelength to the coordinates or to the frequencies we can regard as constant.

Finally, we note that the relations of type (1) have been given quite a definite name in mathematical literature, that is, we say that the function $f(x)$ expressed by Eq. (1) is the convolution of $a(x)$ and $\varphi(x)$. In the physical literature, particular names are sometimes used for the different special cases. For example, in the inves-

tigation of the distorting action of a recording instrument alone, Eq. (1) is called the "general time equation of the spectrometer" in reference 4. For convolutions of two functions there exists a set of mathematical theorems; in particular, convolution possesses the properties of commutation, association, and distribution,[5] i.e.:

$$\int_{-\infty}^{\infty} a(x-y)\varphi(y)\,dy = \int_{-\infty}^{\infty} \varphi(x-y)\,a(y)\,dy;$$

$$\int_{-\infty}^{\infty} g(x-y)\,dy \int_{-\infty}^{\infty} a(y-z)\varphi(z)\,dz$$

$$= \int_{-\infty}^{\infty} \varphi(x-y)\,dy \int_{-\infty}^{\infty} a(y-z)\,g(z)\,dz;$$

$$\int_{-\infty}^{\infty} a(x-y)[g(y)+\varphi(y)]\,dy$$

$$= \int_{-\infty}^{\infty} a(x-y)\,g(y)\,dy + \int_{-\infty}^{\infty} a(x-y)\varphi(y)\,dy. \qquad (4)$$

An important property of convolution consists in the fact that its integral is equal to the product of the integrals of the functions $a(x)$ and $\varphi(x)$:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} a(x-y)\varphi(y)\,dy\,dx = \int_{-\infty}^{\infty} a(z)\,dz \int_{-\infty}^{\infty} \varphi(y)\,dy. \qquad (5)$$

Some other properties of the convolution will be considered below.

It should be borne in mind that for the appropriate use of the concept of the true and the energy distribution over the spectrum we need a definite normalization of the apparatus function $a(x)$. This is connected with the dual role of the slit (or slits) in the spectral apparatus. The finite width of the slit leads to a distortion of the spectral distribution and consequently the slit ought to be infinitely narrow in the ideal apparatus. On the other hand, for an infinitely narrow slit, there is an infinitely small current in the apparatus and it is not possible to operate with real quantities. This difficulty can be avoided if it is contrived that as we reduce the width of the slit we increase the illumination of the spectrum, so that the total energy coming into the apparatus remains unchanged. Mathematically, this means that the apparatus function must be normalized over the area, for example, in the following way:*

$$\int_{-\infty}^{\infty} a(x)\,dx = 1. \qquad (6)$$

*For periodic apparatus functions of interference spectroscopes, the integration is carried out over a single period.

For such a normalization, the total energy of the true distribution is equal to the total energy of the observed distribution. Actually, by integrating (1) over $x'$, and taking (5) and (6) into account, we obtain

$$\int_{-\infty}^{\infty} f(x')\,dx' = \int_{-\infty}^{\infty} a(z)\,dz \int_{-\infty}^{\infty} \varphi(y)\,dy = \int_{-\infty}^{\infty} \varphi(y)\,dy. \qquad (7)$$

Thus, if we assume (6), then the presence of the apparatus function leads only to a redistribution of the energy over the spectrum, i.e., to a change in the shape of the line, the band, etc. This makes it possible to isolate the problem of the distortion of the shape of the distribution from problems connected with the absolute value of the illumination, light intensity, etc. For this purpose it suffices to normalize the functions $f(x)$ and $\varphi(x)$ in a manner similar to (6):

$$\int_{-\infty}^{\infty} f(x)\,dx = \int_{-\infty}^{\infty} \varphi(x)\,dx = 1. \qquad (8)$$

We emphasize that the relation (7) is the direct consequence of the definition of an apparatus function which does not depend either on the form of $\varphi(x)$ or on the nature of $a(x)$. Therefore, the experimental verification of (7), obtained in reference 6, shows only that the region of integration in (7), always finite in the experiment, was taken sufficiently large.

Normalization of (6) and (8) makes it possible to use the theory of $\delta$-functions* for the description of limiting cases — monochromatic radiation and ideal spectral apparatus. If $a(x) = \delta(x)$ then:[7]

$$f(x') = \int_{-\infty}^{\infty} \delta(x'-x)\varphi(x)\,dx = \varphi(x'),$$

i.e., an instrument whose apparatus function is a $\delta$-function is an ideal non-distorting device. In the other limiting case of monochromatic radiation, we have

$$\varphi(x) = \delta(x); \quad f(x') = \int_{-\infty}^{\infty} a(x'-x)\delta(x)\,dx = a(x'),$$

*The $\delta$ function is formally defined in the following way (see, for example, reference 7):

$$\delta(x) = \begin{cases} \infty, & x = 0; \\ 0, & x \neq 0; \end{cases} \qquad \int_{-\infty}^{\infty} \delta(x)\,dx = 1.$$

In what follows we shall take for granted the following property of the function:

$$\int_{-\infty}^{\infty} g(x)\,\delta(x)\,dx = g(0); \quad \delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ix\omega}\,d\omega.$$

in correspondence with the definition of the apparatus function.

3. A relation of the type (1) connects the true and observed quantities not only in the case of spectroscopic measurements but also in many other regions of physical measurement. The distortion of signal presented to the input of an electrical linear system is described by Eq. (1) (see, for example, reference 8) while, by analogy, the apparatus function is the response of the system to an instantaneous pulse. The theory of the phosphoroscope and also of other apparatus with time scanning of rapidly alternating processes can also be reduced to Eq. (1). The methods of Michelson for the determination of the structure of spectral lines and the structure of astronomical objects[9] are quantitatively described by Eq. (1). The methods of x-ray determination of the dimensions of particles are also described in terms of a relation of the type (1) (see, for example, reference 10). Equation (1) arises in a number of problems of astrophysics,[11] the theory of broadening of spectral lines,[11,12] and in other regions. The distortions introduced by real optical apparatus and radio telescopes are described by the two-dimensional analogue of Eq. (1):

$$f(x', y') = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} a(x' - y, y' - y)\varphi(x, y)\, dx\, dy,$$

where (x, y) physically means the distribution of the measured quantity (intensity, current, brightness temperature) for a point source of radiation.[13]

In all these and in many other cases we are dealing with a linear integral relation between the true distribution of some physical quantity $\varphi(x)$ with an arbitrary argument x and the experimentally determined distribution f(x), where the kernel of the equation is characteristic for the given equipment or apparatus function a(x). In spite of the physical diversity of these quantities and the manifold concrete forms of the function a(x), the statement of the problems arising in connection with Eq. (1), and the methods of mathematical solution of these problems have a very general and sometimes almost identical physical measurement in completely different regions. Therefore, many results obtained in other regions can be useful, and are sometimes used directly for the spectral apparatus. This applies particularly to the introduction into the theory of real apparatus the so-called spectral approach or the method of Fourier analysis, which has, as is well-known, a very general significance in the theory of linear electrical systems and in many other cases.

The method of quantitative description of the distorting action of a real spectral instrument set forth above is not the only one possible. Actually, we can construct the observed distribution by the following, more general method. An arbitrary true distribution $\varphi(x)$ is expanded into a sum of certain standard distributions; the distortion of the standard distribution by the real apparatus is taken into account and then the distorted standard distributions are combined forming the observed distribution f(x). In the mathematical technique which was explained above, we used monochromatic radiation as a standard distribution; the real apparatus corresponding to this was described by the apparatus function. Such a form of the standard distribution has a very clear physical meaning and historically was first used for the analysis of the properties of real optical and spectral equipment. However, this by no means signifies that it is impossible to make effective use of other standard distributions. For example, in the theory of linear electrical systems, the step and harmonic distributions are also employed.

The possibility and usefulness of the spectral approach for real optical apparatus, i.e., the use in this case of the harmonic standard distribution was first explicitly shown by Abbe in his theory of the formation of the image of non-luminous objects (see, for example, reference 14). Later, L. I. Mandel'shtam[15,16] and Rayleigh[17] extended the concept of Abbe to the case of partially coherent and luminous objects. Another early application of the spectral approach in optical measurements was associated with the investigation of the hyperfine structure of spectral lines, carried out by Michelson on his double-beam interferometer. Evidently, he was also the first to construct the harmonic analyzer for the analysis of spectroscopic data.[9] However, widespread recognition of the spectral approach in the region of interest to us has come about only during the last 15 — 20 years in connection with the development of information theory and the application of its results and of the mathematical methods for spectral apparatus (see, for example, references 18 — 22).

The fruitfulness of the spectral approach results from the following significant property of the harmonic distribution of the intensity, a property established by L. I. Mandel'shtam.[16] If the true distribution has the form

$$\varphi(x) = \cos(\omega x + \beta), \qquad (9)$$

then the observed distribution will also be harmonic with the same frequency $\omega$ but, generally speaking, with a different amplitude and phase.[16] Actu-

ally, substitution of (9) in (1) quickly demonstrates that

$$f(x) = A\cos(\omega x + \beta'), \tag{10}$$

where the quantities A and $\beta'$ depend on $\omega$ and on the form of the apparatus function. It will be shown below that this is correct in the general case of an arbitrary real apparatus. The inverse is also substantiated, that is, only a harmonic distribution preserves its form under the distorting action of real apparatus.

In connection with the general method of the construction of the observed distribution, let us represent the true distribution in the form of a superposition of harmonic distributions, i.e., in the form of a Fourier integral:[23]

$$\varphi(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \Phi(\omega)\, e^{ix\omega}\, d\omega. \tag{11}$$

Introducing this in (1), and changing the order of integration, we obtain:

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} A(\omega)\,\Phi(\omega)\, e^{ix\omega}\, d\omega, \tag{12}$$

where

$$A(\omega) = \int_{-\infty}^{\infty} a(x)\, e^{-i\omega x}\, dx \tag{13}$$

is the Fourier transform of the apparatus function. It is easily seen from (12) that the Fourier transform of the observed distribution is

$$F(\omega) = \int_{-\infty}^{\infty} f(x)\, e^{-i\omega x}\, dx, \tag{14}$$

i.e., the amplitude of the harmonic component of the observed distribution is equal to

$$F(\omega) = A(\omega)\,\Phi(\omega). \tag{15}$$

The meaning of the transformation of Eq. (1) to Eqs. (12) and (15) is evidently as follows. Each harmonic component of the true distribution with frequency $\omega$ and amplitude $\Phi(\omega)$ is changed over by the real apparatus into the same harmonic component of the observed distribution with the same frequency but, in general, a different amplitude $F(\omega)$, which is given by Eq. (15). The sum of all the harmonics distorted by the apparatus gives the observed distribution (12).

In the case of electrical systems, a relation is valid that is analogous to (15). This relation exists between the amplitude of the harmonic signal at the input of the system $\Phi(\omega)$, and at its output $F(\omega)$. The complex function $A(\omega)$ is known as the phase-frequency characteristic of the system. In optical apparatus generally (in particular in spectral apparatus), this function does not usually have a simple physical meaning, except for the case when the apparatus function is determined only by diffraction, aberrations and slits. In this case, as can be shown, $A(\omega)$ is determined by the amplitude of the electromagnetic field in the plane of the aperture diaphragm of the system, i.e., by the first (according to Abbe) image, and $\omega$ is proportional to the coordinate in this plane.[24] In other cases it is not possible to find such a physical interpretation.

From the mathematical point of view, Eqs. (1) and (15) express a general theorem on convolution and its Fourier transform. Thus, the Fourier transform of the convolution of two functions is the product of the Fourier transforms of these functions. On the basis of the equation for the inversion of a Fourier integral, we can also substantiate the fact that the Fourier transform of the product of two functions is the convolution of the Fourier transform of these functions (see, for example, reference 23).

Besides the methods of analysis of real instruments considered above, another method exists and is rapidly being advanced. It is based on representations and the mathematical techniques of information theory (see, for example, references 19 — 22, 25 — 27). In the present review, however, this approach will not be considered.

