U.D.C. 543.42

Internal Reflection Spectroscopy. Applications in Chemistry and Industry

V.I.Yakutin and O.G.Strukov

Published information on the application of internal reflection spectroscopy (IRS) in chemistry and industry is systematically discussed, and the theory of IRS is briefly reviewed. The apparatus and experimental techniques are described. 297 References.

CONTENTS

I.	Introduction	692
II.	Theoretical basis of internal reflection spectroscopy	693
III.	Apparatus and experimental techniques	696
IV.	Applications of internal reflection spectroscopy	699

I. INTRODUCTION

Many papers dealing with the application of internal reflection spectroscopy (IRS) in chemistry and in related areas of science and industry have appeared in recent years.

The importance of IRS stems primarily from the fact that systems which are difficult or impossible to study by absorption methods can be examined by this method. In contrast to absorption methods, which rely on the transmission of light through the experimental medium, IRS is based on the phenomenon of total internal reflection.

The principle of the method is the following: during total internal reflection, a beam of light can penetrate from the optically denser into the optically less dense medium to a depth of the order of one wave length. If the less dense medium is absorbing, the beam is attenuated and reflection is not total. If the experimental medium is strongly absorbing, its attenuated total reflection (ATR) spectrum can be obtained by measuring with a suitable spectrometer its reflectivity R ($R = I/I_0$, where I_0 is the intensity of the incident light and I is the intensity of the reflected light).

Since total internal reflection does not involve any loss of radiant energy, the method known as multiple attenuated total reflection (MATR)† can be used to measure the spectra of very weakly absorbing media such as thin films and monomolecular layers.

The internal reflection (IRS) spectra of bulk materials, measured under standard conditions, are very similar to their transmission spectra, and in the case of very thin layers the two types of spectrum are practically identical. Hence, IRS spectra can be interpreted in much the same way as transmission spectra. Furthermore, IRS spectra often yield more detailed information on the structure of the sample than transmission spectra.

† OPO and MOPO are the Russian terms for the IRS methods known in English as ATR and MATR (attenuated total reflection and multiple attenuated total reflection). Non-Russian publications sometimes refer to FTR (frustrated total reflection), which is best rendered in Russian as NPVO. The term FMIR (frustrated multiple internal reflection), often encountered in the Western literature, is synonymous with MATR. The physical significance of the methods used in IRS is perhaps most clearly indicated by the terms ATR and MATR (in Russian, OPO and MOPO).

Almost the whole of the spectrum, from ultraviolet to far infrared, can now be explored by IRS.

In practice, the most important results have been obtained by i.r. IRS. The availability of commercial i.r. spectrometers with suitable attachments has greatly increased the scope of i.r. IRS: in particular, chemical, physicochemical, and biochemical processes have been investigated directly in media hitherto inaccessible by conventional methods.

Because its sensitivity and (in some cases) its precision are higher than those of i.r. transmission spectroscopy, i.r. IRS has been used to investigate surfaces, and it has also been applied in analytical procedures. It is now widely used in chemical and related industrial practice as an efficient and reliable method of process control.

The use of total internal reflection to study optical properties of materials is not an entirely new approach. As early as 1914, Mandel'shtam[1] and, somewhat later, Baryshanskaya[2] had used the phenomenon of total internal reflection to investigate fluorescence in thin layers, relying on Eikhenval'd's theoretical model[3]. A much more recent review of the possibilities offered by this method has been published by Hirschfeld[4].

Taylor and Glover[5] used total internal reflection to investigate the spectrum of an aqueous solution of potassium permanganate, and Korobko-Stefanov[6] discussed the advantages of this method in studies of strongly absorbing media.

However, the widespread penetration of IRS into research techniques began in the 1960's, when the remaining theoretical and experimental difficulties were finally overcome.

Unfortunately, existing Russian reviews of the practical application of IRS [7,8] are lacking in both breadth and depth. The only bibliography of the subject[8] dates back to 1967, and is therefore wholly inadequate.

Many review articles have been published outside the Soviet Union[9-17], but none of these consider work published since 1967. However, the number of publications has increased very rapidly in the last few years, and the scope of IRS has grown very significantly. None of this recent work is dealt with in existing reviews, whether Russian or foreign.

The aim of the present review is to discuss as fully as possible the applications of IRS in chemistry and in related areas of science and technology, and to familiarise the reader with the underlying theory, the apparatus, and the experimental methods.

II. THEORETICAL BASIS OF INTERNAL REFLECTION SPECTROSCOPY

Total internal reflection occurs when a light beam strikes the boundary between a medium of high optical density (n_1) and a medium of lower optical density ($n_2 < n_1$) at an angle greater than the critical angle of incidence (θ_c).[18] The critical angle is defined by the expression

$$\sin\theta_c = n_{21} \qquad (1)$$

where n_{21} is the relative refractive index ($n_{21} = n_2/n_1 < 1$), and n_1, n_2 are the absolute refractive indices of the two optically transparent media.

The condition for total internal reflection is written

$$\theta > \theta_c = \arcsin n_{21}. \qquad (2)$$

However, as pointed out by Newton[19], the light penetrates into the optically less dense medium during total internal reflection.

This optical penetration effect, which could not be explained by the corpuscular theory of light, is now clearly understood in terms of the electromagnetic theory.

As pointed out by Eikhenval'd[3], the electromagnetic field associated with the light wave does not suffer a discontinuity at the boundary between the two media during total internal reflection: it penetrates from the medium n_1 into the medium n_2, where it decays exponentially. The decreasing amplitude E of the electrical oscillations of the light wave in the second medium is given by the expression

$$E = E_0 e^{-\gamma z} \qquad (3)$$

where $\gamma = 2\pi(\sin^2\theta - n_{21}^2)^{1/2}/\lambda_1$, E_0 is the amplitude at the interface, z is the distance from the interface into the medium of lower refractive index, λ_1 is the wave length of the light in the denser medium.

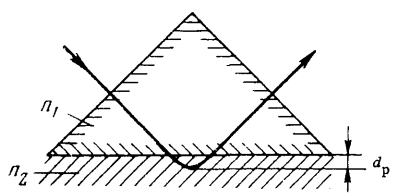


Figure 1. Penetration of light into the medium of refractive index n_2 during total internal reflection (d_p is the depth of penetration).

We must stress that in total internal reflection the intensity of the reflected light (I) is equal to the intensity (I_0) of the incident light: the penetration of the light into the second medium does not cause any loss of radiant energy. According to Eikhenval'd, the incident beam "strays into the second medium" where it follows a curvilinear path "before re-emerging, unaltered, in the first medium as the reflected beam" (see Fig. 1).

Defining d_p as the depth of penetration for which the amplitude E decreases by a factor of e, we obtain

$$d_p = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}^2)^{\frac{1}{2}}} \qquad (4)$$

Examination of Eqn. (4) shows that: 1) for angles $\theta \gg \theta_c$ the depth of penetration is less than one wave length, 2) for $\theta = \theta_c$ the depth of penetration is very large, 3) the depth increases with critical angle, and 4) it increases with the wave length.

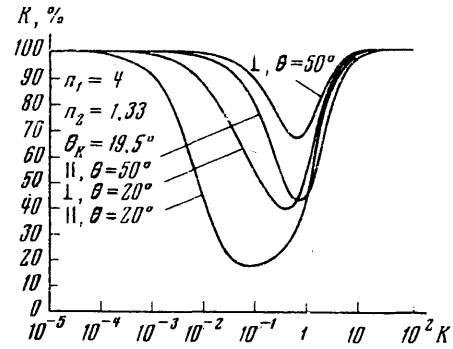


Figure 2. Plots of R against K for different values of θ and for different polarisations.

If the light penetrates into an absorbing medium, then $I \neq I_0$. In this case the reflectance R depends not only on the absorption coefficient K, but also on θ, n_{21}, and λ in Eqn. (4). The functional dependence, as shown in Fig. 2, is very complicated. The variation of R with K, θ, n_{21}, and polarisation of the light can be calculated in two ways. One method is to express the reflectivity as a function of the above variables.

The calculations are usually made by applying the Fresnel formulae, suitably modified for attenuated total reflection conditions. The modifications consist in replacing the refractive index n_2, which adequately characterises the optical properties of a transparent medium, by a complex refractive index[23] n_2^*, which characterises the optical properties of the absorbing medium:

$$n_2^* = n_2(1 - iK), \qquad (5)$$

where n_2 and K are the effective refractive index and the effective absorption coefficient.

The relationship between K and α (the absorption coefficient in the Beer — Lambert law) is given[24] by

$$\alpha = \frac{4\pi n_2 K}{\lambda_0}, \qquad (6)$$

where λ_0 is the wave length of the light in a vacuum, related to the wave length in a denser medium by the expression $\lambda_0 = \lambda_1 n_1$.

For ATR conditions, the Fresnel formulae become[25]

$$R_\perp = \left| \frac{(n_{21}^{*2} - \sin^2\theta)^{\frac{1}{2}} - \cos\theta}{(n_{21}^{*2} - \sin^2\theta)^{\frac{1}{2}} + \cos\theta} \right|^2 \qquad (7)$$

$$R_\parallel = R_\perp \left| \frac{(n_{21}^{*2} - \sin^2\theta)^{\frac{1}{2}} - \sin\theta\tan\theta}{(n_{21}^{*2} - \sin^2\theta)^{\frac{1}{2}} + \sin\theta\tan\theta} \right|^2, \qquad (8)$$

where the subscripts $\perp$ and $\parallel$ indicate that the vector of the electrical oscillations is perpendicular ($\perp$) or parallel ($\parallel$) to the plane of incidence.

Calculations of R as a function of K, θ_c, and θ, and also of polarisation, have been reported and discussed in a number of papers[9,24-29]. We shall confine ourselves to a consideration of some general rules which relate specifically to the practical exploitation of the ATR method.

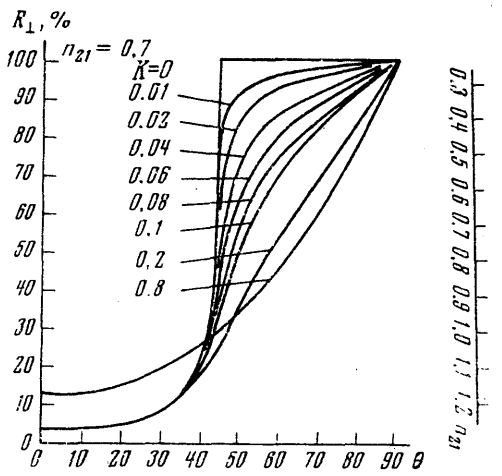


Figure 3. $R_\perp$ as a function of K and θ.

It is evident from Figs. 2, 3, and 4 that the method offers maximum sensitivity in the range $0 < K < 0.2$, which includes the i.r. absorption bands of most organic compounds.

We note also that the reflectivity depends not only on K, but also on θ, θ_c, and polarisation: R decreases as θ decreases and as θ_c increases.

Other conditions being equal, $R_\perp < R_\parallel$.

R falls off sharply as $\theta \to \theta_c$; in other words, the conditions for maximum sensitivity and therefore precision of the ATR method are found[26,28] close to the critical angle of incidence, the best choice of which depends on the value of K.[26]

However, the IRS bands observed at the optimum critical angles are distorted relative to the transmission spectra: they are broadened towards the long-wave end of the spectrum, and their peaks are shifted towards lower frequencies[7,9-11,13,29-31]. Yet, it would be desirable to obtain IRS spectra as similar as possible to the corresponding transmission spectra.