**4.** As has been pointed out, the apparatus function of a real spectral instrument is determined by many and varied factors. Depending on which of these factors plays the decisive role, the apparatus function will have one or another form and will have a varying width. In the most refined instruments, the apparatus function is almost completely determined by diffraction at the aperture.[28,29] If, as is usually the case with spectral instruments, the aperture is rectangular then, as is well-known:[30]

$$a(x) = \frac{1}{s_0}\left[\frac{\sin \pi x/s_0}{\pi x/s_0}\right]^2, \tag{16}$$

where $s_0 = \lambda f/D$, $\lambda$ is the wavelength, D is the width of the cross-section of the beam at the exist of the dispersing system and f is the focal length of the objective. The Fourier transform of such an apparatus function has the form

$$A(\omega) = \begin{cases} 1 - \frac{s_0}{2\pi}|\omega|, & |\omega| \leqslant \frac{2\pi}{s_0}; \\ 0 & |\omega| \geqslant \frac{2\pi}{s_0}. \end{cases} \tag{16a}$$

In a number of instruments there is another limiting case, namely, the apparatus function in them is determined only by the widths of the slits,

and the diffraction, aberrations, etc., can be neglected. The apparatus function of such a spectrograph has the form of a rectangle

$$a(x)=\begin{cases}\frac{1}{s}, & |x|<\frac{s}{2};\\ 0 & |x|>\frac{s}{2},\end{cases} \tag{17}$$

and its Fourier transform is

$$A(\omega)=\frac{\sin s\omega/2}{s\omega/2}. \tag{17a}$$

The apparatus function of a monochromator, taking into account only slit distortions, is the faltung of two rectangular functions:[31]

$$a(x)=\begin{cases}\frac{1}{s_1}, & s_1>s_2,\ |x|\leqslant\frac{s_1-s_2}{2};\\ \frac{1}{s_1s_2}\left[\frac{s_1+s_2}{2}-|x|\right], & \frac{s_1-s_2}{2}\leqslant|x|\leqslant\frac{s_1+s_2}{2};\\ 0 & \frac{s_1+s_2}{2}\leqslant|x|,\end{cases} \tag{18}$$

where $s_2$ is the exit width and $s_1$ is the width of the geometric image of the initial slit. In particular, for the most important case in practice, $s_1 = s_2 = s$, Eq. (18) takes the form

$$a(x)=\begin{cases}\frac{1}{s}\left[1-\frac{|x|}{s}\right], & |x|\leqslant s;\\ 0, & |x|\geqslant s,\end{cases} \tag{19}$$

that is, a(x) has a triangular shape. The Fourier transform of the functions determined by Eqs. (18) and (19) can be written without carryout out direct computations but on the basis of the theorem of the Fourier transform of the convolution of two functions mentioned above. Inasmuch as (18) is the convolution of two rectangular apparatus functions, then its Fourier transform is the product of two functions of the form of (17a):

$$A(\omega)=\frac{\sin s_1\omega/2}{s_1\omega/2}\cdot\frac{\sin s_2\omega/2}{s_2\omega/2}. \tag{18a}$$

For the triangular apparatus function (19) we have

$$A(\omega)=\left[\frac{\sin s\omega/2}{s\omega/2}\right]^2. \tag{19a}$$

Equations (16) — (19) rarely correspond to reality with a sufficient degree of accuracy and, beginning with the researches of Schuster,[32] many attempts were made at a simultaneous account of slit and diffraction distortions. If we consider the slit to be self-luminous and assume, consequently, that the light waves which form the diffraction image of an infinitely narrow element of the slit do not interfere with the waves reaching the image from neighboring elements, then the apparatus function is the convolution of the diffraction and slit apparatus functions. For a spectrograph, for example, we have

$$\left.\begin{aligned}a(x)&=\frac{1}{ss_0}\int_{-s/2}^{s/2}\left\{\frac{\sin[\pi(x-y)/s_0]}{\pi(x-y)/s_0}\right\}^2dy;\\ A(\omega)&=\begin{cases}\frac{\sin s\omega/2}{s\omega/2}\left[1-\frac{s_0}{2\pi}|\omega|\right], & |\omega|\leqslant\frac{2\pi}{s_0},\\ 0 & |\omega|\geqslant\frac{2\pi}{s}.\end{cases}\end{aligned}\right\} \tag{20}$$

The complicated character of these equations makes difficult their practical use and forces us to look for an approximate representation of the apparatus function with the help of elementary functions. For the case $s \gg s_0$, such approximate expressions have been found both for the spectrograph[33,34] and for the monochromator.[35] Account of the partial coherence of illumination of the slit in cases of practical interest leads only to a comparatively small correction to the width of the apparatus function and scarcely changes its form at all.[24,36,37]

The situation is complicated somewhat by the presence of any appreciable aberrations. The few calculations made in recent times[24,38,39] do not permit us to draw any universal conclusions which are valid for a wide class of instruments. Therefore, one usually makes use of an experimentally measured apparatus function which is given either graphically or in tabular form, or of approximate analytic expressions of suitably simple form. In many cases, when the diffraction and aberration distortions are not very large, the Gaussian curve is a suitable approximation for the monochromator:[24,40]

$$\left.\begin{aligned}a(x)&=\frac{2\sqrt{\ln 2}}{\sqrt{\pi}\alpha}\exp\left\{-\frac{4\ln 2}{\alpha^2}x^2\right\};\\ A(\omega)&=\exp\left\{-\frac{\omega^2\alpha^2}{16\ln 2}\right\}.\end{aligned}\right\} \tag{21}$$

For spectrographs of small, medium, and sometimes also of large dispersion, one uses the following approximate representations:[41,42]

$$a(x)=\frac{\alpha/2\pi}{x^2+(\alpha/2)^2};\quad A(\omega)=\exp\left\{-\frac{\alpha}{2}|\omega|\right\}. \tag{22}$$

The possibility of such an approximation is connected with the fact that in the spectrographs mentioned the apparatus function is determined to a significant degree by the scattering of light in the emulsion. The apparatus function of the emulsion is, according to references 43 — 45, well described by the experimental curve

$$\left.\begin{aligned}A(\omega)&=\frac{1}{1+\left[\frac{\alpha\omega}{2\ln 2}\right]^2},\\ a(x)&=\frac{\ln 2}{\alpha}\exp\left\{-\frac{2\ln 2}{\alpha}|x|\right\},\end{aligned}\right\} \tag{23}$$

which in its "wings" is comparatively close to the curve of the dispersion form with the same width $\alpha$.

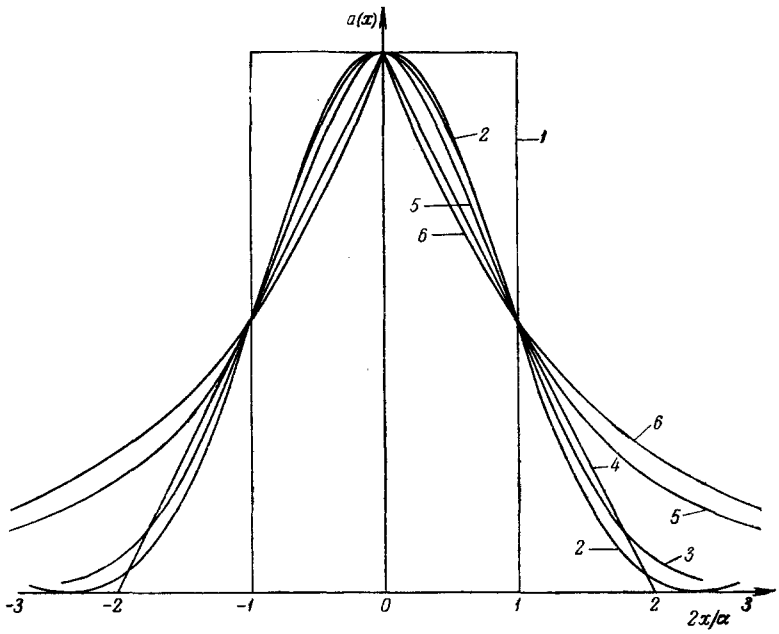


FIG. 2. Apparatus functions for various forms of width $\alpha$: 1) slit shaped (17); 2) diffraction (16); 3) Gaussian (21); 4) triangular (19); 5) dispersion (22); 6) exponential (23).

Recently, a more complicated approximate apparatus function has been employed in a number of works.[46-49] This function is obtained with the help of the Voigt function, which is the convolution of the dispersion and Gaussian functions

$$\left.\begin{aligned} a(x) &= \frac{\sqrt{\ln 2}}{\pi^{3/2}}\frac{\alpha_1}{\alpha_2}\int_{-\infty}^{\infty}\frac{\exp\left\{-\frac{4\ln 2}{\alpha_2^2}y^2\right\}}{(x-y)^2+(\alpha_1/2)^2}\,dy;\\ A(\omega) &= \exp\left\{-\frac{\alpha_1}{2}|\omega|-\frac{\alpha_2^2\omega^2}{16\ln 2}\right\}. \end{aligned}\right\} \quad (24)$$

Graphs are shown in Fig. 2 for the functions under consideration. Their Fourier transforms are shown in Fig. 3. For ease in comparison, all the apparatus functions are given for a single width and for the same value at the maximum.

In the investigation of spectra of Rayleigh and Raman scattering, additional distortions are connected with the non-monochromatic character of the resultant radiation. The observed shape of the line is represented in the form of the convolution of the true line shape and of the observed line shape of the scattering, which is obtained for monochromatic excitation.[50,33] In a number of cases the total apparatus function, which takes into account the distortions just mentioned, virtually coincides with the observed shape of the excitation line.[51,41]

Apparatus functions of interference spectroscopes (the Fabry-Perot etalon, the Lummer-Gehreke plate, the Michelson echelon) are widely known (see, for example, references 2, 52, 53), and we shall not give their expressions here. We

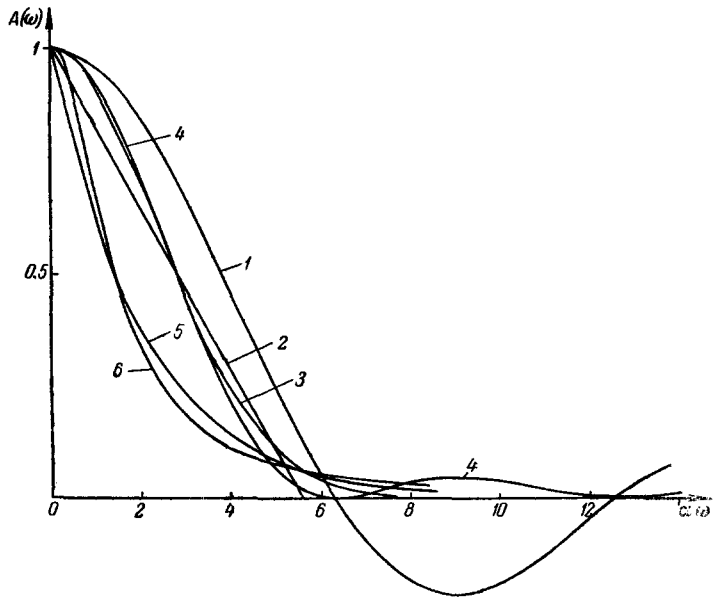


FIG. 3. Fourier transforms of apparatus functions. The number of each curve corresponds to that of Fig. 2.

note only that, in view of the relatively small number of interfering rays in these instruments, we are sometimes obliged to take into consideration the periodic character of their apparatus functions, i.e., to consider the superposition of the interference bands of adjacent orders.

The apparatus function of a recording instrument which is governed by its intertia and the distortions connected with it were considered in references 6, 54 — 58. We shall not dwell on these papers, inasmuch as the fundamental results contained in them were set forth in the review of reference 4. Moreover, as will be seen from what follows (see Sec. 3), the recording conditions must be so chosen that these distortions are small in comparison with the distortions brought about by the apparatus function of the optical part of the instrument, and in comparison with the random errors of measurement. Therefore, we shall only give a few results obtained in reference 58 after reference 4 was published.

A recording instrument equivalent to an RC circuit is described, as is well-known, by the following apparatus function and its Fourier transform:

$$\left.\begin{aligned} a(x) &= \begin{cases} 0, & x<0; \\ \frac{1}{v\tau}\, e^{-x/v\tau}, & x>0; \end{cases} \\ A(\omega) &= \frac{1}{1+iv\tau\omega} = \frac{e^{-i\tan^{-1}v\tau\omega}}{\sqrt{1+(v\tau\omega)^2}}, \end{aligned}\right\} \tag{25}$$

where $\tau$ is a time constant and v is the speed of scanning. For sufficiently slow scanning such an apparatus function reduces to the displacement of a spectrum of arbitrary shape by a quantity equal to

$$\Delta x = v\tau. \tag{26}$$

The condition of sufficient slowness of scanning for the case, for example, of a single line means that $v\tau \ll \delta$, where $\delta$ is the observed line width. If we take into account the shift of the spectrum just noted, then in slow scanning the relative error of recording the illumination at an arbitrary point in the curve is given by the expression

$$p = k(v\tau)^2, \tag{26a}$$

where the coefficient k is determined by the second derivative of the observed distribution at the point in which we are interested. For example, for the maximum of a single line of Gaussian shape, $k = 4 \ln 2/\delta^2$. On the basis of Eqs. (26) and (26a), we can choose the proper conditions for scanning the spectrum (see Sec. 3).

5. We now turn to a consideration of the distorting factors of the third kind, i.e., factors which lead to the appearance of random errors of measurement. A formal generalization of the basic relation (1) of the theory of real instruments, which takes into account the presence of random errors of measurement, evidently consists in the addition to the right side of Eq. (1) of some random function which we shall designate by $\xi(x)$:[24]

$$f(x) = \int_{-\infty}^{\infty} a(x-x')\,\varphi(x')\,dx' + \xi(x). \tag{27}$$

Just as the value of the apparatus function a(x) was necessary for the description of the total effect of the distorting factors of the second group, so must we, for the description of random errors, give statistical mean characteristics of the function $\xi(x)$, which naturally depend on the origin of $\xi(x)$, that is, on those conditions that led to the random errors.

We shall not undertake to set forth the well-known results of the theory of errors nor give any exhaustive analysis of errors for spectroscopic measurements. This is partially connected with the fact that these questions have been exhaustively treated in the literature (see, for example, references 1, 8, 59 — 66). Another basic reason is the circumstance that at the present time analysis of Eq. (27) i.e., the simultaneous consideration of both systematic and random errors, has been carried out in the literature only for a single type of function $\xi(x)$, namely, for the case in which the mean characteristics of $\xi(x)$ do not depend on f(x). In particular, such a situation is realized in contemporary infrared spectrophotometers, where the random errors are almost entirely determined by fluctuation processes in the radiation detector (Johnson noise of the voltmeter, photo-resistance, etc.). In photographic recording, the random errors are obviously proportional to the intensity on the photographic plate,[1] and the theory outlined below is not applicable to this case.

Under the limitations outlined above, the mean values of the errors is equal to zero, so that (6) and (8) are left unchanged by normalization. The random function $\xi(x)$ can be given, with completeness that is sufficient for our purposes, by the correlation function:[8]

$$\psi(|x-x'|) = \overline{\xi(x)\,\xi(x')}, \tag{28}$$

which characterizes the interdependence of random errors in different parts of the spectrogram. For $x = x'$, the correlation function is clearly equal to the mean square error

$$\psi(0)=\overline{\xi^2}=\overline{\Delta f^2}. \tag{29}$$

If the electrical inertia of the radiation detector is much less than the inertia of the recording instrument, which is usually the case, then, as can be shown,[8] the correlation function $\psi(x)$ is equal to

$$\psi(z)=c\int_{-\infty}^{\infty} a_2^*(x)\,a_2(z+x)\,dx, \tag{30}$$

That is, it is expressed by the apparatus function of the recording instrument. The coefficient c is proportional to the mean-square error of recording and can be determined from the condition (29). We recall that the function $f(x)$ satisfies the normalization condition (8) and, consequently, for the transition from $\xi(x)$ to fluctuations in the recording itself, it is necessary to multiply $\xi(x)$ by the integral of the directly recorded observed distribution, and to multiply the mean square combination of the type (28) by the square of this integral.

We can see from Eq. (30) that the correlation function is essentially different from zero in an interval of the order of the time constant of the recording equipment. This means that the random errors are essentially dependent only at points which are distant from each other by intervals of the order of the time constant, which is physically evident. At points at greater distances from each other, the errors are virtually statistically independent.

In spectral language, the description of random errors is given by the Fourier transform of the correlation function

$$\Psi(\omega)=\int_{-\infty}^{\infty}\psi(z)\,e^{-i\omega z}\,dz, \tag{31}$$

usually called the mean spectral density of the intensity of the fluctuations.[8] From the formula for the inversion of the Fourier integral, we have

$$\psi(z)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\Psi(\omega)\,e^{iz\omega}\,d\omega. \tag{32}$$

Setting z equal to 0 in this equation, and taking (29) into account, we obtain:

$$\psi(0)=\overline{\xi^2}=\frac{1}{2\pi}\int_{-\infty}^{\infty}\Psi(\omega)\,d\omega. \tag{33}$$

This equation has the following interpretation. In a recording of the energy distribution over the spectrum, in addition to the "useful signal" [the first term in (27)] with the spectrum $A(\omega)\Phi(\omega)$, there are present fluctuations, the random errors $\xi(x)$, which can be represented in the form of a set of random harmonics, the mean power of which referred to a unit interval of frequency is $\psi(\omega)$. Consequently, we can consider $\psi(\omega)\,d\omega$ as the mean fluctuation power which takes place in an infinitely narrow band of frequencies $d\omega$. The mean square error of the recording is the sum of all these harmonic fluctuations.

We shall now give the expression $\psi(\omega)$ in terms of the Fourier transform $A_2(\omega)$ of the apparatus function of the recording instrument, i.e., in terms of its frequency characteristic. Carrying out the Fourier transformation on the left and right hand sides of Eq. (30), we obtain the result that

$$\Psi(\omega)=c\,|A_2(\omega)|^2. \tag{34}$$

This equation, as also Eq. (30), is valid only when the inertia of the recording instrument far exceeds the electrical inertia of the radiation detector. Such is usually the case for spectroscopic measurements.

In the opposite case, it is necessary to multiply the right hand side of (34) by the spectral density of the fluctuation power in the radiation detector. By virtue of the normalization (8), we have $A_2(0) = 1$. Consequently, c is nothing else than the spectral density of the intensity of the fluctuations at $\omega = 0$:

$$c=\Psi(0). \tag{35}$$

## 2. REDUCTION TO AN IDEAL INSTRUMENT

1. In the analysis of the general equation (27) it is appropriate to consider the limiting case of absolutely accurate measurements, which are described by Eq. (1). The present section is devoted to precisely this case, while Sec. 3 will contain the consequences which follow from the presence of random errors.

Depending on circumstances, various problems connected with Eq. (1) will be of interest, and in correspondence with the physical arrangement of the problem there will be different mathematical problems. Historically, the first statement of the problem was the following: if the true distribution consists of two monochromatic lines which are separated by a distance d, i.e.,

$$\varphi(x)=\frac{1}{2}\left[\delta\left(x-x_0-\frac{d}{2}\right)+\delta\left(x-x_0+\frac{d}{2}\right)\right],$$

then for what value of d at the point $x = x_0$ will there be a minimum of intensity with a definite amount of contrast? This problem is directly connected with the resolution problem or the problem of the determination of the minimum resolved interval of wavelengths, which will be considered in Sec. 4, and is a special case of the more general

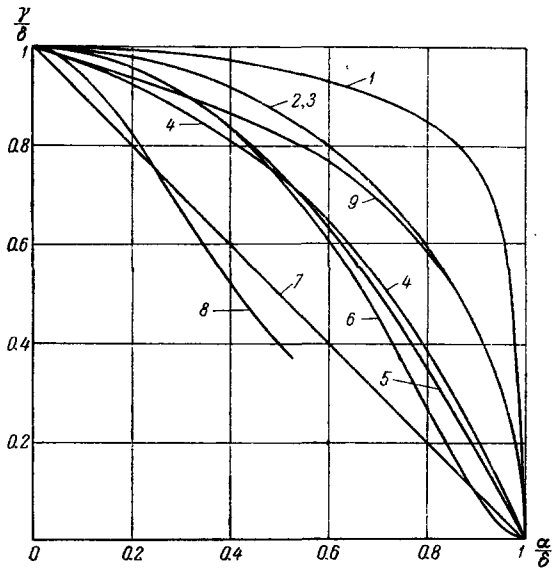


FIG. 4. Relation between the width $\delta$ of the convolution f(x) of the functions $\varphi(x)$ and a(x) with the widths $\gamma$ and $\alpha$ for various forms of and a(x): 1) rectangular ($\alpha$) and diffraction ($\gamma$); 2) slit shaped ($\alpha$) and dispersion ($\gamma$); 3) Gaussian ($\alpha$) and Gaussian ($\gamma$); 4) diffraction ($\alpha$) and dispersion ($\gamma$); 5) Gaussian ($\alpha$) and dispersion ($\gamma$); 6) triangular ($\alpha$) and dispersion ($\gamma$); 7) dispersion ($\alpha$) and dispersion ($\gamma$); 8) exponential ($\alpha$) and dispersion ($\gamma$); 9) Gaussian ($\alpha$) and triangular ($\gamma$).

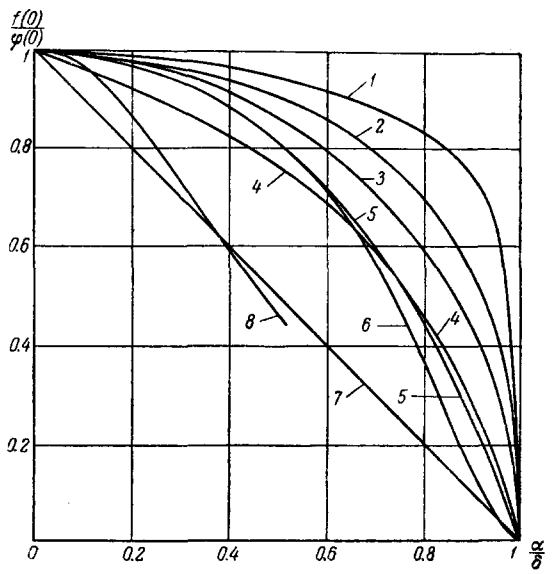


FIG. 5. Maximum value of the convolution f(0) of the functions $\varphi(x)$ and a(x) in dependence on the ratio of the widths $\alpha(\delta)$ of the functions a(x) and f(x). The identification of the curves follows that of Fig. 4.

problem of the calculation of the observed distribution f(x) from the given true distribution $\varphi(x)$ and the apparatus function a(x). In spite of the essential simplicity of the mathematical solution of the problem, which reduces to the calculation of the integral in (1), such calculations rarely lead to simple expressions f(x) in terms of elementary functions. In the majority of cases, one has to be satisfied with graphical or numerical results. Nonetheless, such material is useful in practical research. Therefore, we have plotted in Fig. 4 graphs giving the relation between the widths of the true and observed distributions for various forms of $\varphi(x)$ and a(x). In Fig. 5 there are given the dependences of the intensity at the maximum of the line. These parameters are the most used for all sorts of estimates.

The problem of establishing such distributions $\varphi(x)$, which are transmitted with a real instrument without distortion or in the form of an identical distribution, i.e., distributions for which the following relation holds, is of the utmost importance:

$$f(x) = \lambda\varphi(x). \tag{36}$$

The solution of this problem, which was considered by L. I. Mandel'shtam,[16] consists in the fact that only a sinusoidal distribution satisfies the condition (36) in the general case. Actually the true distribution will not be distorted by a real instrument only in that case in which all its harmonic components will be diminished in amplitude by the same amount, that is, if

$$A(\omega) = \text{const}. \tag{37}$$

The analysis carried in Sec. 1 showed that the Fourier transform of the apparatus functions of real spectral instruments do not satisfy this condition and therefore we can only talk about a sufficiently small difference of f(x) and $\varphi(x)$. However, we can establish a criterion of smallness only upon consideration of random errors of measurement.*

The most important practical problem of the theory is the problem of the reduction to an ideal instrument. By reduction to an ideal instrument we mean the finding of the true distribution for a given observed distribution f(x) and apparatus function a(x).† The particular problem of reduction will be treated in Secs. 2 and 3.

2. As is seen from (1), for absolutely accurate measurements, the reduction leads to a solution of the linear integral equation of first order with a different kernel a(x−y) and the observed distribution f(x) on the left hand side of the equa-

*For certain special forms of $\varphi(x)$ and a(x), the condition (36) will be satisfied (see reference 16 and reference 23, pages 389 and 441, respectively). However, such apparatus functions are not possible in spectral instruments.

†Sometimes other terminology is used, for example, "correction of experimental results for apparatus distortion," "elimination of the apparatus function," etc.

tion. Many different methods of solution in this equation are described in the literature; these will be described below. Here, for a clarification of the connection between the various methods, their advantages and disadvantages, it is appropriate to adopt the point of view of the spectral approach.

A general solution of the problem of reduction from the point of view of the spectral approach consists in the following: each harmonic component of the observed distribution is reduced, that is, $F(\omega)$ is multiplied by $1/A(\omega)$, and all the reduced harmonics are summed. Formally, this reduces to a solution of Eq. (15) relative to $\Phi(\omega)$, and the substitution of the resultant expression in (11):[23]

$$\varphi(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{F(\omega)}{A(\omega)}e^{ix\omega}\,d\omega. \tag{38}$$

Equation (38) gives the general solution of Eq. (16) and, at the same time, the general solution of the problem of reduction for absolutely accurate measurements. However, in recent times, Eq. (38) has rarely been used for direct treatment of experimental data. This is explained by the fact that the spectral instrument does not measure $F(\omega)$ but rather the energy distribution $f(x)$,* and direct use of (38) requires rather difficult preliminary conversion from $f(x)$ to $F(\omega)$. However, with the development of machine-computation technology, this process will not be difficult and perhaps the reduction will be carried out immediately from (38). At the present time in most cases we attempt to select for $F(\omega)$ and $A(\omega)$ simple analytic expressions for which the integral in (38) is computed in explicit form, or so to transform (38) that it would be possible to carry out direct operations on $f(x)$ leading to $\varphi(x)$. In connection with this, the different methods of reduction found in the literature lead to the following classification: (1) analytical methods that start out from a given or an approximate $F(\omega)$ and $A(\omega)$ in terms of simple functions which make possible the integration in (38) in explicit form; (2) methods that reduce the calculation of (38) to a succession of such operations on $f(x)$ (differentiation, integration, etc.), independent of the form $f(x)$; usually these methods are graphical or numerical; (3) finally, there are mixed methods; thus there is, for example, a variant of the method of successive approximations, in which the zeroth approximation is the solution obtained by an analytic method and the subsequent approximations are graphical or numerical.

First we shall consider analytic methods. Approximations of $F(\omega)$ and $A(\omega)$ by expressions of the form

$$\exp\{-\beta_1|\omega|-\beta_2\omega^2\}. \tag{39}$$

have received widespread use. For example, if

$$F(\omega)=\exp\{-\delta|\omega|\};\quad A(\omega)=\exp\{-\alpha|\omega|\}, \tag{40}$$

which corresponds to a description of the observed distribution and the apparatus function in terms of the dispersion curves of the form

$$f(x)=\frac{\delta/\pi}{x^2+\delta^2};\quad a(x)=\frac{\alpha/\pi}{x^2+\alpha^2}, \tag{41}$$

then

$$\left.\begin{aligned}&\Phi(\omega)=\exp\{-(\delta-\alpha)|\omega|\};\\&\varphi(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-(\delta-\alpha)|\omega|+ix\omega}\,d\omega=\frac{(\delta-\alpha)\pi}{x^2+(\delta-\alpha)^2},\end{aligned}\right\} \tag{42}$$

that is, the true distribution also has a dispersion form in which its width $2\gamma$ is equal to the difference in width of the observed distribution and the apparatus function $2\gamma = 2(\delta-\alpha)$. The approximations of (40) or (41) are often applied to the investigation of lines of emission spectra of atoms (see, for example, reference 70), Rayleigh lines and Raman scattering of light,[33,41,51,71,72] in x-rays,[10,73,74] astrophysics,[11,75] and in other cases. In these regions, and also in infrared spectroscopy there is application of another special case of Eq. (39):[4,11,12,33,40,75,76]

$$F(\omega)=\exp\{-\delta^2\omega^2/4\};\quad A(\omega)=\exp\{-x^2\omega^2/4\}, \tag{42'}$$

which corresponds to the approximation of the observed distribution and apparatus function by Gaussian curves

$$f(x)=\frac{1}{\sqrt{\pi}\,\delta}\exp\{-x^2/\delta^2\};\quad d(x)=\frac{1}{\sqrt{\pi}\,\alpha}\exp\{-x^2/\alpha^2\}. \tag{43}$$