Calculations based on the Fresnel formulae have shown that undistorted IRS spectra can be obtained from very weakly absorbing samples only at angles $\theta \gg \theta_c$.[29,30,32]

The values of R for weakly absorbing samples can be calculated by means of simple expressions, derived from Eqns. (7) and (8) by expanding them into a power series and retaining terms up to K^3:[29,32]

$$R_\perp = 1 - \alpha \cdot d_{\text{eff}\perp} \tag{9}$$

$$R_\parallel = 1 - \alpha \cdot d_{\text{eff}\parallel} \tag{10}$$

where d_{eff} is an effective thickness having the same order of magnitude as the wave length.

It follows from Eqns. (9) and (10) that the role of the effective thickness is analogous to that of the optical path length in transmission spectroscopy, and that this parameter can be calculated from the expressions[9,20,29,33,34]:

$$d_{\text{eff}\perp} = \frac{n_{21}\cos\theta\lambda_1}{\pi(1-n_{21}^2)(\sin^2\theta - n_{21}^2)^{\frac{1}{2}}} \tag{11}$$

$$d_{\text{eff}\parallel} = \frac{n_{21}\cos\theta(2\sin^2\theta - n_{21}^2)\lambda_1}{\pi(1-n_{21}^2)[\sin^2\theta(1-n_{21}^2) - n_{21}^2](\sin^2\theta - n_{21}^2)^{\frac{1}{2}}} \tag{12}$$

It is not hard to show that Eqns. (9) and (10) are analogues of the Lambert – Beer equation for the case of very weak absorption[9,35], and therefore they can be re-cast in the form

$$R = e^{-\alpha d_{\text{eff}}} \tag{13}$$

Thus, the Lambert – Beer law is formally applicable to the undistorted IRS spectra[26,32], and we may use these IRS spectra for quantitative measurements in the same way as transmission spectra.

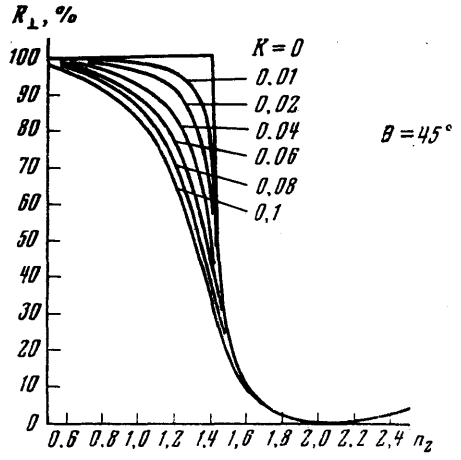


Figure 4. $R_\perp$ as a function of K and n_2.

Although these generalisations of the Fresnel equations provide a theoretical foundation for the practical application of the ATR method, they do not give a physical picture of the interaction of light with the absorbing medium. It should also be noted that the use of Eqns. (7) and (8) in daily laboratory work is complicated by the need for electronic computation[20].

Hence, an alternative solution of the problem could be attractive if it relied on simple mathematical expressions describing the mechanism of light absorption and the main features of IRS spectra in cases of practical interest ($0 < K < 0.2$) without resorting to the use of computers.

Let us consider the case of weak absorption. As stated above, in this case R can be found from Eqns. (9) – (12), whence it follows that d_{eff}, and therefore also n_{21} and θ, are independent of α. From the same equations we can show that the product $\alpha . d_{\text{eff}}$ is simply the fraction of radiant energy absorbed by the medium of lower refractive index. Thus, the behaviour of the electric field in a weakly absorbing medium can be discussed independently of α.[9,20,29,32-34]

According to Harrick[20], the absorption a, i.e. the interaction between the light beam and the weakly absorbing medium over the whole of the penetration path, can be described by the equation

$$a = \alpha \frac{n_{21}}{\cos\theta} \int_0^\infty E^2 dz \qquad (14)$$

where $E = E_0 \cdot e^{-\gamma z}$ is the amplitude of the electric field in the less dense medium relative to the amplitude of the incident light.

From Eqn. (14) we find

$$\frac{n_{21}}{\cos\theta} \int_0^\infty E^2 dz = \frac{a}{\alpha} \qquad (15)$$

where the expression on the left-hand side denotes the effective thickness[9,20,33,34]

$$d_{\text{eff}} = \frac{n_{21}}{\cos\theta} \int_0^\infty E^2 dz \qquad (16)$$

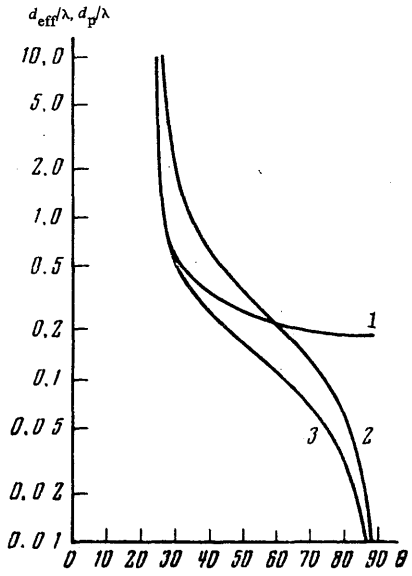


Figure 5. Relative depth of penetration and relative effective thickness as a function of θ (n_{21} = 0.423): *1)* d_p/λ, *2)* $d_{\text{eff}_\parallel}/\lambda$, *3)* $d_{\text{eff}_\perp}/\lambda$.

It follows from Eqn. (14) that the absorption depends not only on the value of α, but also on the value of the integral, which defines the total intensity of the light over the whole of the penetration path. Evidently, this intensity is a function of the amplitude E_0 at the phase boundary on the side of the less dense medium. The value of E_0 as a function of the angle of incidence and of the polarisation of the light can be calculated from the equation for the standing electromagnetic wave produced at the phase boundary on the side of the denser medium by the superposition of the incident and the reflected light. These calculations, carried out by Harrick[20,33,34], have shown that: 1) E_0 is a maximum for $\theta = \theta_c$; 2) E_0 decreases as θ increases; 3) E_0 vanishes for $\theta = \pi/2$; 4) E_0 vanishes for $E_{0\perp} < E_{0\parallel}$.

We shall now discuss the dependence of d_{eff}, and therefore also of the absorption, on the factors which enter into Eqn. (16).

We have two cases, depending on whether the thickness d of the absorbing layer is greater or smaller than the depth of penetration. For "thick" layers ($d > d_p$) we obtain the following formula [from Eqn. (16)] for the effective thickness:

$$d_{\text{eff}} = \frac{n_{21} E_0^2 d_p}{2\cos\theta} \qquad (17)$$

It follows from Eqn. (17) that the effective thickness of "thick" layers depends on four factors. The physical significance of the first three (n_{21}, E_0, and d_p) has already been discussed; the fourth ($1/\cos\theta$) determines the area over which light interacts with the sample.

Fig. 5 shows the variation of d_{eff} (which determines the interaction between the tailing electric field and the weakly absorbing medium) with angle of incidence and with polarisation. It is evident that d_{eff} is greatest near the critical angle, and reaches a maximum [see Eqn. (17)] when the refractive index n_1 of the internal reflection element (IRE)‡ is very close to the true refractive index n_2, i.e. when $n_{21} \to 1$. Hence, to obtain the strongest possible bands in IRS spectra we must choose an IRE with a refractive index close to that of the experimental medium (n_2) at the maximum of the dispersion curve (Fig. 6), and use near-critical angles of incidence[26]. Under these conditions the quantities n_{21}, E_0, and d_p, which determine d_{eff}, have their maximum values.

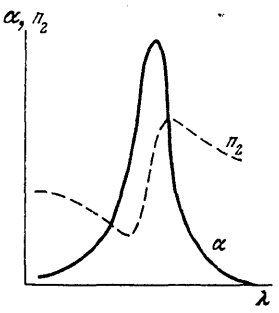


Figure 6. Absorption coefficient α (full line) and refractive index n_2 (broken line) as a function of wave length in the region of the absorption band.

As θ increases, E_0 and d_p fall off, causing a decrease in d_{eff} and hence in absorption[36]. When $\theta = \pi/2$, $E_0 = 0$, and therefore $d_{\text{eff}} = 0$ (i.e. there is no absorption). We note that when $\theta = 45°$, $d_p = (d_{\text{eff}_\perp} + d_{\text{eff}_\parallel})/2$.

It has been shown[20,33-35] that formulae (9) — (13), which are strictly applicable only to weak absorption (they can be obtained from (14) and (17) [20]), can in fact be used over a fairly wide range of K values ($0 < K < 0.2$), since they differ by only 10% from the exact Fresnel formulae when R falls to 10% (see Fig. 2).

‡ In IRS the optically transparent, denser medium is sometimes called the IRE.

Eqn. (17) can be used to explain the difference between the IRS spectra obtained with "thick" layers and the transmission spectra of the same materials. Since d_p increases with λ, the absorption also increases with λ. Hence, the intensity of the bands in the IRS spectra increases with wavelength[10,11,20,29,33,34].

As stated above, IRS spectra obtained with θ close to θ_c appear distorted. To identify the cause of the distortion we turn to Fig. 6, whence it is evident that n_2 (as well as α) varies with wave length. The largest value of n_2 is found on the long-wave side of the absorption band. Since the critical angle reaches a maximum and the difference $\theta - \theta_c$ (for a given θ) reaches a minimum on the long-wave side of the absorption peak, it is not surprising to find an increase in n_{21}, E_0, and d_p (and therefore an increase in absorption) on the long-wave side of the peak. As a result, the absorption maximum is shifted towards lower frequencies, and the band shows some broadening in the same direction[7,9-13,29-31].

Obviously, the distortion of the IRS spectra arises from the fact that the ATR method is sensitive to changes in both the optical constants K and n_2. This suggest that IRS can be used to evaluate these constants[24,25,28,37-49].

In order to obtain an IRS spectrum free from the distortion associated with anomalous dispersion we must choose conditions such that d_{eff} is not sensitive to changes in the coefficient n_2. It can be seen from Fig. 5 that when the angle θ is much greater than θ_c, i.e. when the difference $\vartheta - \theta_c$ is large, the fluctuations in this difference due to changes in the critical angle have very little influence on the depth of penetration. The same can be said of E_0, which is insensitive to changes in θ_c if $\theta \gg \theta_c$, as demonstrated by Harrick[9]. Therefore, it is essential to work with an angle of incidence much greater than the critical angle if the aim is to obtain an IRS spectrum almost identical to the transmission spectrum. However, small differences in frequency (of the order of a few cm^{-1}) are nevertheless to be expected[50].

Starting from the refractive index n_2 of the experimental medium, measured by normal refractometric methods, the expected absorption coefficient K, and the condition[29] $K/(\sin^2\theta - n_{21}^2) \ll 1$, it is possible to choose an angle of incidence and an IRE refractive index such that the IRS spectrum is free from the distortion associated with anomalous dispersion. We can readily show that this condition is satisfied for small K values, and as K increases for $\theta \gg \vartheta_c$.

However, the IRS spectrum plotted at large angles of incidence has a low intensity[7,9-11,30,35,51]. Stronger bands can be obtained by the MATR method, which produces spectra both undistorted and intense[7,9-11,30,35,52-56].

In this method, d_{eff} is increased in proportion to the number of reflections (N), and therefore the absorption is increased by a factor of N. Evidently, Eqn. (13) for the MATR method must be re-written[20,35]

$$R^N = e^{-\alpha \cdot d_{eff} N} \tag{18}$$

Clearly, by adopting the MATR method we can not only increase the intensity of the IRS method but also use it at higher sensitivity.

We shall now turn to the case of "thin" layers ($d < d_p$). In this case the electric field penetrates beyond the thin absorbing layer into the underlying optically transparent medium§. Since the layer is very thin, the electric field may be assumed to be constant within the film[20]. Then, using Eqn. (16), we obtain

$$d_{eff} = \frac{n_{21} E_0^2 d}{\cos\theta} \tag{19}$$

Thus, with "thin" layers as with "thick" layers the parameter d_{eff} depends on four factors. We can evaluate d_{eff} for a "thin" layer using the formulae proposed by Harrick[9,20,33,34]¶:

$$d_{eff\,\perp} = \frac{4n_{21} \cdot \cos\theta \cdot d}{1 - n_{31}^2} \tag{20}$$

$$d_{eff\,\parallel} = \frac{4n_{21}\cos\theta\,[(1 + n_{32}^4)\sin^2\theta - n_{31}^2]\,d}{(1 - n_{31}^2)[(1 + n_{31}^2)\sin^2\theta - n_{31}^2]} \tag{21}$$

where $n_{21} = n_2/n_1$; $n_{32} = n_3/n_2$; $n_{31} = n_3/n_1 < 1$ are the relative refractive indices. Formulae (20) and (21) are accurate when

$$\frac{2\pi d}{\lambda_1} < 0{,}1 \text{ and } K_2 < 0{,}1$$

Eqns. (19) – (21) lead to a number of generalisations applicable to IRS spectra obtained with "thin" layers.

It follows from Eqn. (19) that d_{eff} is independent of the depth of penetration. Hence, the intensity of the bands in the IRS spectra of "thin" layers does not increase with wave length. Furthermore, we can see from Eqns. (20) and (21) that d_{eff} is limited for $\theta = \theta_c$, where θ_c = arc sin n_3/n_1. Clearly, the IRS spectrum of a "thin" layer—unlike the spectra of "thick" layers—is free from anomalous dispersion distortions and is practically identical to the transmission spectrum.

It is important to note that the IRS spectrum of "thin" layers can be obtained even when the true refractive index of the thin layer is greater than the refractive index of the IRE. Furthermore, and in contrast to "thick" layers for which $d_{eff\,\parallel} > d_{eff\,\perp}$, the parameter $d_{eff\,\parallel}$ can be greater or smaller than $d_{eff\,\perp}$ in "thin" layers, depending on whether the ratio n_{32}^4/n_{31}^2 in Eqn. (21) is greater or smaller than unity.

It follows from (20) and (21) that d_{eff} for "thin" layers can be much greater than the physical thickness of the layer if $n_3/n_1 \to 1$. By using MATR, the sensitivity of the method can be dramatically increased[58] to $\sim 10^{-14}$ mole.

We had previously stated that light polarised in a parallel direction interacts more strongly with the absorbing medium than light polarised at right angles[59], which is true only for isotropic media. In anisotropic media the interaction will depend on the orientation of the dipoles. Hence, ATR and MATR methods can be used to study anisotropic media[20,25,27,60-62].

III. APPARATUS AND EXPERIMENTAL TECHNIQUES

The apparatus used to record IRS spectra consists of a standard spectrophotometer with a special attachment in the cell compartment. The optical system of the attachment is designed according to the optical and geometrical features of the IRE and of the spectrometer. Depending on the IRE, the attachment can provide single or multiple reflections. In single-reflection attachments the IRE may

§ The theory of multilayer systems, with reference to the ATR method, has been discussed by Hansen[57].

¶ Formulae (20) and (21) are given[20] without proof, but a derivation of these formulae was published later[25]. However, formula (21) is somewhat different from the corresponding formula obtained in Ref. 25.

be in the form of a prism[15,54,63-65] (mainly for work in the u.v. and visible regions), a hemisphere, or a hemicylinder[24,35,37,66-71] (for i.r. measurements).

The use of a hemicylinder is convenient because it allows an arbitrary choice of angle of incidence and hence it can replace several prisms with different angles of incidence. Furthermore, it is easy to obtain a parallel beam within the hemicylinder[9,24,25,35,68,70] over a wide range of angles of incidence, and therefore the angle of incidence can be calculated unambiguously and with great precision (~0.5′)[66]. This level of precision is essential, for example, in determinations of optical constants by the two-angle method[25,46].

Attachments using a hemicylindrical IRE have been designed for the IKS-14,[67] Hilger H-800,[68] and UR-20 [70] spectrophotometers. The operation of these attachments is easily understood from Fig. 7.

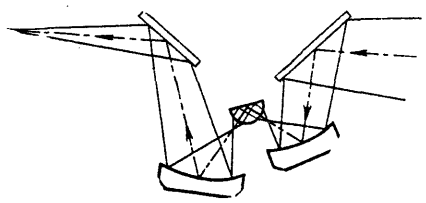


Figure 7. Single reflection attachment.

Single-reflection attachments have one serious drawback: they cannot produce intense, undistorted spectra. This drawback is overcome in multiple-reflection attachments, which can accept IRE's of different geometrical configurations such as plates with fixed or variable angles of incidence, and with single[10,11,15,72-77] or double[9,15,20,78] light transmission. IRE's can be trapezoidal[79] or rosette-shaped[80], with multiple light transmission, or in the form of a light-guide[15,81]. An IRE with a curved surface has been described[82,83]. The most commonly used of these elements is the multiple internal reflection (MIR) plate with fixed angle of incidence and single light transmission. This is because both the construction and the calculations are simpler with these plates. In the simple geometry of the plate, the number of reflections is easily calculated:

$$N = \frac{L}{t}\cot\theta \qquad (22)$$

where L is the length and t is the thickness of the plate.

It follows from Eqn. (22) that the number of reflections increases as the angle of incidence decreases. The number of reflections increases in proportion to the length, and in inverse proportion to the thickness of the plate. However, it should be remembered that the length of the plate cannot be increased indefinitely without total extinction of the light beam as a result of optical imperfections in the polished surfaces. The scattering by these imperfections is a function of wave length, and is most pronounced in the u.v. region[58]. Hence, the reflectivity of the plate depends on the quality of its optical finish[35,54]. The thickness of the plate, also, is limited, and cannot be decreased below the width of the spectrometer slit[10,11,35].

It should be noted that any divergence of the light beam within the plate causes ambiguity in the angle of incidence[9,35] even though it may be beneficial in ensuring total illumination of the surface of the plate[10,11].

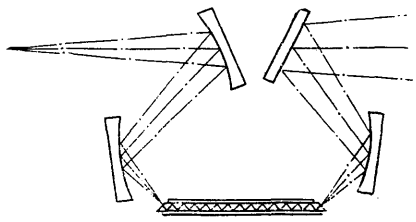


Figure 8. Multiple reflection attachment.

MIR plates are now commonly used in commercial attachments (see Fig. 8), made both in the Soviet Union and abroad. Attachments for the IKT-14,[71] UR-20 [84,85], and various Perkin — Elmer spectrometers[54-56] have been described in detail.

Attachments using an MIR plate as the IRE are used in the u.v. and the visible region[54], and also in the i.r. region[76] and in the far infra-red[86]. MIR plates giving up to 50 — 300 reflections have been constructed[87-89].

Cells for special investigations have been developed using MIR plates. Some of these, produced[54,55] by the firm of Wilks Scientific Corporation (USA), are particularly interesting because they are equally suitable for analytical work and for physicochemical research.

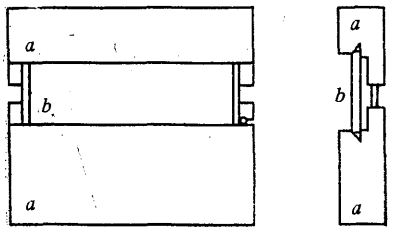


Figure 9. Cell for viscous liquids: (*a*) Teflon holder, (*b*) IRE plate.

Fig. 9 shows a cell for the analysis of high-boiling compounds (lubricants, oils, adhesives, and other viscous materials). The cell consists of a Teflon holder and an IRE in the form of a plate. The IRS spectrum is obtained by spreading the material on the surface of the plate. 25 reflections are possible.

The microcapillary cell (Fig. 10) is used to examine fractions isolated by gas — liquid chromatography. It consists of a Teflon holder and two thin MIR plates, between which the substance to be analysed is placed. Because of the large number of reflections (~50), the sample size can be very small (~10^{-4} g).

The cell shown in Fig. 11 is used for liquid samples. The gap between the MIR plate and the metal holder is not critical, because the absorption does not depend on the thickness of the layer of sample.

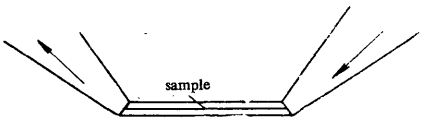


Figure 10. Micro-capillary cell.

The combined cell and reaction vessel (Fig. 12) and the flow-through cell (Fig. 13) have been designed for studies of the kinetics and mechanisms of chemical reactions[88].

In spectrophotometric studies of powders, paper, tissues, rubber, polymers, films, and various coatings, the solid-sample cell shown in Fig. 14 is used. Mechanical pressure is applied to increase the area of contact between the plate and the experimental material.

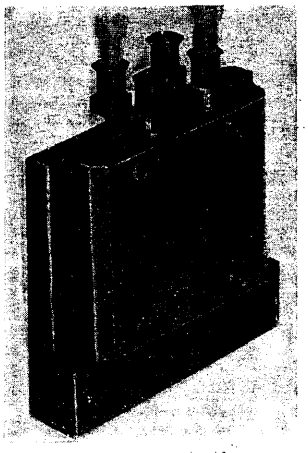


Figure 11. Liquid sample cell.

Cells for direct spectroscopic studies of aerosol particles[90], and for measurements in high vacuum[9] and at high temperatures[54,55], have also been described. Special attachments in which the IRE extends beyond the cell compartment of the apparatus have been developed for studies on large samples[10,11].

Differential spectra can be obtained, if necessary, by using single and multiple reflection cells. However, it is not always possible to compensate exactly for the differences between two IRE's. With isotropic media, the residual background absorption can be compensated with polarisers[91] or variable-area cells[54]. In addition to the various attachments, special spectrometers for IRS spectroscopy have been described[10,11,54,55,92], but in every case the essential component, which determines the quality of the spectra, is the IRE. Obviously, the material used to fabricate the IRE must have some special optical, physical, and chemical properties.

The material must have: 1) a high refractive index, so as to give undistorted spectra with samples of widely different refractive indices; 2) high purity and optical transmission, since the length of the optical path in the MIR

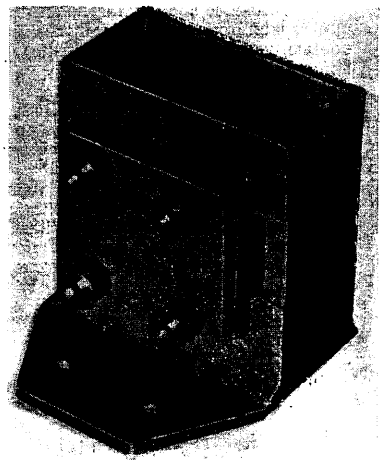


Figure 12. Reaction cell.

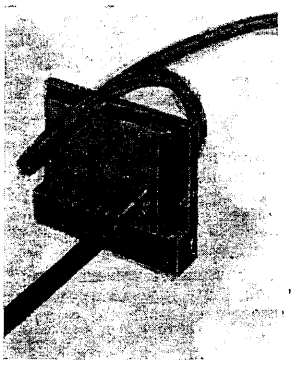


Figure 13. Flow-through cell.