In this case the true distribution also has a Gaussian form

$$\Phi(\omega)=\exp\{-(\delta^2-\alpha^2)\omega^2/4\};$$

$$\varphi(x)=\frac{1}{\sqrt{\pi(\delta^2-\alpha^2)}}\exp\{-x^2/(\delta^2-\alpha^2)\}, \tag{44}$$

and its width is equal to

$$2\gamma=2\sqrt{\delta^2-\alpha^2}. \tag{45}$$

Use of the complete expression (39), that is, the approximation

$$\left.\begin{aligned}&F(\omega)=\exp\{-\delta_1|\omega|-\delta_2^2\omega^2/4\};\\&A(\omega)=\exp\{-\alpha_1|\omega|-\alpha_2^2\omega^2/4\},\end{aligned}\right\} \tag{46}$$

*An exception in this relation is the determination of the structure of a line by means of a double beam interferometer,[9] where $|F(\omega)|$ coincides with the "visibility curve," and the treatment of the results consists of the harmonic analysis of the "visibility curve." It should be noted that in references 67, 68 there are applied several improvements of the method, which permit us to avoid the well-known indeterminacy which takes place in the experiments of Michelson.[69]

leads to a similar form for $\Phi(\omega)$ and a representation of the true distribution $\varphi(x)$ by means of the Voigt function

$$\left.\begin{aligned}\Phi(\omega)&=\exp\{-(\delta_1-\alpha_1)|\omega|-(\delta_2^2-\alpha_2^2)\omega^2/4\};\\ \varphi(x)&=\frac{\delta_1-\alpha_1}{\pi\sqrt{\pi(\delta_2^2-\alpha_2^2)}}\int\limits_{-\infty}^{\infty}\frac{\exp\{-y^2/(\delta_2^2-\alpha_2^2)\}}{(x-y)^2+(\delta_1-\alpha_1)^2}\,dy.\end{aligned}\right\}\quad(47)$$

In spite of the rather rough expression for $\varphi(x)$, treatment of the experimental data by this method is comparatively simple, thanks to the excellent tables of the Voigt function in reference 77. In references 12, 47 — 49, and 75 methods are worked out in detail for the determination of the parameters $\alpha_1$, $\alpha_2$, $\delta_1$, $\delta_2$ from observed quantities; these parameters are necessary for the calculation of $\varphi(x)$ by (47).

A characteristic feature of the foregoing methods and of other methods (see references 51, 74, 78, 79) is the description of the initial curves by relatively simple expressions that depend on one or two parameters, wherein, in the introduction of the second parameter, the calculations as a rule become significantly more complicated. It must be assumed that introduction of still another parameter would not be appropriate. Moreover, in many cases the approximations considered are inadequate. In connection with this, more flexible methods have been developed, directly connected with the specific form of the observed distribution.

3. Consideration of approximate universal methods of reduction is properly begun with such a transformation of Eq. (38) that we isolate that part which is connected with a non-ideal instrument. The apparatus function of an ideal instrument is a $\delta$-function, while its Fourier transform is equal to unity:

$$\int\limits_{-\infty}^{\infty}\delta(x)\,e^{-i\omega x}\,dx=1.\quad(48)$$

Therefore, it is natural to add and subtract unity to $A^{-1}(\omega)$ under the integral sign in (38); we then have

$$\varphi(x)=\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}F(\omega)\,[A^{-1}(\omega)-1]\,e^{i\omega x}\,d\omega+\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}F(\omega)\,e^{i\omega x}\,d\omega$$

$$=f(x)+\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}[A^{-1}(\omega)-1]\,F(\omega)\,e^{i\omega x}\,d\omega.\quad(49)$$

The second term in this equation is often a relatively small correction which vanishes in an ideal instrument, and the major part of approximating methods reduced to some particular variation of calculation of this term.

It should be emphasized that $A(\omega)$ is characteristic for the function of the given instrument, while both the energy distribution over the spectrum and, consequently, the function $F(\omega)$ can be extremely varied. In connection with these methods, it is natural to base the reduction only on assumptions concerning the properties of $A(\omega)$, but not of $F(\omega)$. Therefore, a majority of the approximate universal methods of solution of Eq. (1) obtained with the help of the expansion of $A^{-1}(\omega) - 1$ in functional series.

Let us first consider an expansion in a power series

$$A^{-1}(\omega)-1=\sum_n b_n\omega^n.\quad(50)$$

We substitute this expression in (38) and change the order of integration and summation:

$$\varphi(x)=f(x)+\sum_n b_n\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}\omega^n F(\omega)\,e^{i\omega x}\,d\omega.$$

We can compute the resultant integrals by differentiating $f(x)$ n times:

$$\frac{d^nf}{dx^n}=\frac{d^n}{dx^n}\left\{\frac{1}{2\pi}\int\limits_{-\infty}^{\infty}F(\omega)\,e^{i\omega x}\,d\omega\right\}=\frac{i^n}{2\pi}\int\limits_{-\infty}^{\infty}\omega^n F(\omega)\,e^{i\omega x}\,d\omega.$$

Consequently,

$$\varphi(x)=f(x)+\sum_n\frac{b_n}{i^n}\frac{d^nf}{dx^n}.\quad(51)$$

Thus, expansion of $A^{-1}(\omega) - 1$ in a power series corresponds to the expression of $\varphi(x)$ in terms of $f(x)$ and its derivatives, while the coefficients are determined only by the apparatus function. Solution in the form (51) was obtained by Eddington,[80] Hardy and Young,[81] and other authors[49,82,83] for certain specific forms of the apparatus functions of spectral instruments. In reference 84 an attempt was made to correct the distortions introduced by the inertia of the thermal light detector with the aid of a differentiating network, which is a customary method for high-frequency correction in radio-electronics. It is easy to see that this corresponds to the calculation of the first term of Eq. (51).

Equation (51) takes an especially simple form upon elimination of the apparatus function of a photographic emulsion. According to (23), only $b_2$ differs from zero in this case, that is,[49]

$$\varphi(x)=f(x)-\left[\frac{\alpha}{2\ln 2}\right]^2\frac{d^2f}{dx^2}.\quad(52)$$

Transforming this result, we can set up the problem of finding such an approximate function for the apparatus function that the expansion (50) contains two terms, i.e., that all $b_n = 0$ except, for example, $b_2$ and $b_4$. If the following expression is given for $A(\omega)$:

$$A(\omega)=[1+\alpha_1^2\omega^2]^{-1}\,[1+\alpha_2^2\omega^2]^{-1},\quad(53)$$

then the exact solution of Eq. (1) will have the form

$$\varphi(x) = f(x) - (\alpha_1^2 + \alpha_2^2)\frac{d^2f}{dx^2} + \alpha_1^2\alpha_2^2\frac{d^4f}{dx^4}. \qquad (54)$$

The apparatus function which corresponds to (53) is (see, for example, reference 85)

$$a(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{e^{ix\omega}\,d\omega}{(1+\alpha_1^2\omega^2)(1+\alpha_2^2\omega^2)}$$

$$= \frac{1}{2(\alpha_1^2-\alpha_2^2)}[\alpha_1 e^{-|x|/\alpha_1} - \alpha_2 e^{-|x|/\alpha_2}]. \qquad (55)$$

A graph of this function, in contrast to (23), has an extremum at the point $x = 0$, while the presence of two parameters enables us to change the form for "adjustment" in the apparatus function of real instruments within certain limits.

The insufficiency of the solution of the form (51) is that calculation of the derivatives according to the curve measured experimentally, a curve obtained with a certain error, is actually very difficult and in essence reduces to the calculation of finite differences. Below (Sec. 3), it will be seen that this difficulty is not accidental but in principle takes place in any method of reduction which can be shown to be exact for some form of the apparatus function.

A natural generalization of the derivation of Eq. (51) is the following. Let $A^{-1}(\omega) - 1$ be expanded in a certain functional series

$$A^{-1}(\omega) - 1 = \sum_n b_n u_n(\omega). \qquad (56)$$

Substituting (56) in (49), and changing the order of summation and integration, we obtain

$$\varphi(x) = f(x) + \sum_n b_n \frac{1}{2\pi}\int_{-\infty}^{\infty} u_n(\omega) F(\omega) e^{ix\omega}\,d\omega. \qquad (57)$$

In analogy to the case considered above, we can say that the multiplication of the Fourier transform $F(\omega)$ of the function $f(\omega)$ by some function $u_n(\omega)$ means a definite operation on the same function $f(x)$. If $u_n(\omega) = \omega^n$, then this operation is an n-fold differentiation; if $u_n(\omega) = \exp\{-ina\omega\}$, then the corresponding operation consists in a shift along the x axis by a distance na, etc. Of course, multiplication of $F(\omega)$ by $A^{-1}(\omega)$ can also be regarded as a certain operation. The meaning of the approximate methods is also that the operator $A^{-1}(\omega) - 1$ is replaced by a set of operators $u_n(\omega)$, which define operations that are more suitable (in some fashion or other) than the operations determined by the same operator $A^{-1}(\omega) - 1$.

We shall consider other methods of solution from this point of view. Historically, the first method to be developed was that of finite differences. This method is obtained by the following expansion:

$$A^{-1}(\omega) - 1 = \sum_n b_n \sin^n\frac{a\omega}{2}. \qquad (58)$$

Calculating the first term of a series in (57),

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\sin\frac{a\omega}{2}F(\omega)e^{ix\omega}\,d\omega$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{1}{2i}[e^{i(x+a/2)\omega} - e^{i(x-a/2)\omega}]F(\omega)\,d\omega$$

$$= \frac{1}{2i}[f(x+a/2) - f(x-a/2)] \equiv \frac{1}{2i}\Delta_a^1 f(x),$$

we conclude that multiplication $F(\omega)$ by $2i\sin\frac{a\omega}{2}$ corresponds to the operation of taking the finite difference of $f(x)$ over the interval a, while multiplication by $(2i)^n\sin^n\frac{a\omega}{2}$ is an n-fold application of this operation, i.e., the taking of the finite difference $\Delta_a^n f(x)$ of order n in the interval a (see, for example, reference 82). Thus we obtain the following expression for $\varphi(x)$:

$$\varphi(x) = f(x) + \sum_n \frac{b_n}{(2i)^n}\Delta_a^n f(x). \qquad (59)$$

This method was advanced by Rayleigh in 1871[84] for the reduction of observed spectra for infinitesimally narrow slits of a monochromator; there he limited himself only to the first non-vanishing correction. Thereafter, the method was developed by Paschen and Runge,[87,88] who took into consideration higher approximations. In subsequent investigations, the case was considered of a monochromator with different widths of the input and exit slits,[89] the change of the dispersion over the range of the width of the slit[90] was considered and, finally, a generalization of the method of finite differences for other "non-slit" apparatus functions was given.[91]

The method of finite differences is applied at present to a wide variety of cases. Widespread use of this method of reduction is accounted for in a significant degree by the extraordinary simplicity of the calculation of corrections with the aid of a geometrical construction also given by Rayleigh. In reference 92, a correction was carried out according to coefficients for a parabolic interpolation of the observed distribution. This method, being equivalent to the construction of Rayleigh, is significantly less useful practically and is rarely employed.

It is interesting to note that the parameter a in Eqs. (58) and (59) was never specified and can be chosen arbitrarily; in particular, for $a \to 0$, the method of finite differences transforms into the method of Eddington. In the expressions obtained by Paschen and Runge,[87,88] the finite difference is taken over an interval equal to the width of the slit s of the monochromator, while Rayleigh used an interval equal to $s/\sqrt{2}$.[86] In Sec. 3 we shall see that this is arbitrarily removed in a

reasonable manner only upon calculation of random errors of measurement. If we represent $A^{-1}(\omega) - 1$ in the form of a trigonometric series

$$A^{-1}(\omega) - 1 = \sum_n b_n e^{-ian\omega}, \qquad (60)$$

then the solution of Eq. (1) has the following form:

$$\varphi(x) = f(x) + \sum_n b_n f(x - an), \qquad (61)$$

inasmuch as $u_n(\omega) = \exp\{-ian\omega\}$ is the "displacement operator." Thus it is easy to see that the latter two methods are quite related, since we can express $\sin^n \frac{a\omega}{2}$ in terms of multiple harmonics, and go from (58) to (60). From the practical point of view, these methods are different, since they define different operations on the real distribution $f(x)$ in the calculation of a finite number of terms: in (59) we shall limit ourselves to the finite difference of a particular order, say the second, while in (61) we shall limit ourselves to values of the functions at points that are a sufficiently large distance from the point x, for example, $\pm 2a$.

We can achieve the solution in the form (61) by different means. In many researches where such a form has been advanced, the author started out from the approximate substitution of the integral equation (1) by a system of linear algebraic equations with the aid of various formulas of approximate integration; then this system was solved in some fashion or other.[93-95] In a number of papers use has been made of trigonometric expansions for solution of Eq. (1). Such an expression can be obtained if we write

$$A^{-1}(\omega) - 1 = \sum_n b_n \delta\left(\omega - \frac{n}{a}\right). \qquad (62)$$

then, obviously,

$$\varphi(x) = f(x) + \frac{1}{2\pi} \sum_n b_n F\left(\frac{n}{a}\right) e^{i\frac{n}{a}x}, \qquad (63)$$

that is, the expansion (62) corresponds to replacing the integral (49) by a series or, in practice, by a sum of a finite number of terms. This method is usually applied in x-ray research,[96,97] and, as is pointed out in reference 98, it can be suitable for the investigation of spectral lines by the Fabry-Perot etalon (by virtue of the periodicity of its apparatus function.)