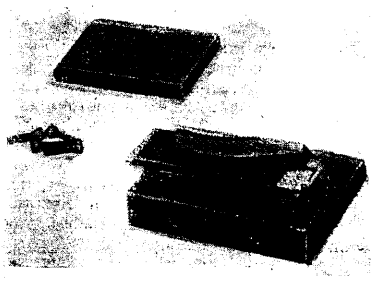


Figure 14. Solid-sample cell.

plate can be 100 mm or more; 3) high elasticity, hardness, and mechanical strength, since the IRE must not be easily deformed, scratched, or bent; 4) chemical stability, since the IRE material must not dissolve in or react with the material being analysed.

Characteristics of materials.

No.	Material	Chemical composition	n_D	θ^*_K	Spectral region, μm	Max. temp., °C	Remarks
1	Germanium		4.0	14.5	2—11.5	125	Hard, brittle, chemically stable. Used in the i.r. region.
2	Silicon		3.5	16.6	2—6.5 40—300	300	Hard, brittle, chemically stable. Used in the i.r. and far i.r. region.
3	KRS-5	42%—TlBr 58%—TlI	2.5	23.6	1—40	125	Elastic, soft, insoluble in many solvents. Sparingly soluble in water. Used in the i.r. region.
4	Irtran-4	ZnSe	2.4	24.6	2—16	300	Hard, stable, insoluble in water. Used in the i.r. region.
5	KRS-6	40% TlBr 60% TlCl	2.2	27.0	0.4—25	100	Softer,than KRS-5. Used in the i.r. region. Can be used in the visible.
6	Silver chloride	AgCl	2.0	30.0	1—20	200	Very soft, insoluble in water. Used in the i.r. region.
7	Sapphire	Al_2O_3	1.7 (above 2 at $\lambda < 0.2$ μm)	36.0	0.18—6		Very hard. Used in the u.v. and visible region.
8	Quartz (fused)	SiO_2	1.43 (1.65 at $\lambda < 0.2$ μm)	44.4	0.18—0.75		Used in the u.v. and visible region

*θ_K values calculated relative to air.

In addition, the IRE material must: 5) be easy to grind and polish, and 6) retain its transparency at high temperatures.

Because of these stringent requirements, the materials used to obtain transmission spectra are not always suitable for IRS. The literature dealing with materials for internal reflection spectroscopy is extensive[9-17,34,54-56,72,85,93]. Some properties of materials commonly used in IRS are listed in the Table.

IV. APPLICATIONS OF INTERNAL REFLECTION SPECTROSCOPY

As stated above, internal reflection spectra are qualitatively similar to transmission spectra if the distortion resulting from anomalous dispersion can be overcome. (Suitable conditions are discussed in Section II). Hence, existing data on the transmission spectra of related compounds can often be used to interpret IRS spectra. This allows IRS methods to be applied to a wide variety of problems, including the identification of various compounds, studies of their structure and reactivity, and a wide range of associated problems.

However, IRS has a number of advantages over transmission spectroscopy: it is unique in its ability to examine materials in any state of aggregation, of any consistency, and of practically any size or thickness.

1. Types of Material

The IRS method has no special advantage over transmission spectroscopy in work with liquids and some solutions, but in practically every other case it is greatly superior, and in some cases it is the only possible method.

Powders. The study of powders by i.r. spectroscopy is a very common problem. Conventional techniques (pressing into tablets with alkali halides, preparation of mulls, etc.)[94] are laborious and often unsatisfactory: they tend to contaminate the sample and to disturb its crystal structure, and chemical interaction between the sample and the matrix cannot always be avoided. Furthermore, the spectra are sometimes incomplete or otherwise unsatisfactory, due to scattering or masking by the bands of the diluent.

IRS methods are free from all these drawbacks. The only pre-treatment needed is to spread the sample on an adhesive tape[54], which is then pressed against the IRE. With amorphous powders the procedure is even simpler: the sample is deposited directly on the internal reflection plate[54]. Sands, various precipitates[95], and other fairly coarse (up to 300 μm particle size) powders have been analysed in this way, and have always yielded high-quality spectra (Fig. 15).

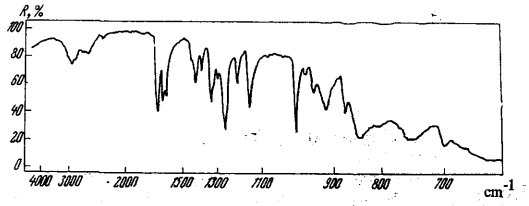


Figure 15. Internal reflection spectrum of sorbic acid powder. IRE—Ge plate (25 reflections).

Solid bodies. Solid bodies cannot be examined directly by transmission spectroscopy. A sample must first be removed, finely powdered, and examined by a standard method. In some cases (e.g. coal analysis[96]) the preparation of the sample may take up to 8 hours.

On the other hand, the study of solid bodies (including coals[97]) by IRS methods is quite straightforward: special attachments have been developed[10,11,54] for recording spectra from samples of any size.

The difficulties encountered in studying single crystals by transmission spectroscopy[98] are well known: again, this type of sample can yield IRS spectra without difficulty[60,99-103]. The IRS method is particularly effective in studies of anisotropic media: in particular, it is greatly superior to transmission spectroscopy for studying dichroism[60-62,99].

Films. The examination of fairly thick films by the classical spectroscopic methods presents a number of difficulties. Even at thicknesses of a few tens of microns[98] analysis of the film by classical methods may become impossible. In direct contrast, films are perhaps the best type of sample for IRS studies (Fig. 16). In addition to solving various problems in the physics of films[104], these methods have been used successfully for film identification[54] (including films of metal hydroxides[7,105]). Coatings on films[7] are easily analysed, including measurements of thickness[107] and composition[106,107]. IRS methods are seen at their best in the analysis of multilayer films[7,108,109], since they can yield identifiable spectra for the individual layers.

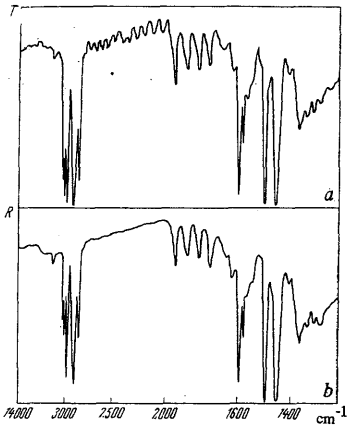


Figure 16. Transmission (*a*) and IRS (*b*) spectra of a polystyrene film. IRE—KRS-5 plate (25 reflections).

Viscous materials. Viscous materials are not easily studied by transmission spectroscopy in their natural form, yet they are almost the ideal type of sample for IRS[54]. For example, IRS spectra for a large number of adhesives have been obtained very easily[79], including industrial adhesives[110,111] and adhesive coatings[112].

Melts. Fairly complicated techniques are available for measuring the i.r. spectra of melts. They become very much simpler when IRS methods are used[113,114].

Liquids and solutions. In studies of the i.r. spectra of liquids, and some solutions, the use of IRS methods is hardly justifiable. However, the u.v. transmission spectra of liquids and concentrated solutions are almost impossible to measure. Furthermore, the scope of i.r. spectroscopy of solutions is often limited by the difficulty of finding a suitable solvent, since most solvents have strong absorption bands and therefore they can only be used over a limited region of the spectrum. Water is one of these solvents, and in many cases aqueous solutions are the only form in which the material of interest can be investigated. With biologically active substances and their model compounds aqueous solutions are vitally important because they most closely resemble natural (*in vivo*) conditions. However, the study of aqueous solutions still presents considerable difficulties[115], and several important regions of the spectrum remain inaccessible even with the thinnest available cells.

With the introduction of IRS methods the scope of aqueous i.r. spectroscopy has become much wider, and at the same time the experimental procedures have been simplified. The i.r. spectra of aqueous solutions can now be measured over practically the whole of the spectral region by using the available range of crystals (KRS-5,[115] AgCl,[116,117] Irtran-2,[118] Ge [95])†, by choosing the ATR[116-122] or the MATR[115,123,124] method as required by the problem, and by taking advantage of the most up-to-date equipment[117,119].

The possibilities and the advantages of the IRS method in comparison with the transmission method have been demonstrated by measurements on aqueous solutions of acetylcholine[125], various aminoacids[115,116,118-120], and carbohydrates[115,120,126]. IRS methods are widely used to study aqueous solutions of inorganic and organic acids and their salts[16,115,117,118,120-122,127-132], and other compounds[115,120], and also the structure of water itself[121,129,133]. IRS methods are particularly effective in studies of multiphased systems, e.g. aqueous emulsions of disperse and turbid media, etc.[95,118,120], which cannot as a rule be examined by conventional transmission methods. The IRS spectra of concentrated aqueous solutions have also been examined in the u.v. region[72,81].

The IRS technique has greatly extended the range of solvents which can be used in i.r. spectroscopy. Thus, universally acceptable solvents such as alcohols, dimethylformamide, dimethylsulphoxide, etc. can now be exploited by the i.r. spectroscopist. A comparative study[134] of the solvents most commonly used in chemistry has shown that their transmission bands are much broader in i.r. IRS spectra than in conventional i.r. absorption spectra.

2. Applications

Because of the unique features of the IRS method, its potential applications in chemistry and in related areas of science and technology are many. Some examples of the application of IRS in areas where the method appears particularly promising are discussed below.

a) Study of chemical reactions

Molecular spectroscopy is undoubtedly one of the most powerful methods of studying various types of chemical change, and important problems in chemical kinetics and reaction mechanisms. However, the scope of transmission spectroscopy in this particular area is severely limited. Thus, it is seldom possible to study a reaction without a solvent, or in concentrated solutions; unfortunately the commonest solvents are strongly absorbing, and therefore the reaction systems cannot be studied by transmission methods even in dilute solutions.

All these difficulties can be fully or partially overcome by resorting to IRS methods, whose extensive technical arsenal (various crystals with different angles of incidence and number of reflections, special reaction vessels[54,55]) allows almost any reaction to be investigated either in solution (in one of the increasing number of usable solvents[134]) or without a solvent.

A good example of the advantages of IRS over ordinary transmission methods is provided by Roberts' work[135] on

† It must be noted that KRS-5 is sparingly soluble in water, particularly in hot water[95], and that AgCl can react with aqueous solutions giving rise to corrosion of the steel parts of the cell[16,95].

reactions involving carbonium ions, based on measurements of u.v. IRS spectra. Carbonium ions absorb very strongly in the u.v., and they can be studied only at high dilution. On the other hand, they are so highly reactive that unwanted side-reactions with the solvent are almost unavoidable. For these reasons, the study of carbonium ion reactions by normal u.v. spectroscopy is not a practical proposition.

On the other hand, IRS methods have been found very effective in this case, and studies of carbonium ion reactions (including intermediates) have been successfully carried out by these methods over a range of concentration, temperature, and pressure.

Infrared IRS is widely used to study polymerisation reactions[76,136-138], including high-temperature polymerisation[138], which do not lend themselves to conventional transmission spectroscopic investigation (Fig. 17).

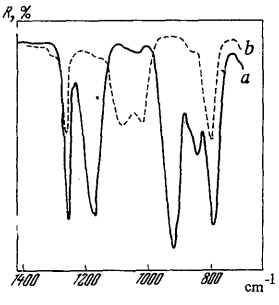


Figure 17. IRS spectra of hexamethylcyclotrisilazane during hydrolysis: (*a*) initial compound, (*b*) hydrolysis product. IRE—KRS-5 plate (25 reflections).

IRS is one of the most effective methods of monitoring surface reactions on opaque materials. For example, the effect of u.v. radiation on the stability of polymers and the effect of inhibitors on the course and the rate of reactions on polymer surfaces have been studied[139] by IRS spectroscopy. The behaviour of modifiers and other polymer additives under the influence of light has also been examined[140]. IRS has been used to study surface oxidation[141], the oxidative polymerisation reactions involved in the drying of certain oils[142], and various other processes on polymer surfaces[143].

b) Surface phenomena and adsorption

The future of IRS in the study of these important chemical problems is assured[144,145]. In particular, IRS methods are among the few which can give information on surface states in semiconductors and on their influence on the electrical properties of the surface[144]. In this case the application of the method stems from the fact that the reflectivity is a function of the electric charge at the surface, which is itself influenced by external electric fields or by adsorption. Harrick[27,53,82,146] was the first to use IRS in the study of surface states, but the method was soon adopted by other workers[147-149]. More recently, IRS has been used to study a wide range of problems in semiconductor surface chemistry, including the chemical nature and the behaviour of solid and liquid surface films formed by the action of electrolytes, during etching, etc.[73,150-157], and also adsorption processes on semiconductors[27,158].

Adsorption is the branch of chemistry where the advantages of IRS are most clearly evident, as shown by the large number of papers published on this subject. Among the most interesting are studies of the adsorption of hydrocarbons[82], fatty acid derivatives[154-159], and other organic and inorganic substances[159-161] including gases[27,158].

The various modifications of carbon are technically important as adsorbents, but the study of these materials by the traditional methods of transmission and reflection spectroscopy (particularly in the i.r. region) often presents insuperable practical difficulties arising from their very strong absorption[162] (which can exceed the absorption of organic compounds by 10^2-10^3). However, by using multiple reflection techniques in very sensitive spectrometers we can identify the functional surface groups which determine the adsorption properties of the different carbons, measure their concentration, and examine various problems bearing on the nature of the adsorption process. In particular, we can answer questions such as: how do adsorbates affect the structure of the surface, which functional groups are involved in sorption processes, what is the nature of the sorption bond, etc.[96,141,162-164].

c) Electrochemistry

The most important problems in electrochemical research are to establish the mechanism of the electrode reactions, to identify the intermediate activated states of the products formed by electron transfer, etc. Information of this type cannot be obtained directly from electrochemical measurements. Other methods, including transmission spectroscopy, are also unsuitable.

IRS, on the other hand, is ideally suited to the study of electrochemical processes *in situ*.

The theory of IRS developed by Hansen[165] for multilayer systems has been widely applied in studies of electrochemical reactions by u.v. and i.r. internal reflection spectroscopy.

The electrode for studies in the u.v. region usually consists of a glass prism or plate coated with a thin conducting layer of tin oxide[166-169], gold[149,170-172], platinum and palladium[173], or antimony[171]. For work in the i.r. region the electrode is either pure germanium[174] or germanium coated with a metallic film (e.g. gallium)[88,175].

A good example of the successful application of u.v. IRS in electrochemistry is a series of studies[166-168,173] of the electrochemical oxidation of *o*-toluidine, in which the kinetics and the mechanism of the reaction were examined under different conditions, the electrolysis products were identified on the electrode surface, and their concentration was measured. A similar study of eosin-Y has also been published[165,170,171].

Other examples of the use of IRS in the u.v. region for electrochemical studies include an investigation of discrete states at the electrode — solution interface[147,176,177] and studies of the reduction of 8-quinolinol, tetramethylbenzidine, and various carbonyl compounds[88,175]. Electrolysis mechanisms were investigated, the reduction products were identified, and their concentration was determined. The effect of electrode potential on the intensity of the spectral bands due to intermediate products was also found (Fig. 18).

d) Biochemistry, clinical chemistry, and pharmacology

Molecular spectra (and, in particular, vibrational spectra) are widely used in biochemical research. Significant advances have been made in recent years[178-180],

but the preparation of samples for spectroscopic measurements remains a complicated and laborious procedure[180], involving many preliminary operations such as homogenisation, dehydration, and pressing into alkali halide disks, which can lead to losses and contamination of the sample. However, the most serious shortcoming of these techniques is the danger of altering the properties of delicate biological samples.

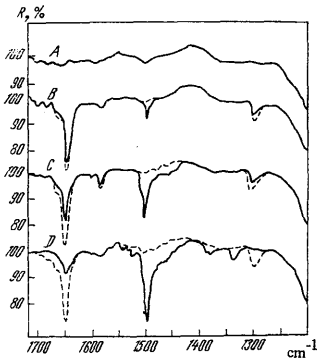


Figure 18. IRS spectra of *p*-benzoquinone (broken line) and its electrolysis products (full line): *B* at 0.7 V, *C* at 1.1 V, *D* at 2.0 V. *A* is the spectrum of the solvent. IRE—germanium plate (25 reflections) coated with a layer of gallium.

IRS methods have opened an entirely new chapter in biochemistry and clinical chemistry, because they enable biological tissues to be examined without pre-processing. Thus, spectra have been obtained from whole blood[126], bone tissues and collagens[181], tendons[181,182], etc.

One of the main advantages of the IRS methods is their unique ability to examine not only the tissues themselves but also numerous processes occurring within the tissues as a result of various influences. For example, spectra have been obtained from the upper integument of the brain cortex of the white rat, undergoing narcosis[76]. IRS methods have been used also to study stimulated chemical changes in animal tissues under the influence of biologically active preparations[183]. One of the most important discoveries has been the selectivity of these preparations towards different organs: for example, spectral changes were detected in kidney and liver tissues after the injection, but not in other tissues. Thus, IRS methods can, in principle, monitor the distribution of biologically active substances within the organism, and therefore they can be used to study the mechanism of biological interactions[183].

The use of IRS in biochemical studies of normal and pathogenic animal and human tissues may lead to significant advances in the diagnosis and study of various diseases. Results so far obtained are extremely promising. Thus, spectra have been obtained from normal and from pathological erythrocytes in human blood[76]. Infrared IRS spectra have been recorded, and studied, from the tissues of various human organs[184]: spleen, liver, blood vessels, etc. Significant differences have been found between the spectra of the aorta of a new-born infant and that of an adult suffering from arteriosclerosis. We may therefore classify IRS among the methods available for comparative studies of the chemical composition and properties of healthy and of pathological tissues. The use of IRS to study healthy and diseased tissues in the human eye (cornea, and crystalline lens) has also been proposed[184].

New prospects in biochemical and clinical research (e.g., in the diagnosis of skin diseases) may be expected from the latest refinements in the design of IRS apparatus. Thus, special attachments have been developed[185] to take IRS spectra from the surface of practically any part of the human body. These provide detailed information on the skin retention of ointments, creams, and other preparations, and on the nature of their interaction with the skin (Fig. 19).

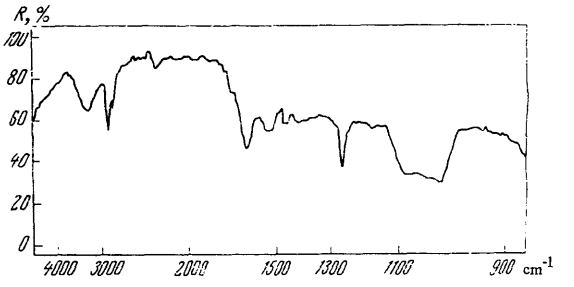


Figure 19. IRS spectrum of human skin treated with an ointment. IRE—AgBr plate.

One of the most interesting biochemical applications of IRS is the study (and, in some cases, the identification) of micro-organisms such as bacteria and algae. By using special membrane filters to "accumulate" the micro-organisms, their spectra can be recorded[95,186,187], and furthermore the organisms can be identified, since the spectra of, say, two varieties of algae show some distinct differences[95]. In principle, mixed cultures can be analysed from their IRS spectra with the help of a computer.

Among the many other biological applications of IRS, the following are particularly interesting: a study of the structure of liquid water in crystalline animal haemoglobin[76], a study of the surface reactions of bio-polymers[188,189], and also measurements of the u.v. spectra of chlorophyll[79] and of the i.r. spectra of carbohydrates[120,126,190], aminoacids[118-120], steroid hormones[191], and various biologically active substances and preparations[160,192,193].

IRS methods are very attractive in pharmacology[194], since they can be used in the structural analysis and quality control of medicinal preparations[195].

e) Chromatography

Infrared spectroscopy is one of the most effective methods of analysis and identification of chromatographic fractions. However, this method cannot always be applied: in order to achieve the optimum separation conditions, it is often necessary to work with very small samples, which may lie below the limits of sensitivity of standard methods of analysis.

In gas chromatography, the problem can be overcome by using the capillary multiple reflection cell described in the previous Section[54,185,196], which may be connected

directly to the chromatographic fraction collector. This method overcomes the loss of sample which is unavoidable in normal methods, and it offers very high sensitivity (down to 0.01 μl) by virtue of the large number of reflections possible (up to 50)[196]. The apparatus can be used with substances covering a wide range of boiling point (60 — 200°)[185, 196].

Typical examples of the use of IRS in chromatography include the analysis of fractions of steroids[191], pesticides[192], adhesives[110], and other substances[112], with samples weighing only a few microgrammes[192] (see Fig. 20).

Thin-layer chromatography and paper chromatography also involve very small samples, which cannot be analysed by normal i.r. spectroscopy after being fractionated and extracted from the substrate. Larger samples are sometimes collected by combining several peaks[192], but the procedure is time-consuming.

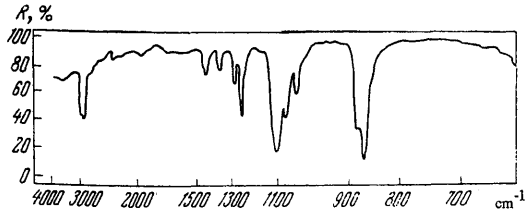


Figure 20. IRS spectrum of a chromatographic dioxan fraction isolated from a 0.7 μl sample of dioxan — acetone mixture. IRE—KRS-5 (50 reflections).

Considerable time saving, and simpler experimental procedures, can be achieved by resorting to IRS methods. Thus, it is sometimes possible to record spectra and to identify the fractions directly from the surface of the chromatogram, and even to analyse a mixture quantitatively[197]. In other cases[191,192] the chromatographic spot is extracted with a suitable solvent and the solution is applied to the IR plate. With this technique, a few microgrammes of sample are sufficient to give a strong spectrum, particularly if a plate capable of 50 or more reflections is used[54].

f) Industry

The important new features of IRS (as compared with transmission spectroscopy) offer great scope not only in scientific and research work but also in industrial laboratories responsible for the analysis of production runs. Molecular spectroscopy may now find general application as a method of process control and quality assurance in industry, whereas until relatively recently the method had been applied only in a few specialised areas.

The outlook can be illustrated by some examples.

1. Paper. IRS methods are already widely applied in the analysis of various types of paper, cardboard, etc. They are used also in the analysis of pulp and unbleached paper[198,199], and to identify and to determine the composition of paper coatings[200,201] including bonding[7,202-204] and colouring agents[16,106]. Different types of article have been analysed: paper-coated aluminium foil[205], cardboard boxes and labels[199], stamps[206]. IRS methods have been applied to specific problems such as identifying the contaminants of the matting in paper-making machinery[199], and also in determining the stability of paper coatings under the influence of temperature, light, etc.[54,204].

2. Wood. IRS methods have been used to solve problems related to the composition of wood, and to analyse various wood coatings[126].