We shall now consider the method of successive approximations put forth by Berger and van Cittert,[99,100] and frequently applied in the reduction to an ideal instrument in various cases.[75,82,92,98] This method corresponds to an expansion of $A^{-1}(\omega) - 1$ in a geometric progression:[82,93,101]

$$\frac{1}{A(\omega)} - 1 = \frac{1 - A(\omega)}{1 - [1 - A(\omega)]} = \sum_{n=1}^{\infty} [1 - A(\omega)]^n. \qquad (64)$$

In contrast to the cases considered previously, the operator is an integral operator. Actually, in accordance with the theorem given above on the representation of a function whose Fourier transform is equal to the derivative of the transform of two other functions, we have, calculating for example the first term of the series in (64),

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} [1 - A(\omega)] F(\omega) e^{ix\omega} d\omega = f(x) - \int_{-\infty}^{\infty} a(x - y) f(y)\, dy.$$

If we can consider the n first terms of the series (52), then we can represent the solution in the form

$$\varphi(x) = f(x) + \{nf(x) - \int_{-\infty}^{\infty} U_n(x - y) f(y)\, dy\}, \qquad (65)$$

where the resolvent $U_n(x)$ is expressed in the following fashion:

$$\left.\begin{aligned} U_n(x) &= \frac{(n+1)n}{2!} a(x) - \frac{(n+1)n(n-1)}{3!} a_1(x) + \ldots + (-1)^n a_{n-1}(x); \\ a_1(x) &= \int_{-\infty}^{\infty} a(x - y) a(y)\, dy; \quad a_k(x) = \int_{-\infty}^{\infty} a(x - y) a_{k-1}(y)\, dy. \end{aligned}\right\} \qquad (66)$$

For each particular instrument the resolvent can be calculated beforehand and the reduction leads to calculation of the integral in (65). Special integrators[99,102] have been prepared for computation of corrections by the method of successive approximations. These permitted rapid computation of integrals of the type (66).

In the practical employment of the method of successive approximations, the following notes can be useful. Under real conditions, the width of the slit of a spectral apparatus is frequently changed in correspondence with the widths of the lines and bands investigated, and for other reasons. In order that it not be necessary to recompute the resolvent for each value of the slit width, successive elimination of slit and non-slit distortions is carried out. In many cases, we can consider the former in terms of the simpler method of finite differences of (59). A second remark is connected with the fact that the roughness with which $f(x)$ and $a(x)$ are known gets worse in the higher approximations, i.e., for large n. Therefore, as

the authors of the method point out, the solution will be satisfactory if we can limit ourselves to the first approximation.

In addition to the methods discussed above, there is a series of other methods of solution of Eq. (1), which, however, have not found application in spectroscopy. There are methods consisting of the simultaneous application of the operators of displacement and differentiation,[82] and also a method (which is interesting from the mathematical point of view) of expansion into the orthogonal polynomials of Hermite and Bernoulli.[103]

We pause on the problem of the choice of zeroth approximation. As was discussed above, in many cases we have unity for the zeroth approximation in the expansion of $A^{-1}(\omega)$; in this connection, the zeroth approximation for the solution of Eq. (1) is the observed distribution f(x). The rational form of the expansion of $A^{-1}(\omega)$ is fundamentally determined by the properties of the apparatus function. In a number of cases, however, when the higher approximations have large values, it can be shown to be appropriate to take into consideration the character of the observed distribution. This can be done in the following way. Let us represent

$$f(x) = f_0(x) + f_1(x); \quad a(x) = a_0(x) + a_1(x), \qquad (67)$$

where $f_0(x)$ and $a_0(x)$ are certain functions, given in analytical form, for which the solution $\varphi_0(x)$ of Eq. (1) is known, and which satisfactorily reproduce the curve of the functions f(x) and a(x), respectively, so that we can consider $a_1(x)$ and $f_1(x)$ to be small. For example, for $f_0(x)$ and $a_0(x)$, we can take the Gaussian or the dispersion curve. We get the function $\varphi_0(x)$ as a zeroth approximation. Substituting (67) in (1), we get the following equation

$$f_1(x) - \int_{-\infty}^{\infty} a_1(x-y)\,\varphi_0(y)\,dy = \int_{-\infty}^{\infty} a(x-y)\,\varphi_1(y)\,dy \qquad (68)$$

relative to the function $\varphi_1(y) = \varphi(y) - \varphi_0(y)$. We can now solve this equation by the methods considered above; its solution will determine the correction to the zeroth approximation.

**5.** In concluding this section, let us note some special cases of reduction which are not included in the scheme set forth above. First, we have the interesting reduction method advanced in reference 104 for the case of the Fabry-Perot etalon. The apparatus function of the Fabry-Perot etalon, as was shown in reference 104, can be represented in the form of a superposition of equidistant contours of the dispersion shape with identical intensities:

$$a(x) = \frac{(1+r)/(1-r)}{1+\frac{4r}{(1-r)^2}\sin^2\pi x} = \sum_{-\infty}^{\infty} \frac{\alpha/\pi}{(x-m)^2+\alpha^2}; \quad \alpha = \frac{1}{2\pi}\ln\frac{1}{r}. \qquad (69)$$

It then follows that for the dispersion form of the true distribution, the observed distribution is also expressed in terms of a series of dispersion curves, similar to (69), which can, after some transformations, lead to the following expression:

$$f(x) = \sum_{-\infty}^{\infty} \frac{\delta/\pi}{(x-m)^2+\delta^2} = \frac{\coth\pi\delta}{1+\left[\frac{\sin\pi x}{\sinh\pi\delta}\right]^2}; \quad \delta = \gamma + \alpha, \qquad (70)$$

where $\gamma$ is the width of the true distribution. Thus, determining the parameters $\delta$ and $\alpha$ of the observed distribution and the apparatus function, we can compute the true line width. Equations (69) and (70) take into consideration the superposition of neighboring interference maxima and make more precise the usual method,[53] in which the apparatus function of the etalon is approximated only by a single dispersion curve. We note that the expansion (70) can also be shown to be useful in the treatment of the almost periodic structure of rotational spectra.

A second special case relates to the measurement of absorption spectra. Here Eq. (1) connects the true, $\varphi(x)$, and the observed, f(x), transmission. The characteristic of the material is not the transmission but the absorption coefficient, which is determined according to Bouguer's law by the relation

$$k(x) = \frac{1}{d}\ln\frac{1}{\varphi(x)} \equiv \frac{1}{d}D(x), \qquad (71)$$

where d is the thickness of the absorbing specimen and D(x) is its optical density. Consequently, the true form of the band absorption, which is determined by the function $1-\varphi(x) = 1-e^{-dk(x)}$, will not dpend on d only for small values of dk(x). In this connection, some authors have considered an equation in which the unknown function is the optical density directly, i.e., the following nonlinear integral equation:

$$D_{obs}(x) = -\ln\left\{\int_{-\infty}^{\infty} a(x-y)\,e^{-D(y)}dy\right\}, \qquad (72)$$

where $D_{obs}(x) = \ln\frac{1}{f(x)}$ is the observed value of the optical density[35,105,106]. Expansion of the right hand side of the equation allows us to simplify this expression to a certain degree, representing $D_{obs}(x)$ in the form of a power series in the value of the true absorption.[35,107] For example, for the case of a single absorption line, (72) takes the following form

$$D_{obs}(x) = J_1(x)\, D_m - \beta_1(x)\, D_m^2 + \ldots, \qquad (73)$$

where $D_m$ is the true density at the maximum of the line, and the coefficients $J_1$, $\beta_1, \ldots$ must be considered in terms of the known apparatus function of the monochromator and the curve $k(x)$ of the true absorption coefficient, whose form is also assumed to be known. If these data change then, by numerical or graphical integration in (72) or, what is simpler, use of the series (73), we can tabulate known values of the absorption and line widths as functions of the observed function and band width and the width of the apparatus function. The results of detailed calculations of such a type were given in references 35 and 107 for the case of a triangle-shaped apparatus function and a dispersion of the form $k(x)$. In the general case, in which the form of the case of the true absorption coefficient is unknown and the problem consists in finding this coefficient, use of Eqs. (72) and (73) do not simplify but greatly complicates the calculations. Here it is more appropriate to solve Eq. (1) relative to the transmission $\varphi(x)$ by the universal methods previously considered, and to transform to the densities by taking the logarithm of the latter.

All the methods described in the present section refer to the determination of the total true distribution $\varphi(x)$. In a number of cases, especially for macroscopic measurements for analytical purposes, values of less than complete characteristics of the true spectrum are sufficient, for example the integral absorption coefficient, "effective width" of the line, intensity at the maximum of the line, etc. Not going into details, we refer only to references 1, 24, 75, 105, and 107, where the methodology is considered and such "non-total" reduction is actually carried out.

## 3. UNIQUENESS AND ACCURACY OF REDUCTION* TO AN IDEAL INSTRUMENT

1. The problem of the uniqueness of the reduction is fundamental in the theory of reduction. The importance of this problem is evident, inasmuch as only its complete evaluation permits us to judge objectively the experimental data and to make them the basis for any conclusions.

In the limiting case of absolutely accurate measurements, the problem of the uniqueness of the reduction reduces to a statement of the condition for the uniqueness of the solution of Eq. (1). It has been shown by Bracewell and Roberts[101] and Toraldo di Francia that Eq. (1) does not have a unique solution if the Fourier transform $A(\omega)$ of the apparatus function $a(x)$ vanishes at certain points (or in a certain region). Actually, if the function $A(\omega)$ vanishes at the points $\omega = \omega_j$, $A(\omega_j) = 0$, then $\Phi(\omega)$ is indeterminate, since Eq. (15) is satisfied not only by the function

$$\Phi_1(\omega) = F(\omega)\, A^{-1}(\omega), \quad \omega \neq \omega_j, \qquad (74)$$

but also by functions of the form

$$\Phi_2(\omega) = \Phi_1(\omega) + \sum_j a_j \delta(\omega - \omega_j), \qquad (75)$$

where $a_j$ is an arbitrary number. If $A(\omega)$ vanishes in a region of frequencies $\omega_1 < \omega < \omega_2$, then

$$\left.\begin{aligned} &\Phi_2(\omega) = \Phi_1(\omega) + \sum_j a_j \delta(\omega - \omega_j) + b(\omega)\, s(\omega); \\ &s(\omega) = \begin{cases} 1, \omega_1 < \omega < \omega_2; \\ 0, \omega_1 > \omega;\ \omega > \omega_2, \end{cases} \end{aligned}\right\} \qquad (76)$$

where $b(\omega)$ is an arbitrary function. Taking the inverse Fourier transform, we obtain the following equation $\varphi_2(\omega)$:[101]

$$\varphi_2(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Phi_1(\omega)\, e^{ix\omega} d\omega + \frac{1}{2\pi} \sum_j a_j e^{i\omega j y} + \frac{1}{2\pi} \int_{\omega_1}^{\omega_2} d(\omega)\, e^{i\omega x} d\omega. \qquad (77)$$

Thus, if the Fourier transform $\Phi(\omega)$ of the investigated distribution $\varphi(x)$ contains harmonics whose frequencies coincide with the zeroes of the Fourier transform $A(\omega)$ of the apparatus function, then these harmonics do not affect the observed distribution $f(x)$ and, consequently, can in no way be "recovered" from this distribution.

From this point of view let us consider specific expressions for the apparatus functions given in Sec. 2. If, for example, the apparatus function is determined only by the finiteness of the slit width [see (17) and (17a)], then its Fourier transform vanishes at the point

$$\omega_j = \pm \frac{2\pi}{s} j, \quad j = 1, 2, 3, \ldots$$

Consequently,

$$\varphi_2(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Phi_1(\omega)\, e^{ix\omega} d\omega + \frac{1}{2\pi} \sum_{j=1}^{\infty} \left[a_j e^{i\frac{2\pi}{s} ix} + a_{-j} e^{-i\frac{2\pi}{s} jx}\right],$$

i.e., $\varphi_2(x)$ is determined with accuracy up to periodic functions whose period is equal to the slit width $s$ and whose mean value is zero. However, this indeterminacy is not irremovable in principle. Actually, changing the width of the slit, we can change the period of the indeterminate term in $\varphi_2(x)$ and thereby determine experimentally its presence or absence. A similar situation holds for the purely slit apparatus function (18) of the monochromator.

*We remind the reader that the term "reduce" is used here solely in the sense of "restore" or "bring back" rather than "contract" or "decrease" – Tr.

We now return to the other limiting case, when the apparatus function is determined only by diffraction. Unusually, we assume that the apparatus function for a slit-shaped aperture is given by Eq. (16), while its Fourier transform is given by (16a). Consequently, in this case,

$$\varphi_2(x) = \frac{1}{2\pi}\int_{-2\pi/s_0}^{2\pi/s_0} \Phi_1(\omega)\, e^{ix\omega} d\omega + \frac{1}{2\pi}\int_{-\infty}^{-2\pi/s_0} b(\omega)\, e^{ix\omega} d\omega + \frac{1}{2\pi}\int_{2\pi/s_0}^{\infty} b(\omega)\, e^{ix\omega} d\omega.$$

In connection with such a situation, the conclusion was reached in references 101 and 108 that unique reduction to an ideal instrument is impossible and, consequently, diffraction phenomena in the apparatus lead to a limitation on its possibilities as an instrument for the investigation even of absolutely precise measurements in the limiting case.

However, there is an inner contradiction in the reasoning leading to this conclusion. The fact is that Eq. (16a) for $A(\omega)$, which is obtained in the solution of the diffraction problem by the Kirchhoff method, is an approximate expression which is suitable only with a definite degree of accuracy. Consequently, in the investigation of the limiting case of the complete absence of random errors of measurement, Eq. (16a) cannot be used, and must be replaced by the exact expression. On the other hand, it was shown in reference 109 that in the strict analysis of the diffraction problem the exact Fourier transform of the apparatus function cannot vanish over the whole frequency range (see also reference 24). Thus, in contrast to the conclusions of references 101 and 108, it should be emphasized that the diffraction phenomena in a real apparatus do not lead to non-unique reduction in the case of absolutely accurate measurements.