The chemical composition of its surface determines many important properties of wood, such as its ability to bond to other surfaces. IRS spectral studies of different types of wood[207] have shown that the chemical composition of wood near a cut surface is very dependent on the angle of the cut. In particular, the xylene content of the surface region can vary by a large factor, depending on the angle of the cut.

3. Textiles. The development of IRS methods has led to the solution of a number of problems in the textile industry. Thus, both natural[54,105,208-210] and synthetic[54,99,126,210,211] fibres and fabrics have been successfully identified, glass fibres have been studied[105], and the composition of their surface coatings has been determined[105,111,208]. Because of the high sensitivity of the IRS methods, minor components of surface coatings can be detected[111] at concentrations below 1%. Other successful applications of IRS include the quantitative analysis of fibre compositions (for example, the ratio of cotton to nylon in semi-synthetic fabrics[31]), and the analysis of residues of finishing materials[208], which may include impurities harmful to the fabric[111].

4. Leather. The different types of natural[212] and synthetic[7,111] leather can easily be identified by IRS methods; it is possible also to analyse coatings and residues of finishes on the leather surface.

5. Polymers. Articles made from polymers are extensively used in industry and in everyday life. They can all be identified and analysed by IRS methods. These methods can also be applied for process control in the production of polymers[76,136,213], and for the analysis of finished articles[7,24,69]. In conjunction with special pyrolysis attachments, IRS methods can give useful information on polymer additives and fillers[185,211,214,215].

The use of IRS methods to analyse and identify polymers in the footwear industry[110], and also in the packaging and other industries[108], has also been reported.

6. Foodstuffs. I.r. IRS spectra have been measured on many food products, including margarine, gelatin[70,126], and milk powder[182]. By using membrane filters[187], components present in suspension in liquid foodstuffs can be analysed (for examples, yeasts in different types of beer[186]). In principle, IRS enables the quality of any foodstuff to be assessed and the presence of adulterants to be detected.

7. Cosmetics. The analysis of cosmetic articles by IRS methods is much more effective than analysis by the classical transmission spectroscopy methods, used until recently[216]. The most varied types of cream can be analysed[189,217] (including cream present on the skin[185]), and also toothpaste[182,217], liquid soap[218], foam[54], shampoo[218], domestic liquid detergents[218], and others[219].

The importance of i.r. spectroscopy as an operational method of quality assurance and process control in industry is well known[220]. The development of IRS has

greatly extended the scope and the range of the industrial applications of i.r. spectroscopy: as stated above, i.r. spectroscopy can now be applied in the paper, textile, food, and other industries as an analytical method. IRS may have an important part to play in the solution of some urgent industrial problems (e.g. effluent analysis[95,115]).

In the chemical industry, IRS offers exciting new prospects in the area of direct process control (e.g., on-line product analysis[24,221,222]).

Problems of these types can seldom be solved by the classical methods of spectroscopic analysis, which are severely limited by the need to use extremely thin optical cells. On the other hand, analysers based on the IRS principle can be used in a wide variety of automatic process control loops handling any type of liquid system, including very viscous liquids.

Industrial i.r. IRS analysers have been developed[223,224], and have been used successfully under factory conditions[224].

g) Trace analysis

One of the main attractions of the IRS method is its very high sensitivity, which enables quantities of the order of $10^{-6}-10^{-7}$ [54,87,95,191,193] or even 10^{-9} [35] g of sample to be detected and identified. It is thought[58] that even lower limits of detection may be practical. Hence, the IRS method is very attractive for the detection of very small concentrations of harmful and dangerous substances (a very important problem in chemical plant, storage areas, etc.).

An IRS trace analyser[139] has been developed for the detection of toxic vapours from rocket fuels, which may build up to dangerous concentrations in rocket storage sheds. A more recent modification of this equipment is used[160] to detect traces of organo-phosphorus compounds in air. The key component of the apparatus is a germanium multiple reflection plate coated on both sides with a thin platinum film which acts as the adsorption surface. Under the best conditions (film thickness 500 — 800 Å, surface temperature 15 — 20°) the apparatus can detect the presence of 10^{-7} g litre^{-1} of dimethylmethylphosphonate in air in 30 s.

The function of the platinum coating is to ensure that the adsorption is reversible: the adsorbate can be removed from the surface in a few seconds, simply by flushing the apparatus with air, and the sensitivity of the surface remains constant over long periods.

Similar devices can be used[90] to detect solid particles.

3. Quantitative Measurements

It was pointed out in Section II that the reflectivity of the surface can be approximately described by an equation analogous to the Lambert — Beer law if the refractive index and the angle of incidence of the IRE are correctly chosen. The formal optical density $\ln(R_0/R)$ then becomes a linear function of the concentration c.

From Eqn. (13) we have

$$\ln\left(\frac{R_0}{R}\right)_\nu = \alpha_\nu \cdot c \cdot d_{\text{eff}} \qquad (23)$$

Eqn. (23) can be used to calculate the concentration of the material of interest by the procedures and methods of quantitative transmission spectroscopy.

The practical aspects of quantitative analysis by IR spectroscopy were discussed by Wilks[31], who examined the dependence of the precision, reproducibility, and sensitivity of the method on factors such as the material of the plate, the number of reflections, the angle of incidence, the area of the plate covered by the sample, the position and uniformity of the sample, and the effectiveness of the contact.

It should be noted that, because of the linear dependence of the effective thickness upon wave length, the IRS band intensities are not directly comparable with those of transmission spectra. It can be shown, however, that the integral intensity of a band in the IRS spectrum is equal to the G integral in the transmission spectrum, obtained by integrating over the logarithm of the frequency[46,76]. Thus, the IRS method offers a simple way of determining the integral band intensities in the spectra of pure liquids and solutions[32].

The ATR and, particularly, the MATR method show great promise in routine analysis, when absolute methods are very seldom necessary and the main objective is to establish the effect of varying many factors. Relative methods are fully adequate in these circumstances. Typical applications of IRS methods in routine analysis include the quantitative analysis of aqueous and alcoholic solutions[72,95,112,117,118,124,127], and of coatings on paper[201,203], fabrics[203], and films[107,219]. Other reported applications of quantitative IRS methods include the compositional analysis of alkyd resins[215] and adhesives[112], semi-synthetic fabrics[31], and paper pulp[198]. Quantitative analyses of medicinal products[195], cosmetics[218,219], chromatographic fractions[197], and mixtures of powders[31] have also been mentioned. It has been shown that the method can measure the concentration of electrochemical reaction products on electrode surfaces[197], and the concentration of functional groups on adsorbent surfaces[164], and that it can be used to monitor polymerisation processes quantitatively[138]. Lastly, analysers for the quantitative control of continuous industrial processes have been developed[223,224].

The precision of quantitative IRS methods is always of the order of a few per cent[117,124,198,215,218], which is as good as in ordinary transmission spectroscopy. However, the former technique has a number of advantages over the latter, such as freedom from interference errors (Fig. 16). IRS methods also have some operational advantages by being less time consuming than transmission methods (mainly because of the simpler sample preparation procedures).

---o0o---

Many examples of the successful application of IRS in important areas of science and technology have been listed in this review. However, the list is by no means exclusive. It may be said, without exaggeration, that the scope of IRS, and therefore the area of application of ATR and MATR methods, is almost limitless. It would be difficult to enumerate all the areas of science and technology in which IRS methods have been successfully applied.

IRS has been used to study the liquid-crystal state[225], electrophoresis[54] and diffusion[9], and in mineralogy[103]; it has also been used to analyse asphalt[226] and tiles[156]. ATR and MATR methods are used to analyse pollutants in air[227], to determine the composition of cigarette smoke[95] and exhaust gases[186], and to identify inks[186] and wire coverings[54]. IRS methods have been proposed for the analysis of sludge deposits[95] and lunar dust[87]. There are reports of the successful use of IRS in philately[75,206] and in forensic science[10]. IRS methods may be useful in establishing the authenticity of paintings from the composition of the paints[185], which may be determined by direct IRS measurements on the painting itself. Wilks, one of the

founders of practical IR spectroscopy, rightly points out that the limitations of the IRS methods, and the specific areas of science and technology where these methods can be applied, are mainly determined by the ingenuity of the investigator.

In conclusion, we note that IRS methods can be generally recommended, in all cases where the conventional methods of transmission spectroscopy are difficult or impossible to apply. The number of such cases is ever-increasing: many new problems in science and technology are soluble in principle, but they present insuperable difficulties arising from the limitations of transmission spectroscopy methods. Therefore, a more extensive penetration of molecular spectroscopy into chemistry and industry is almost unthinkable unless accompanied by a wider application of IRS methods in research and industrial laboratories.

---o0o---

Many new publications have appeared while the present review was being prepared. The most important is undoubtedly Harrick's monograph[228], translated into Russian with an appendix by V. M. Zolotarev in which IRS equipment commercially available in the Soviet Union is described.

Two reviews[229,230] deal with general problems, and discuss some practical aspects of the application of IRS methods. In the latter, formulae for calculating effective thickness are obtained from a new mathematical treatment[231] of the problem.

Many interesting review papers can be found in the proceedings of a conference on applied spectroscopy held in 1970 in the USA.[232]

Section III of the present review, dealing with apparatus and techniques, would be incomplete without mention of some multi-purpose attachments for plotting u.v. and i.r. spectra[233], for adsorption studies[234], for low-temperature work[235,236], for studies of solids undergoing pyrolysis[237], and also of an attachment in which the light passes twice through the IRE.[238]

Mention must be made also of a number of interesting papers dealing with experimental methods, including the possibility of applying compensation measurements in IRS,[239] the optimum conditions for recording the spectra[240], and still further examples of the use of internal reflection spectroscopy with widely different types of sample including disperse media[241], suspensions[242], single crystals[243,244] and powders[245,246], and in particular metal oxides[247].

The practical applications of IRS methods continue to grow, as shown by the large number of papers published in the recent past. Among the most noteworthy we include IRS studies of paints[248] and textiles[249], of cellulose[250], of various foodstuffs[251], and of organic impurities in water[252].

IRS methods are being used on an increasing scale to study chemical reactions. Some of the more recent examples include studies of the interaction of proteins with polysaccharides[253], or resorcin with formaldehyde[254], and studies of the formation of elastomers in the solid phase[255] and studies of electrochemical reaction mechanisms[256-260].

In biochemistry the MATR method has recently been used in process control (separation of steroids by thin-layer chromatography[261]); in pharmacology it has been used to identify medicinal compounds and preparations[262-264].

IRS continues to be widely used in studies of surface phenomena and adsorption. The most recent papers on these topics deal with the physiochemical processes occurring in the surface layers of polymers during photochemical oxidation[265-267], under the influence of a corona discharge[268], in the presence of ozone[269,270], and they also describe further studies of various processes in polymers[271-274]. Adsorption[234], surface phenomena on semiconductors[275-279], and corrosion inhibitors[280] have also been investigated. In addition, IRS has been used to study the surface orientation of polymers[281] and biopolymers[282,283], the behaviour of surface-active molecules at an interface[284], solutions of alkali metals in liquid ammonia[285], adhesion between epoxy resins and cellulose[286,287], the hydrolysis of glass surfaces[288], and also a number of films and surface coatings[289-291].

Furthermore, the ATR method continues to be widely used to measure optical constants[292-297].

REFERENCES

1. L. I. Mandel'shtam, "Pol'noe Sobranie Trudov" (Collected Papers), Vol. 1, Izd. Akad. Nauk SSSR, Moscow, 1948, p. 261.
2. F. S. Baryshanskaya, Dokl. Akad. Nauk SSSR, 17, 99 (1937).
3. A. A. Eikhenval'd, "O Dvizhenii Energii pri Polnom Vnutrennem Otrazhenii" (The Motion of Energy During Total Internal Reflection), Vol. 2, Izd. Izv. Moskov. Inzhener. Uchrezhd., 1908.
4. T. Hirschfeld, Canad. Spectroscopy, 10, 128 (1965).
5. A. M. Taylor and A. M. Glover, J. Opt. Soc. Amer., 23, 206 (1933).
6. A. A. Korobko-Stefanov, Uspekhi Fiz. Nauk, 42, 433 (1950).
7. S. Polchlopek, Symposium "Prikladnaya Infrakrasnaya Spektroskopiya" (Applied Infrared Spectroscopy), Izd. Mir, Moscow, 1970, p. 299.
8. V. M. Zolotarev, Zhur. Prikl. Spektrosk., 7, 286 (1967).
9. N. J. Harrick, "Internal Reflection Spectroscopy", N. Y., 1967.
10. P. A. Wilks and T. Hirschfeld, Appl. Spectroscopy Rev., 1, 99 (1967).
11. P. A. Wilks and T. Hirschfeld, "Applied Spectroscopy Reviews", N. Y. — London, 1968, p. 99.
12. J. Merka, Canad. Spectroscopy, 10, 93 (1965).
13. P. A. Wilks, Chim. Anal., 48, 456 (1966).
14. N. A. Puttnam, Spectrovision, No. 15, 11 (1966).
15. W. W. Wendlandt and H. G. Hecht, "Reflectance Spectroscopy", N. Y., 1966.
16. J. A. Pawlak, G. Fricke, and H. Szymanski, "Progress in Infrared Spectroscopy", v. 3, N. Y., 1967, p. 39.
17. P. A. Wilks, "Modern Aspects of Reflectance Spectroscopy", N. Y., 1968, p. 170.
18. G. S. Landsberg, "Optika" (Optics), GITL, Moscow — Leningrad, 1940.
19. Sir I. Newton, "Optics" (Translated into Russian), Vol. 2, Ch. 1, GITL, Moscow, 1954, p. 46.
20. N. J. Harrick, J. Opt. Soc. Amer., 55, 851 (1965).
21. C. Schaefer and G. Groos, Ann. Physik, 32, 648 (1910).
22. F. Goos and H. Hanchen, Ann. Physik, 6, 333 (1947).
23. A. Sommerfeld, "Optics" (Translated into Russian), Inostr. Lit., Moscow, 1953.
24. J. Fahrenfort, Spectrochim. Acta, 17, 698 (1961).
25. J. Fahrenfort, Proceedings of the Fourth Conference on Molecular Spectroscopy, London, 1968, p. 111.

26. V. M. Zolotarev and L. D. Kislovskii, Optika i Spektrosk., 19, 623 (1965).
27. N. J. Harrick, Ann. N. Y. Acad. Sci., 101, 928 (1963).
28. J. Fahrenfort, "Infra-red Spectroscopy and Molecular Structure", Amsterdam, London, N. Y., 1963, p. 377.
29. W. N. Hansen, Spectrochim. Acta, 21, 815 (1965).
30. V. M. Zolotarev and L. D. Kislovskii, Optika i Spektrosk., 19, 809 (1965).
31. P. A. Wilks, Appl. Spectrosc., 23, 63 (1969).
32. P. A. Flournoy, J. Chem. Phys., 39, 3156 (1963).
33. N. J. Harrick and F. K. du Pre, Appl. Optics, 5, 1739 (1966).
34. N. J. Harrick, "Modern Aspects of Reflectance Spectroscopy", N. Y., 1968, p. 207.
35. V. M. Zolotarev, see Ref. 7, p. 322.
36. P. A. Wilks, Appl. Spectrosc., 22, 782 (1968).
37. J. Fahrenfort and W. M. Visser, Spectrochim. Acta, 18, 1103 (1962).
38. W. N. Hansen, ISA Transaction, 4, 263 (1965).
39. W. N. Hansen, Spectrochim. Acta, 21, 209 (1965).
40. J. Fahrenfort and W. N. Visser, Spectrochim. Acta, 21, 1433 (1965).
41. A. Engelsrath and E. V. Lowenstein, Appl. Optics, 5, 656 (1966).
42. V. M. Zolotarev, Dokl. Akad. Nauk SSSR, 170, 317 (1966).
43. G. M. Irons and H. W. Thompson, Proc. Roy. Soc., A298, 160 (1967).
44. J. A. Horton and W. N. Hansen, Analyt. Chem., 39, 1097 (1967).
45. V. M. Zolotarev, B. A. Mikhailov, L. I. Al'perovich, and S. I. Popova, Optika i Spektrosk., 27, 790 (1969).
46. A. C. Gilby, J. Burr, W. Krueger, and B. Crawford, J. Phys. Chem., 70, 1525 (1966).
47. B. M. Zolotarev, Zhur. Prikl. Spektrosk., 5, 62 (1966).
48. J. M. Bennet, J. L. Stauford, and E. J. Ashley, J. Opt. Soc. Amer., 60, 224 (1970).
49. T. Hirschfeld, Appl. Spectroscopy, 24, 277 (1970).
50. E. F. Young and R. W. Hannach, see Ref. 17, p. 218.
51. M. K. Withers, Austral. Paint J., 14, No. 11, 9 (1969).
52. M. K. Withers, Austral. Paint J., 14, No. 12, 10 (1969).
53. N. J. Harrick, Phys. Rev. Letters, 4, 224 (1960).
54. Techmation Analytex Seminars, 1969.
55. "Internal Reflection Spectroscopy", v. 1, Wilks Scientific Corp., 1965.
56. Techmation Application Bulletin No. 2.
57. W. H. Hansen, J. Opt. Soc. Amer., 58, 380 (1968).
58. T. Hirschfeld, Appl. Spectrosc., 20, 336 (1966).
59. A. H. Reed and E. Yeager, Appl. Optics, 7, 451 (1968).
60. K. Gottlieb, Z. Inst., 75, 125 (1967).
61. P. A. Flournoy and W. J. Schaffers, Spectrochim. Acta, 22, 5 (1966).
62. P. A. Flournoy, Spectrochim. Acta, 22, 15 (1966).
63. W. N. Hansen and J. A. Horton, Analyt. Chem., 36, 783 (1964).
64. W. N. Hansen, Analyt. Chem., 37, 1142 (1965).
65. S. Toda, M. Nakamura, Y. Nihei, and S. Tanaka, Spectrochim. Acta, 26A, 937 (1970).
66. A. C. Gilby, J. Burr, and B. Crawford, J. Phys. Chem., 70, 1520 (1966).
67. V. M. Zolotarev and L. D. Kislovskii, Pribory i Tekh. Eksper., No. 5, 175 (1964).
68. V. M. Zolotarev, V. A. Karinskii, and Yu. D. Pushkin, Opyt.-Mekh. Prom., No. 8, 24 (1966).
69. D. E. McCarthy, Appl. Spectrosc., 22, 460 (1968).
70. D. S. Bulatov, Pribory i Tekh. Eksper., No. 1, 145 (1969).
71. V. A. Nikitin, Zhur. Prikl. Spektrosk., 12, 583 (1970).
72. T. Hirschfeld, Canad. Spectroscopy, 11, 102 (1966).
73. V. M. Zolotarev, "Struktura i Rol' Vody v Zhivom Organizme" (Structure and Role of Water in the Living Organism), Vol. 1, Izd. Leningrad. Univ., 1966, p. 108.
74. J. Dechant and K. Frigge, Experim. Tech. Phys., 17, 221 (1969).
75. A. J. Barnes, Instrument News, 21, No. 1, 1 (1970).
76. V. M. Zolotarev, Thesis, Leningrad, 1966.
77. N. J. Harrick, Analyt. Chem., 37, 1445 (1965).
78. N. J. Harrick, Appl. Optics, 5, 1 (1966).
79. T. Hirschfeld, Appl. Optics, 6, 715 (1967).
80. N. J. Harrick, Appl. Optics, 5, 1236 (1966).
81. W. N. Hansen, Analyt. Chem., 35, 765 (1963).
82. N. J. Harrick, J. Phys. Chem., 64, 1110 (1960).
83. N. J. Harrick and A. F. Turner, Appl. Optics, 9, 350 (1970).
84. D. Schmitz, Plaste Kaut., 16, 936 (1969).
85. G. Kortum, "Reflexionsspektroskopie", Berlin, 1969.
86. G. L. Carlson and W. G. Fateley, Appl. Spectrosc., 23, 374 (1969).
87. N. J. Harrick and N. H. Riederman, Spectrochim. Acta, 21, 2135 (1965).
88. D. R. Tallant and D. H. Evans, Analyt. Chem., 41, 835 (1969).
89. V. A. Bershtein and V. V. Nikitin, Dokl. Akad. Nauk SSSR, 190, 823 (1970).
90. N. J. Harrick, Appl. Optics, 9, 349 (1970).
91. V. M. Zolotarev, Optika i Spektrosk., 29, 519 (1970).
92. N. J. Harrick, Appl. Optics, 4, 1664 (1965).
93. N. J. Harrick, Appl. Optics, 36, 188 (1964).
94. S. A. Fridmann, see Ref. 16, p. 1.
95. J. S. Mattson and H. B. Mark, Environment. Sci. Technol., 3, 161 (1969).
96. R. Fridel, see Ref. 17, p. 164.
97. R. Bent and W. R. Ladner, J. Fuel Sci., 44, 243 (1965).
98. R. Ebinden, "Infrared Spectroscopy of High Polymers" (Translated into Russian), Izd. Mir, Moscow, 1966.
99. K. Gottleb and B. Schrader, Z. analyt. Chem., 216, 307 (1966).
100. N. Yamada and K. Suzuki, Spectrochim. Acta, 23A, 1735 (1967).
101. K. Tsuji, N. Yamada, K. Suzuki, and I. Nitta, Spectrochim. Acta, 26A, 475 (1970).
102. A. M. Deane and E. W. Richards, Spectrochim. Acta, 22, 1253 (1966).
103. G. Rigault and D. Aquilano, Period. Mineral., 33, 445 (1964).
104. "The Physics of Thin Films" (Translated into Russian), Izd. Mir, Moscow, 1970.
105. T. S. Hermann, J. Appl. Polymer Sci., 9, 3953 (1965).
106. R. J. McGowan, Analyt. Chem., 35, 1664 (1963).
107. K. H. Reichert, Farbe Lack, 72, 13 (1966).
108. W. Morris, J. Assoc. Offic. Agric. Chem., 48, 497 (1965).
109. C. A. Lucchesi, Offic. Digest, 35, 975 (1963).
110. W. Fischer and G. Leukroth, Adhesion, 11, 247 (1967).