2. However, the position is changed when we take into account random errors of measurement and, accordingly, we go from Eq. (1) to the more complete expression (27). In these cases, phenomena occur which are essentially equivalent to the non-uniqueness of the reduction. Van de Hulst noted in particular[103] that as the accuracy of the reduction method is increased, the reduced distribution ceases to be "smooth," and "peaks" and "troughs" connected with the measurement errors appear. Van de Hulst calls this phenomenon the "instability" of the solution, and emphasizes that it is inherent in the integral equation and is not due to any particular method of its solution. Unfortunately, confirmation of the instability of the solution in reference 103 is treated as an empirical fact to which no explanation or foundation is given.

The nature of the instability of the solution and the relation of this phenomenon to the uniqueness of the reduction can easily be clarified in the following manner.[24] As was observed above (Sec. 2), reduction to an ideal instrument is equivalent to multiplication of the Fourier transform of the observed distribution $F(\omega)$ by $A^{-1}(\omega)$, a quantity that is the inverse of the Fourier transform of the apparatus function. But this operation is unavoidably connected with a randomly-fluctuating component of $F(\omega)$, and each harmonic component of the noise power $\Psi(\omega)$ will be multiplied by $|A^{-1}(\omega)|^2$. Consequently, the error of the reduced distribution will be

$$\overline{\Delta\varphi^2} = \frac{1}{2\pi}\int_{-\infty}^{\infty} \Psi(\omega)\,|A^{-1}(\omega)|^2\, d\omega. \qquad (78)$$

It is not difficult to see that this integral always diverges. Actually, in accord with (34), the mean spectral density of the power of the fluctuation $\Psi(\omega)$ is proportional to the square of the modulus of the frequency characteristic $A_2(\omega)$ of the recording instrument. On the other hand, this same frequency characteristic acts also on the observed distribution, i.e., $A(\omega)$ is the product of $A_2(\omega)$ by the Fourier transform of an apparatus function of optical origin [see (3)]. Denoting the latter quantity by $A_1(\omega)$, we have

$$\overline{\Delta\varphi^2} = \frac{C}{2\pi}\int_{-\infty}^{\infty} |A_1(\omega)|^{-2}\, d\omega. \qquad (79)$$

Inasmuch as $|A_1(\omega)|$ tends to zero upon increase in $\omega$, the integral diverges.

It follows directly from what has been said above that the question as to what sort of error $\overline{\Delta\varphi^2}$ is to be expected if the value of the error $\overline{\Delta f^2}$ in the observed distribution is given — a problem which is common to a whole number of physical measurements — has, in the general case of reduction to an ideal instrument, an unpleasant answer: the error can be arbitrary. This means, furthermore, that the presence of random errors leads essentially to a non-unique reduction. Elimination of this lack of uniqueness is possible only by gathering additional evidence on the investigated distribution, evidence obtained in an independent fashion.

In spectroscopic measurements (and in many other cases), in addition to the evidence obtained in experimental data in the form of recordings of the observed distribution $f(x)$, one frequently assumes additional information on $\varphi(x)$. For example, the form of the true energy distribution over the spectrum of $\varphi(x)$ may be known (single or double lines of Gaussian shapes — Doppler effect; a single line of dispersion shape — natural and

Lorentz damping, etc.). Here it remains to determine only the parameters of the true distribution (the intensity at the maximum, line width and position, distance between lines in the case of several lines, etc.,), and not the whole distribution, and we can speak about the accuracy of the measurement of these parameters in the usual sense. Mathematically, this is expressed by the fact that for a previously known form of $\varphi(x)$ we can determine the integral in (1), and the reduction will be carried not to a solution of the integral equation, but to a solution of an algebraic or transcendental equation, or of a system of equations relating the unknown parameters of the true distributions.[24,27]

In many cases we shall not assume sufficiently detailed information on the true distribution so as to impose so rigid an a priori limitation on $\varphi(x)$ as the postulation of its shape. However, it is shown that for "stabilization" of the solution, in order that the reduction be unique and that we can speak in the usual sense about the accuracy of measurement of the reduced quantities, it suffices to apply to $\varphi(x)$ significantly less stringent requirements, namely an assumption on the behavior of the Fourier transform of the true distribution for large values of $\omega$.[24] Actually, the integral (79) diverges because of the high frequencies. Consequently, the mean error of the reduced distribution will be finite if the high-frequency harmonics of the observed distribution are not only not reduced but on the contrary are significantly suppressed in the process of reduction. But such a reduction will be approximate and, consequently, will be justified only when the Fourier transform $\Phi(\omega)$ of the true distribution does not contain high harmonics. Thus a sufficient condition of the uniqueness of the reduction is a postulate on the smallness of the amplitudes of the harmonics of the true distribution which lie outside of a certain finite frequency integral. If such a postulate is taken into account, then the problem of reduction to an ideal instrument has a definite meaning: it is necessary to restore elements inside of this frequency range and to suppress the harmonics outside of it as much as possible or, in the limiting case, not to restore them.

We shall not consider here the problem of the physical basis of the conditions just pointed out. In actual cases these can be very different. For example, the lower boundary of the width of a single line and, consequently, the upper boundary of the width of the Fourier transform of the true distribution can be controlled by the Doppler effect. For our purposes the problem of establishing the postulate is not significant; of principal value is the very necessity of such a form of the postulate.

3. The methods of reduction that are well known in the literature (see Sec. 2) essentially reflect the described state of affairs, i.e., in all of them, the reduction* is of importance only in some limited frequency interval. For example, the expansion $A^{-1}(\omega) - 1$ in powers of $\sin\frac{a\omega}{2}$, which corresponds to the method of finite differences, is periodic with period $\frac{4\pi}{a}$, as is not difficult to see. Consequently, for a given value of the parameter a it is not the whole Fourier transform of the observed distribution that is generally reduced, but only harmonics with low frequencies.[82,91] The same considerations apply to the expansion (60). In the expansion of the solution in a trigonometric series [see (63)] only a finite number of terms N is used. This is equivalent to the fact that, in corresponding expansion (62) for $A^{-1}(\omega) - 1$, it is assumed that $b_n = 0$ for all $n > N$, that is, once again the high frequency harmonics are not reduced.[96] So far as expansions in power series and the expression of $\varphi(x)$ in terms of $f(x)$ and $\frac{d^n f}{dx^n}$ are concerned, we should note that in practice use is made of approximate values of the derivatives, and this is equivalent either to their replacement by finite differences,[91] or to the bounding of the limits in the integrals $\int \omega^n F(\omega) e^{ix\omega} d\omega$,[84] that is, in this case also the problem becomes that of regular reduction in a finite frequency interval. In this connection we have not included those methods of reduction in which the apparatus function is approximated by analytical expressions. For example, we can consider the approximation of the true distribution of the apparatus function for Voigt profiles as the expansion $\ln A(\omega)$ and $\ln F(\omega)$ in powers of $\omega$,[47] where the first two terms of the expansion are used; this is sufficient only at low frequencies.

For a smooth representation of the considerations given above it is appropriate to introduce a graphical illustration. In Fig. 6 there are shown schematically the graphs of the Fourier transforms

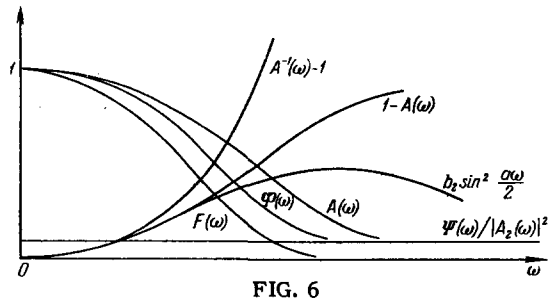


FIG. 6

*See footnote on p. 260.

entering into the consideration of the functions: $\Phi(\omega)$, $A(\omega)$, $F(\omega)$, $A^{-1}(\omega)-1$, and $\Psi(\omega)/|A_2(\omega)|^2$. Furthermore, the given curves corresponding to the first terms of the expansion of $A^{-1}(\omega)-1$ in the methods of Rayleigh and of successive approximations $\left[b_2 \sin\frac{a\omega}{2}\right.$ and $\left.1-A(\omega)\right]$ From Fig. 6 it is seen first of all that in the reduction process the random errors of measurement are increased and that this increase is the more significant the wider the frequency range in which the observed distribution is reduced. Consequently, decrease of systematic apparatus distortions is achieved at the price of increase of random errors in the reduced distribution in comparison with the observed. Conversely, the tendency to transform random errors insignificantly means a bad reduction and, consequently, a large departure of the reduced distribution from the true, i.e., large remaining systematic errors.

From what we have said, the question naturally arises as to the estimate of such an "optimal" method of reduction, by which we would minimize the total mean-square deviation $P^2$ of the reduced distribution from the true, made up of the remaining systematic errors and the random errors arising in the reduction process. It is not difficult to write down this condition mathematically. If we denote by $G(\omega)$ the approximate expression for the Fourier transform of the apparatus function, that which is obtained in the reduction, then $P^2$ has the form[24]

$$P^2=\frac{1}{2\pi}\int_{-\infty}^{\infty}|G(\omega)|^{-2}\Psi(\omega)\,d\omega + \left|\frac{1}{2\pi}\int_{-\infty}^{\infty}[1-A(\omega)G^{-1}(\omega)]\Phi(\omega)e^{ix\omega}\,d\omega\right|^2. \quad (80)$$

The first term of this expression is the random error, the second — the remaining systematic error. Consequently, estimating the optimal method of reduction means such a selection of the function $G(\omega)$ for which the expression (80) has a minimal value. In this case, as is seen from (80), $\Phi(\omega)$, $A(\omega)$ and $\Psi(\omega)$ must be fixed, i.e., the object of investigation and the instrument must be fixed.

Another statement of the problem is possible. We can fix $\Phi(\omega)$ and the method of reduction, i.e., the form of $G(\omega)$, and concern ourselves with the choice of the parameters of the instrument. Such an arrangement of the problem is of practical importance for the following reasons. In the first place, different approximation methods of reduction, as will be seen, lead to approximately identical values of $P^2$. On the other hand, in spectral instruments there are parameters which have a significant effect both on the apparatus function and on the value of the random errors of measurement, and at the same time can easily be varied by the experiment (widths of the slits, rate of scanning, time constant, thickness of the absorption layer etc.). Therefore it is very important to know for what values of these parameters we can carry out measurements in order that $P^2$ would be minimal.

By way of an illustration, let us consider (following reference 58) a choice of a slit width s of the monochromator, a time constant $\tau$, and a scanning rate v in the measurement of the intensity at the maximum of a single line. For simplicity, we assume that the reduction to the ideal instrument is not carried out [i.e., $G(\omega)=1$], that the apparatus function is determined only by the slits of the monochromator, and that s is much smaller than the width of the line. For a recording instrument which is equivalent to an RC network, and for slow scanning $P^2$ is expressed in the following way:

$$P^2=\frac{c^2}{s^4\tau}+[as^2+b(v\tau)^2]^2. \quad (81)$$

The first term in (81) describes the random errors of measurement, while the second gives the systematic error connected with the apparatus functions of the monochromator and the recording instrument. The coefficients a, b, and c are determined by the shape, width, and brightness of the line and also by the properties of the radiation detector. For a line of Gaussian shape of width $\gamma$ and for approximation of the apparatus function by a Gaussian curve of width a = s [see (21)] it is shown that

$$a=1/2\gamma^2;\quad b=4\ln 2/\gamma^2. \quad (82)$$

The optimal values $s=s_m$ and $\tau=\tau_m$, which make $P^2$ a minimum, are found from the conditions $\partial P/\partial s=0$, $\partial P/\partial\tau=0$, whence we easily obtain the following expressions for $s_m$, $\tau_m$, and $P_{min}$:

$$\left.\begin{aligned} s_m^9&=\frac{8}{5}\sqrt{\frac{b}{a^5}}vc^2=16\gamma^4vc^2;\\ \tau_m v&=\frac{1}{2}\sqrt{\frac{a}{b}}s_m=0.21s_m;\\ P_{min}&=1.86\left[\sqrt{b}\,a^2vc^2\right]^{2/9}=1.53\left(\frac{v}{\gamma}\right)^{2/9}\left(\frac{c}{\gamma^2}\right)^{4/9}. \end{aligned}\right\} \quad (83)$$

On the right-hand sides of these expressions we substitute the values of a and b from (82) for functions of Gaussian shape.

As is easily seen from (81), the minimum of p in the parameter v is obtained for v = 0, since the error decreases monotonically with decrease of the scanning rate. Consequently, the choice of v is determined only by the general time meas-

urement T and the frequency interval scanned. Inasmuch as this interval is obviously proportional to $\gamma$, then the ratio $\gamma/v$ is proportional to T and in the same fashion turns out to be a given quantity since T must be fixed for each particular case. Consequently, $P_{min}$ has the form

$$P_{\min} = \frac{P_0}{T^{2/9}M^{4/9}}, \qquad (84)$$

where $P_0$ is a coefficient of proportionality which depends neither on the characteristics of the instrument nor on the width and brightness of the line. Thus $P_{min}$ depends on the ratio of "signal to noise" $M = \gamma^2/c$ for $s = \gamma$ $\tau = 1$ and on the general time of measurement T, that is, only on such characteristics of the object, apparatus and other conditions of the experiment on which, starting out from the same general considerations, we usually expect the errors to depend for a reasonable choice of the conditions of measurement.

From (81) and (83) we easily obtain the fact that, under optical conditions, the systematic error $bv^2\tau^2$ produced by the inertia of the recording instrument is four times smaller than the distortion due to the apparatus function of the monochromator. This important consequence is directly connected with the fact that random errors are proportional to $1/s^2\sqrt{\tau}$, that is, that the exponent for s is four times larger than the exponent for $\tau$. Furthermore, inasmuch as $s_m$ and $P_{min}$ are very weakly dependent on the scanning rate (as $v^{1/9}$ and $v^{2/9}$, respectively) then it becomes clear that the choice of $\tau$ is not very critical, that is, the difference of $\tau$ and $\tau v$ from their optimal values does not lead to any material increase in the error. From this it follows that in practical measurements and for the analysis of more complicated cases than the example considered (application of an exact or approximate reduction etc.,), we can assume that the inertia distortions must be negligibly small in comparison with the systematic errors from the apparatus function from the monochromator and we can consider $\tau$ as fixed.

The recommendations given above rarely contradict the results obtained in the researches of references 110 to 112, where such a problem of the choice of the parameters of the arrangement is discussed. This is connected with two circumstances. In the first place, errors due to apparatus function of the monochromator are not considered in references 110 and 111. In the second place, the parameters of the instrument are chosen in references 110 to 112 by starting from a completely different criterion, and this is very important. In references 110 and 111, for example, the requirement for minimizing the total mean-square error does not apply here, and the random and systematic error values are given independently. The operating conditions determined by this criterion are of course not optimal from the point of view of minimum P.

The scheme given above for the selection of the parameters of the instrument can in principle be applied in very different cases. At the present time such calculations are still very infrequent; however, they have already permitted us to make a number of important conclusions.

The question of the choice of slit widths of the monochromator and the thickness of the absorbing layer for the reduction of optical density at the maximum of a single line of Gaussian form has already been considered in references 56 and 76.* It was shown that the values of these parameters ought to be different in the employment of different methods of reduction. Furthermore, it turned out that for a typical infrared instrument, use of the first correction in the Rayleigh method of reduction (59) guarantees 1.5 — 2 times less accuracy in comparison with those cases in which the form of the line is known beforehand and the reduction completely eliminates the systematic errors.

The latter result permits us to make an important comparison of the various methods of reduction. Actually, if the first correction in the Rayleigh method leads to practically the same result as the "exact" method of reduction, then we must assume that all approximate methods will give (approximately) the same result. Thus random errors of measurement and their transforms in the reduction process smooth out differences in accuracy between the various reduction methods, and the choice of the reduction method should be based only on simplicity and ease of application.

It appears that this conclusion holds only for the correct choice of the slit width and for the other parameters of the system. Furthermore, it is obtained for a definite apparatus and form of the distribution under consideration. Therefore the application of the above results to other cases requires additional justification.

A resume of the present paragraph can be made in the following way. In the limiting case of absolutely accurate measurements, reduction to an ideal spectral instrument is unique, and in this sense, the presence of only the apparatus function for the real instrument does not lead to any limitation of

*The time constant is chosen fixed and the inertial distortion is not considered. By virtue of the reasons set forth above, this is entirely correct.

its possibilities. Actually, random errors are finite and this leads to the impossibility of a unique calculation of the true distribution from the observed distribution $f(x)$. Practically, this nonuniqueness manifests itself in the fact that as the accuracy of the method of solution of Eq. (27) in the reduced distribution increases, there appears a certain false structure. To establish the nonreality of this structure, there is a paramount need of additional information on the distribution $f(x)$ under consideration, a distribution which is obtained independently of the method of the given experiment. In many cases, the additional information on $\varphi(x)$ permits us to consider the reduction to be unique and in the usual sense of the word permits us to speak about the error of computation of the true distribution.

It is important to emphasize that, with the exception of those cases in which the form of the true distribution is reliably known and in which we deal only with measurements of a finite number of parameters — in all remaining cases, the presence of random errors of measurements leads to a situation in which it is impossible to establish the problem of obtaining data completely independent of the apparatus, and we can only speak of the estimation of such a method of reduction and such conditions of measurement in which the difference between the true and the reduced distributions is minimal (for example, in the sense of the mean-square deviation).

## 4. THE PROBLEM OF RESOLUTION

1. The resolution criterion given by Rayleigh[30] and the concept of the resolving power of a spectral instrument which was introduced by him were first applied only to the visual observation of two monochromatic lines in instruments whose apparatus function was determined only by the diffraction on the rectangular aperture of the diaphragm, that is, it has the form $\frac{1}{s_0}\left[\frac{\sin \pi x/s_0}{\pi x/s_0}\right]^2$. This criterion, as is well known, reduces to the following; two monochromatic lines of different intensity are considered resolved if the distance $d$ between them is not less than $s_0 = \lambda f/D$. In this case the maximum of the intensity in the diffraction curve of one line coincides with the first minimum in the diffraction curve of the other line, while the intensity of the middle of the resulting curve is equal to $8/\pi^2 \cong 0.81$ of the maximum intensity.

Subsequently, there appeared a large number of papers in which the problem was considered of the development and the generalization of the Rayleigh concept of resolving power. Generalizations applied first of all to the application of the resolution criterion to instruments whose apparatus function differed from the diffraction one. Schuster[32,113] considered the case of a spectroscope in which the apparatus function was determined by the diffraction as a finite width of the slit. As a criterion of resolution he kept the condition that the intensity at the middle point of the total distribution of the two lines should be 81% of the maximum intensity.

For the ratio $\lambda/\Delta\lambda$, where $\Delta\lambda$ is the minimal resolved interval of wavelengths for finite slit of the width, Schuster introduced the special name of "purity" of the spectrum. However, this terminology is rarely employed, and most authors apply the term resolving power both in the case considered above and in other cases when various forms of the apparatus function are employed. A similar criterion of resolution was applied for the characteristics of the Fabry-Perot etalon,[2,53,114] which have the apparatus function (69). The small difference, which consists in the fact that the value of the "gap" in the total distribution from two monochromatic lines is taken here to be 20%, has no practical significance.

Further development of the resolution criterion is connected with the fact that the eyes, the photographic plate and other radiation detectors are capable of observing much smaller changes in the intensity than 20%, i.e., the change which is applied on the basis of the Rayleigh criterion (see, for example, reference 115). In connection with this fact, several visual resolving criteria have been suggested based on various premises. The simplest development is the postulation of a value of the gap different from 20%, for example 5%. Such a criterion was considered in reference 116 in an application to an apparatus function of the dispersion form. In references 52 and 117, the minimum resolving interval of wavelengths was assumed to be equal to the width of the apparatus function. For such a criterion, in the case of various shapes of the apparatus function, the value of the "gap" turns out to be different. For example, for the dispersion shape it is equal to 17%, that is, it differs insignificantly from the Rayleigh criterion, while for a diffraction distribution it has a gap of 2%, and in correspondence with this the resolving power for such a criterion is 13% larger than the Rayleigh value. We recall, finally, the criterion of Sparrow,[118] who considered that two lines are at the limit of resolution if the distance between them is such that the second derivative at the central point of the total distribution of the intensity of the two lines vanishes, that is, that the gap between

| Apparatus function | $\frac{\Delta\lambda_R}{\alpha}$ | $\frac{\Delta\lambda_5}{\alpha}$ | $\frac{\Delta\lambda_S}{\alpha}$ |
|---|---|---|---|
| Diffraction* | 1.13 | 1.02 | 0.94 |
| Triangular | 1.20 | 1.05 | 1.00** |
| Gaussian | 1.13 | 0.99 | 0.85 |
| Dispersion | 1.05 | 0.80 | 0.58 |

*The quantities $\alpha$, $\Delta\lambda_R$, $\Delta\lambda_S$ in the calculation of diffraction and finite slits were considered in references 24, 25, 32, 36, 118, and 121.

**For a triangular apparatus function, the second derivative at the central point of the total distribution is always equal to zero. In the table, in line with the basic idea of Sparrow, that value of $\Delta\lambda_S$ is given for which the gap only just vanishes, although in reference 25 the value of 1.156 $\alpha$ is given.

the lines only just vanishes. This criterion was applied for various shapes of the apparatus function[118-120,25] and, as an experimental investigation has shown,[118] very closely corresponds to visual determination of the presence of a gap between the lines. A comparison is given in the table of the resolving criteria stated above for the forms of the apparatus function met most frequently in practice. Here $\alpha$ is the width of the apparatus function and $\Delta\lambda_R$, $\Delta\lambda_S$, and $\Delta\lambda_5$ denote the minimal resolving intervals of wavelengths for the Rayleigh criterion, the Sparrow criterion and a criterion in which the minimum value of the gap is set equal to 5% of the maximum intensity, respectively.

In a number of researches there have been considered the dependence of the value of the gap on such factors as the difference in the intensity of two monochromatic lines,[118] the finiteness of the width of the line,[25] the level of "background" of constant intensity, etc. In these cases also, the authors call the ratio $\lambda/\Delta\lambda$ the resolving power, where $\Delta\lambda$ is the minimum distance between still resolved lines. Consideration of these circumstances is necessary in the analysis of concrete real instruments, the experimental determination of their limiting characteristics, and in other problems. However, analysis in these cases reduces to the establishment of those criteria of resolution which were considered above and do not lead in principle to new ideas on the resolution problem.

It must be remarked that inclusion of the random errors of measurement in the resolution problem is very important on the one hand, but on the other presents well known difficulties. Variation of the depth of the gap for a constant apparatus function cannot be considered a completely satisfactory receiver. The complexity of the problem lies in the fact that the value of the random errors of measurement and the width of the apparatus function are not independent. For example, in an expansion of the slit, the width of the line increase and the value of the gap quickly decreases. However, the errors of measurement decrease simultaneously and, consequently, a gap of given depth is recorded with greater reliability. Therefore, in the determination of the resolved intervals of wavelengths, it is necessary to take into consideration simultaneously both the random errors and the apparatus function and their mutual interaction. In application to visual methods of application and for diffraction slit apparatus function, the analysis of this important factor has been carried out qualitatively by Schuster[32,113] and van Cittert.[36] For photoelectric methods of recording, such an analysis is generally lacking at the present time. The first step in this direction was taken in reference 122 for the case of infrared absorption spectra. Those values of the absorption and width of the slits of the monochromator were computed for which the ratio of the depth of the gap to the mean square of measurement had a maximum value. In this case a triangular shape was taken for the apparatus function and a dispersion shape for the absorption coefficient. Calculations lead to a somewhat unexpected result. That is, the width of the slit, $s_m$, for which the best resolution (in the sense given above) takes place is almost entirely determined by the distance between the lines d from which it is shown that

$$s_m \cong \frac{1}{2} d$$

for lines of practically any width.

2. The characteristic feature of all the researches considered above on the resolving power of spectral instruments is that in the examination of the energy distribution of the two lines and in the comparison of this distribution with that of a single, strictly monochromatic, line, i.e., with an apparatus function, all attention was devoted to the single item of obtaining a distribution and to ascertaining whether it has a maximum or minimum. Such an approach is quite natural: if the apparatus function is a maximum at the middle point and the observed distribution is the minimum, then it is clear that this distribution is brought about by nonmonochromatic radiation. It is not difficult to see, however, that the inverse confirmation is not valid. In other words, such an approach assumes in principle that on the basis of the resolution criterion a certain qualitative difference should be established between the observed distribution and the apparatus function, a difference that is noted at first glance,

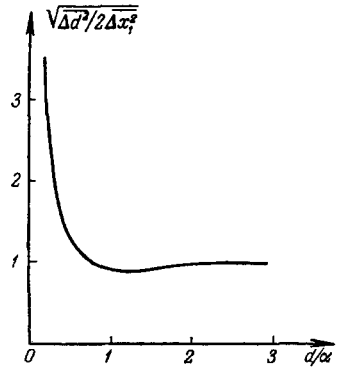


FIG. 7

without quantitative measurements of the entire energy distribution of the spectrum. Moreover, at all points of the curve there will be some quantitative difference which can be measured and used for establishing the spectral composition of the radiation under consideration.[123] Thus, the resolution criteria considered above are slanted primarily to qualitative observations and the magnitudes of the resolving powers obtained on the basis of such criteria only determine the order of magnitude of the distance between the lines which can be achieved for a given real instrument.

As an illustration, let us consider the following example. The observed distribution from two monochromatic lines for an absolutely accurate measurement has the form

$$f_1(x) = I_1 a(x - x_1) + I_2 a(x - x_2). \qquad (81')$$

For the sake of simplicity, we shall assume that the apparatus function is known with absolute accuracy, while the observed distribution $f(x)$ from two monochromatic lines is measured with some random roughness. This real recording is naturally approximated by the function $f_1(x)$ and the problem consequently reduces to the determination of the four parameters $I_1$, $x_1$, $I_2$, and $x_2$. We shall make a choice of these parameters by the method of least squares, i.e., we shall consider as the most probable values of $I_1$, $x_1$, $I_2$, $x_2$, those values for which the total mean square deviation of the real signal $f(x)$ from the approximating function $f_1(x)$ has a minimum value,* that is,

$$\int_{x_1}^{x_2} [f(x) - f_1(x)]^2 dx = \min.$$

From the point of view of the resolution problem there is interest in the error of measurement of the distance $b = x_2 - x_1$ between the lines as a function of the value of this distance and width of the apparatus function. Simple calculations carried out under the assumption of the Gaussian form of the apparatus function [see (21)] and equal intensities of the lines ($I_1 = I_2$), lead to the following expression for the mean square error in the determination of d:

$$\overline{\Delta d^2} = 2\overline{\Delta x_1^2} \times \frac{1 + \exp\left\{-2\ln 2 \frac{d^2}{\alpha^2}\right\}}{1 - \exp\left\{-4\ln 2 \frac{d^2}{\alpha^2}\right\} + 4\ln 2 \frac{d^2}{\alpha^2} \exp\left\{-2\ln 2 \frac{d^2}{\alpha^2}\right\}}, \qquad (82')$$

where $\overline{\Delta x_1^2}$ is the mean square error of the determination of the position of the maximum of a single line. If $d \gg \alpha$, i.e., the lines are not superimposed, then, as is to be expected, $\overline{\Delta d^2} = 2\overline{\Delta x_1^2}$. If $d \ll \alpha$, then (82′) takes the form

$$\overline{\Delta d^2} = 2\overline{\Delta x_1^2} \frac{1}{4\ln 2} \frac{\alpha^2}{d^2}, \qquad (83')$$

That is, the error increases rapidly in the case of small distances between the lines in comparison with the width of the apparatus function. The general form of the curve $\sqrt{\overline{\Delta d^2}/2\overline{\Delta x_1^2}}$ as a function of $\sqrt{\overline{\Delta d^2}}$ is given in Fig. 7. It can be seen that the sharp increase of $\sqrt{\overline{\Delta d^2}}$ begins only for $d < \alpha/2$, when there is no sort of "gap" at the center point of the observed distribution $f_1(x)$ (Fig. 8).

This smallest distance between lines, $d_{min}$, which can still be measured in the case under consideration, is obtained from the condition $\sqrt{\overline{\Delta d^2}} = d_{min}$. Employing Eq. (83′), we obtain:

$$\frac{d_{min}^2}{\alpha^2} = \sqrt{\frac{1}{2\ln 2} \frac{\overline{\Delta x_1^2}}{\alpha^2}}. \qquad (84')$$

For example, if the error in the determination of the position of a single line amounts to one tenth of the width of the apparatus function, that is, $\sqrt{\overline{\Delta x_1^2}/\alpha^2} = 1/10$, then $d_{min} = 0.29\,\alpha$, which is 3 or 4 times smaller than the smallest resolved

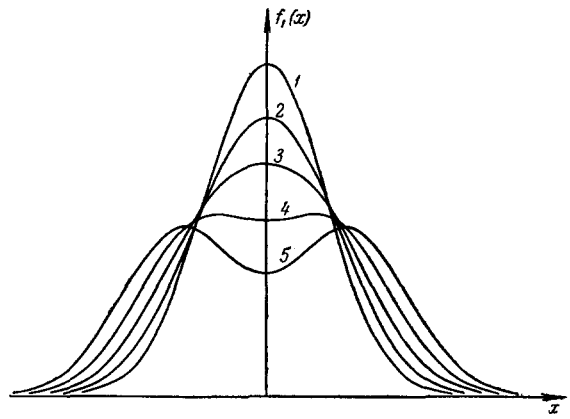


FIG. 8. Total distribution for the intensity for two monochromatic lines of equal intensity and for Gaussian shape of the apparatus function of width α: 1) d = 0; 2) d = 0.5α; 3) d = 0.72α; 4) d = 0.96α; 5) d = 1.20α.

*Similar consideration for the case of a single line was given in references 24 and 26.

interval determined by different criteria of resolution (see the foregoing table). If the accuracy of measurement is high, then the difference between $d_{min}$ and $\alpha$ will be still larger.

The example considered shows clearly that with quantitative measurements and subsequent mathematical treatment of the observed distribution the possibilities of real instruments are not limited by what the Rayleigh criterion (or any other sort of criterion based on the analysis of the behavior of the total distribution at a single points) gives, but can be more fruitful if one takes into consideration the difference between f(x) and a(x) at all points of the curve.

The non-correspondence of the Rayleigh concept of resolving power (and its modifications considered above) to experiments with quantitative measurements has lead in recent years to a wide generalization of the concept of resolution, which is directly connected with the application in optical measurements of the modulation method. We have in mind the researches of G. S. Gorelik and his colleagues[124-126] on the improvement of accuracy of measurement in a different type of interference experiments. His general considerations can be applied without difficulty to spectroscopic measurements.[124]

If in the papers referred to, the problem of resolution appears as a problem of finding in an observed distribution some feature of the true distribution — the extension of the light source, splitting of a spectral line when a magnetic field is applied to the light source, number of lines, etc. In other words, by resolving ability is meant the capacity to note, on a real instrument, a difference between the observed distribution and the apparatus function which arises as a result of the given difference of the true distributions from a $\delta$-function.

It should first of all be noted that in such an approach we are not talking about any qualitative indication such as the absence of a minimum, but about a quantitative difference of two distributions. For example, if two spectral lines are considered, then the limit of resolution corresponds to such a distance between them that the departure of the observed distribution from the apparatus function is equal, say, to the mean square error of measurement.

Furthermore, by the problem of resolution is understood not only the possibility of establishing the presence of two monochromatic lines of equal intensity, but also many other problems connected with finding in an observed distribution some indication of the true distribution. In such an approach, it is especially clear that quantities of the type of the resolving power are not characteristics of the apparatus only but depend essentially on the distribution being measured and determine the sensitivity of the instrument only in the measurement of a given distribution, giving very little information as to what the situation would be in another case.

In the approach to the resolution problem that we have made, there is a special case of the general problem of reduction to a real instrument considered in Secs. 2 and 3.* Actually, for known form of the true distribution $\varphi(x)$, the reduction reduces to the calculation of parameters characterizing $\varphi(x)$ (the width of the line, its intensity, distance between lines, etc.), starting out from the observed distribution f(x). As a result of the crudeness of measurement, the parameters of the true distribution are made known with some error; this error is the greater the wider the aperture function. For sufficiently gross measurements, or a sufficiently small value of the parameter of interest to us, the error of its determination is shown to be equal to the magnitude itself. This value of the measured parameter also characterizes the resolving ability of a real instrument in the investigation of a distribution of a given type. Thus the magnitude of the resolving power (in the sense considered) characterizes the conditions of the experiment (the apparatus and the object measured) in which the reduction to an ideal instrument no longer has meaning.

The connection shown between the problems of reduction and resolution permit us to explain one very widespread misunderstanding which amounts, roughly speaking, to the following. It is frequently desirable to make use of the value of the resolving power as an explanation of the limiting possibilities of an instrument in the case of differences of the true distributions of different and, generally speaking, unknown shapes. For example, one wants to know for what conditions one can distinguish on the given real instrument a set of three neighboring lines from a single line of finite width, and so forth.

Such an arrangement of the problem means in essence the use of the concept of the resolving power beyond the limits of its applicability. Actually it was shown in Sec. 3 that for finite errors of measurement the possibility of reduction to an ideal instrument depends essentially on additional information about the true distribution which was obtained independently of the given experimental procedures. It was explained in particular that only for a previously known form of the true distribution could

*The example considered at the beginning of the present section is an excellent illustration of this.

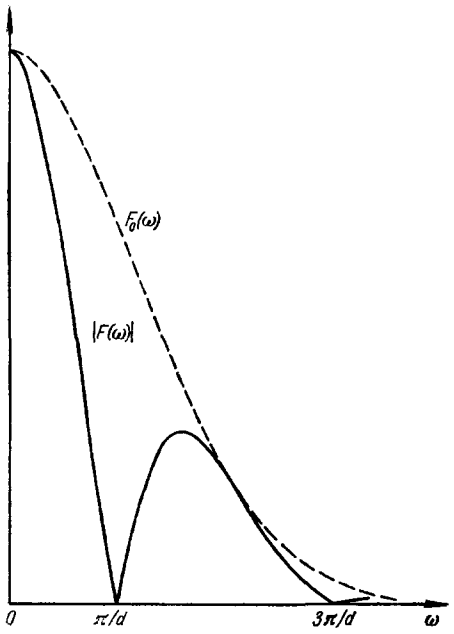


FIG. 9

one completely eliminate systematic distortions connected with the apparatus functions. In the case of the absence of such detailed information, reduction does not permit us to obtain data completely independent of the apparatus.

Everything pointed out of concerning reduction refers (perhaps with still greater firmness) also to the limiting possibilities of reduction and consequently to the resolving power. The concept of resolution under consideration relates exclusively to that case in which the form of the true distribution is known beforehand, and where we are speaking only about measurements of its parameters. In the absence of such information, this concept apparently loses its previous meaning and must be redetermined in a corresponding fashion. This redetermination will be different for information of a different type. At the present time, however, this question has not been discussed in the literature.

**3.** In conclusion, let us consider briefly several possibilities which the spectral approach opens up in the resolution problem. First of all, we have in mind the research of D. S. Rozhdestvenskiĭ,[115] in which, for analysis of the quality of spectral instruments, use is made of a harmonic energy distribution over the spectrum. The advantage of this method lies in the fact that it is comparatively easy experimentally to obtain the harmonic distribution by means of a combining of the spectral instrument with a double ray interferometer. In this case, without consideration of the effect of distortion factors of the first group (see Sec. 1), a point harmonic distribution exists. At the same time, employment of linear spectra for this purpose frequently becomes complicated (especially for instruments of comparatively high resolving power) by virtue of the presence of hyperfine line structure and other factors.

Essentially the Rozhdestvenskiĭ method consists of following the amplitude distribution while increasing frequency of the harmonic distribution (in practice, while increasing the difference of path between the rays of the interferometer) until frequencies are reached when the "visibility" of the interference picture vanishes. In other words, making use of the terminology given here, we are dealing with the discovery of the zeroes of the Fourier transform $A(\omega)$ of the apparatus function. For example, if the apparatus function is determined by diffraction then, in accordance with Eq. (16a), $A(\omega) = 0$ for $|\omega| \geq 2\pi/s_0$, that is, beginning with the period of the harmonic distribution equal to the Rayleigh minimum resolution distance. If $A(\omega)$ has no zeroes, then they extend to those frequencies in which the visibility becomes equal to the errors of measurement.

The principle set forth as the basis of the Rozhdestvenskiĭ method is employed in many widely different cases. A. I. Salishchev has carried out several measurements by the Rozhdestvenskiĭ method with the purpose of explaining the effects of defects of preparation of the instrument on its resolving power.[127] Rozhdestvenskiĭ himself has shown[127] that his method coincides in principle with the well-known method of Michelson[9] of measurement of the angular dimensions of stars. In an interesting paper[128] on the foundation of the same principle, the question was considered of the measurement of spectral width of slits and the resolving power of infrared spectrometers. The universally adopted method of measurement of resolving power of photo objectives by means of periodic patterns (see, for example reference 129) is also based on the method of Rozhdestvenskiĭ. This is connected with the fact that the effect of the apparatus function is primarily to decrease the amplitudes of the higher harmonics of the Fourier transform of the transmission function of the patterns. Therefore an arbitrary periodic pattern, with an arbitrary distribution of transmission over the range of the period, will give in practice a harmonic observed distribution of intensity at frequencies close to the limit of resolution, while the second and higher harmonic play virtually no role at all. Finally, it can be shown by the work of reference 130 (in which the resolving power of the photographic emulsion was determined directly by means of a harmonic distribution of illumination obtained by interference from two point sources).

An interesting application of the spectral approach to the problem of the resolution of two lines was given by G. G. Petrash. It is not difficult to show that the Fourier transform $F(\omega)$ of the observed distribution of two lines of identical intensity is

$$F(\omega) = F_0(\omega)\cos\omega d/2, \qquad (85)$$

where $F_0(\omega)$ is the Fourier transform of the distribution of a single line, d is the distance between the lines. As is easy to see, $F(\omega)$ vanishes at the points (Fig. 9).

$$\omega_k = (2k-1)\frac{\pi}{d}, \qquad k = 1, 2, \ldots, \qquad (86)$$

while in the vicinity of the lines, the values $\omega_k$ "move away" in the direction of larger and larger frequencies. Thus, if harmonic analysis of the intensity is carried out even when there is no "gap" at the central point, then we can decide on the existence of two lines by the presence of a zero in $F(\omega)$. Two circumstances prevent the zeroes of the function $F(\omega)$: decrease of the Fourier transform $F_0(\omega)$ of a single line upon increase in frequency and the presence of random errors of measurement. The limit of resolution corresponds to such a closeness of the lines in which the first maximum, after the frequency $\omega_1 = \pi/d$, where $F(\omega)$ first goes to zero, becomes equal to the error of the measurement. Consideration of concrete examples shows that such a method of finding two lines leads to a smaller resolved interval than the Sparrow criterion. For example, in the case of a dispersion line shape we can easily distinguish two lines if the distance d between them is equal to one half of their width $\gamma$, while the "gap" at the central point of the observed distribution vanishes for $d = 0.58\gamma$ (see the table on page 266).

We note that the Petrash criterion, as also the Rayleigh, Sparrow, and other criteria, is based on the observation of a single point, with only this difference, that in the latter cases this point is selected in the observed distribution, while in the former it is from its Fourier transform. However, the Petrash criterion possesses this important advantage that upon infinite increase in the accuracy of measurement, the minimum resolved interval tends to zero while in the other criteria this natural requirement is not satisfied.

It is interesting to note that the method of estimation of the resolving power of a spectral instrument considered here is essentially the generalization of that approach which is undertaken in the analysis of the resolving power of the well-known method of investigation of the line structure by means of a double beam interferometer employed by Michelson and other authors.[9,67,68] Actually, the visibility curve V of the interference bands according to which one judges the line structure is the modulus of the Fourier transform of the energy distribution over the spectrum. In the case of two identical lines, consequently, the visibility curve has the form

$$V(\omega) = |F(\omega)| = \left|F_0(\omega)\cos\frac{\Delta\lambda\omega}{2}\right|,$$

and the minimum observed difference of wavelengths $\Delta\lambda$ is determined by the condition that the visibility band beyond $\omega = 2\pi/\Delta\lambda$ does not exceed the random errors of measurement.

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Translated by R. T. Beyer