111. W. Krentz, Melliand Textilber., 50, 557 (1969).
112. E. Medeck, Canad. Spectroscopy, 13, 76 (1968).
113. A. Bondy, J. P. Devlin, R. Burger, and B. McCay, Rev. Sci. Instr., 35, 1206 (1964).
114. J. P. Devlin, K. Williams, and G. Austin, J. Chem. Phys., 44, 2203 (1966).
115. K. Burner, Z. analyt. Chem., 243, 68 (1968).
116. F. P. Robinson and S. N. Vinogradov, Appl. Spectroscopy, 18, 62 (1964).
117. R. N. Wilhite and R. F. Ellis, Appl. Spectroscopy, 17, 168 (1963).
118. B. Katlafsky and R. E. Keller, Analyt. Chem., 35, 1665 (1963).
119. F. S. Parker, Nature, 200, 1093 (1963).
120. G. Peters, Z. analyt. Chem., 215, 41 (1966).
121. L. V. Ivanova and V. M. Zolotarev, Zhur. Strukturnoi Khim., 9, 385 (1968).
122. J. J. Fripiat, F. Van Cauwelaert, and H. Bosmans, J. Phys. Chem., 69, 2458 (1965).
123. J. D. S. Goulden and D. J. Manning, Nature, 203, 403 (1964).
124. C. P. Malone and P. A. Fluorney, Spectrochim. Acta, 21, 1361 (1965).
125. F. G. Canepa and E. F. Mooney, Nature, 207, 78 (1965).
126. Instrument News, 14, No. 1, 1 (1962).
127. G. E. B. Y. Ahlijah and E. F. Mooney, Spectrochim. Acta, 25A, 619 (1969).
128. G. E. B. Y. Ablijah and E. F. Mooney, Spectrochim. Acta, 22, 547 (1966).
129. E. F. Roger, Diss. Abs., B28, 960 (1968).
130. J. D. S. Goulden and D. J. Manning, Spectrochim. Acta, 23A, 2249 (1967).
131. J. P. Devlin and P. P. J. Cooney, J. Chem. Phys., 52, 5495 (1970).
132. L. V. Ivanova and V. M. Zolotarev, "Struktura i Rol' Vody v Zhivom Organizme" (Structure and Role of Water in the Living Organism), Vol. 2, Leningrad, 1968, p. 30.
133. V. A. Mikhailov and V. M. Zolotarev, "Struktura i Rol' Vody v Zhivom Organizme" (Structure and Role of Water in the Living Organism), Vol. 2, Leningrad, 1968, p. 43.
134. B. Katlafsky and R. E. Keller, Instrument News, 15, No. 2, 1 (1964).
135. G. L. Roberts, Appl. Spectroscopy, 23, 165 (1969).
136. V. M. Zolotarev, Zhur. Prikl. Spektrosk., 7, 743 (1967).
137. T. S. Hermann and L. J. Leng, J. Appl. Polymer Sci., 12, 2725 (1968).
138. K. Fujimoto and K. Wataya, J. Appl. Polymer Sci., 13, 2513 (1969).
139. T. J. Gedemer, Appl. Spectroscopy, 19, 141 (1965).
140. D. A. Olsen and A. J. Osteraas, J. Polymer Sci., 7, part 1, 1927 (1969).
141. J. S. Mattson, L. Lee, H. B. Mark, and W. J. Weber, J. Colloid Interface Sci., 33, 284 (1970).
142. A. E. Rheineek, R. H. Peterson, and G. M. Sastry, J. Paint Technol., 39, 484 (1967).
143. D. J. Carlsson and D. M. Wiles, Canad. J. Chem., 48, 2397 (1970).
144. "Elektronnye Yavleniya na Poverkhnosti Poluprovodnikov" (Electronic Phenomena on Semiconductor Surfaces), Izd. Naukova Dumka, Kiev, 1968.
145. L. Little, "Infrared Spectra of Adsorbed Molecules" (Translated into Russian), Izd. Mir, Moscow, 1969.
146. N. J. Harrick, Phys. Rev., 125, 1165 (1962).
147. H. Seliger, Phys. Letters, 30A, 278 (1969).
148. G. Chiarotti, G. del Signore, A. Frova, and G. Samoggia, Nuovo Cimento, 26, 403 (1962).
149. W. N. Hansen and A. Prostak, Phys. Rev., 174, 500 (1968).
150. T. G. Rawlins, J. Electrochem. Soc., 111, 810 (1964).
151. K. H. Beckmann, Phys. Verhand, 16, 19 (1965).
152. K. H. Beckmann, Angew. Chem., 80, 213 (1968).
153. K. H. Beckmann, Surface Sci., 5, 187 (1969).
154. L. H. Sharpe, Proc. Chem. Soc., 461 (1961).
155. L. H. Sharpe, Bull. Lab. Record, 40, 62 (1962).
156. L. H. Sharpe, Instrument News, 15, No. 4, 1 (1965).
157. D. N. Shchepkin and A. L. Belozerov, Proceedings of the Symposium on the Application of Spectroscopy to Chemical Production Control, Dzerzhinsk, 1967, p. 8.
158. G. E. Becker and G. W. Gobell, J. Chem. Phys., 38, 2942 (1963).
159. M. J. Prager, Amer. Ind. Hyg. Assoc. J., 27, 272 (1967).
160. M. J. Prager and C. N. La Rosa, Appl. Spectrosc., 22, 449 (1968).
161. P. Peyser and R. R. Stromberg, J. Phys. Chem., 71, 2066 (1967).
162. J. S. Mattson and H. B. Mark, J. Colloid Interface Sci., 31, 131 (1969).
163. J. S. Mattson, H. B. Mark, and W. J. Weber, Analyt. Chem., 41, 355 (1969).
164. J. S. Mattson, H. B. Mark, M. D. Malbin, W. J. Weber, and J. C. Critenden, J. Colloid Interface Sci., 31, 116 (1969).
165. W. N. Hansen, "Modern Aspects of Reflectance Spectroscopy", N. Y., 1968, p. 182.
166. W. N. Hansen, T. Kuwana, and R. A. Osteryong, Analyt. Chem., 38, 1810 (1966).
167. W. N. Hansen, R. A. Osteryong, and T. Kuwana, J. Amer. Chem. Soc., 88, 1062 (1966).
168. T. Kuwana and J. W. Strojek, Discuss. Faraday Soc., No. 45, 134 (1968).
169. N. Winograd and T. Kuwana, J. Electroanalyt. Chem., 23, 333 (1969).
170. A. Prostak, H. B. Mark, and W. N. Hansen, J. Phys. Chem., 72, 2576 (1968).
171. V. S. Srinivasan and T. Kuwana, J. Phys. Chem., 72, 1144 (1968).
172. A. S. Prastak, Diss. Abs., B30, 2115 (1969).
173. B. S. Pons, J. S. Mattson, L. O. Winstrom, and H. B. Mark, Analyt. Chem., 39, 685 (1967).
174. H. B. Mark and B. S. Pons, Analyt. Chem., 38, 119 (1966).
175. D. R. Talant and D. H. Evans, Abstract of Papers 157th National Meeting American Chemical Society, Minneapolis, April, 1969.
176. K. H. Beckmann, Ber. Bunsengesellschaft phys. Chem., 70, 842 (1966).
177. A. H. Reed and E. Jeager, Electrochim. Acta, 15, 1345 (1970).
178. L. May, "Progress in Infrared Spectroscopy", v. 2, N. Y., 1964, p. 213.
179. F. S. Parker, see Ref. 16, p. 75.
180. E. Fahr and W. Rohlfing, Z. analyt. Chem., 243, 43 (1968).
181. H. Furedi and A. G. Walton, Appl. Spectrosc., 22, 23 (1968).
182. B. Sherman, Appl. Spectrosc., 18, 7 (1964).
183. T. S. Hermann, Analyt. Biochem., 12, 406 (1965).
184. F. S. Parker and R. Ans, Analyt. Biochem., 18, 414 (1967).

185. P. A. Wilks, "Modern Aspects of Reflectance Spectroscopy", N. Y., 1968, p. 192.
186. R. H. Hannah and J. L. Dwyer, Analyt. Chem., 36, 2341 (1964).
187. R. D. Jonson, Analyt. Chem., 38, 160 (1966).
188. R. Baier and W. A. Zisman, Macromolecules, 3, 462 (1970).
189. R. Baier and W. A. Zisman, Macromolecules, 3, 70 (1970).
190. F. S. Parker and R. Ans, Appl. Spectroscopy, 20, 384 (1966).
191. E. L. Saier, Appl. Spectroscopy, 22, 445 (1968).
192. T. S. Hermann and S. R. Harvey, Abstract of Papers 157th National Meeting American Chemical Society, Minneapolis, 1969.
193. T. S. Hermann, Appl. Spectroscopy, 19, 10 (1965).
194. D. Johnson and P. Reinhart, see Ref. 7, p. 105.
195. B. Peutrell and J. S. Wragg, Analyst, 95, 225 (1970).
196. P. A. Wilks, "Gas Chromatography and Infrared Spectroscopy", American Laboratory, March 1969.
197. S. Tanaka, T. Matsui, and F. Yogyu, Japan Analyst, 18, 1125 (1969).
198. J. Marton and H. E. Sprarks, Tappi, 50, 363 (1967).
199. "Internal Reflection Spectroscopy at Work", No. 2, Wilks Scientific Corp.
200. J. P. Deley, R. G. Gigi, and A. J. Liotti, Tappi, 46, 188a (1963).
201. G. Jayme and E. M. Rohmann, Papier, 20, 1 (1966),
202. G. Jayme and G. Traser, Papier, 23, 694 (1969).
203. G. Jayme and E. M. Rohmann, Papier, 19, 497 (1965).
204. O. Schwab, Papier, 19, 115 (1965).
205. B. H. Baxter and N. A. Puttman, Nature, 207, 288 (1965).
206. A. C. Gilby, J. Cassels, and P. A. Wilks, Appl. Spectroscopy, 24, 539 (1970).
207. R. N. O'Brain and K. Hartman, Pulp Paper Mag. Canada, 70, No. 8, 67 (1969).
208. E. R. McCall, S. H. Miles, and R. T. O'Connor, Amer. Dyestuffs Rep., 55, 40 (1966).
209. T. Hirschfeld, Appl. Spectroscopy, 21, 335 (1967).
210. E. Loeser and M. Schutz, Melliand Textilber, 46, 1412 (1966).
211. J. W. Cassel, Appl. Spectroscopy, 22, 477 (1968).
212. D. A. Pettit and A. R. Carter, J. Soc. Leather Trades Chem., 48, 476 (1964).
213. G. Brown and C. A. Murray, Plastics Technol., 11, No. 9, 45 (1965).
214. S. E. Polchlopek, W. J. Menosky, and L. G. Dalli, "Modern Aspects of Reflectance Spectroscopy", N. Y., 1968, p. 242.
215. R. L. Harris and G. R. Svoboda, Analyt. Chem., 34, 1655 (1962).
216. D. Rogers and Z. Tot, see Ref. 7, p. 131.
217. N. A. Puttnam, S. Lee, and B. H. Baxter, J. Soc. Cosmetic Chemists, 16, 607 (1965).
218. N. A. Puttnam, B. H. Baxter, S. Lee, and P. L. Stott, J. Soc. Cosmetic Chemists, 17, 9 (1966).
219. N. A. Puttnam, Proc. Analyt. Chem., 2, 158 (1965).
220. R. Chrysler, see Ref. 7, p. 202.
221. L. Bartz and G. Rule, see Ref. 7, p. 225.
222. L. Hirscher, see Ref. 7, p. 7.
223. A. M. Bartz, Analyt. Instrumentation, No. 4, New York, 1967, p. 113.
224. K. G. Karr-Brion and J. A. Godsden, J. Sci. Instr., 2 (ser. 2), 155 (1969).
225. V. M. Zolotarev, N. B. Belyavskaya, and Ya. S. Bobovich, Optika i Spektrosk., 28, 195 (1970).
226. J. S. Mattson, H. B. Mark, R. L. Kolpack, and C. E. Schutt, Analyt. Chem., 42, 234 (1970).
227. F. M. Nooman and B. Linski, Atoms. Environ, 4, 125 (1970).
228. N. J. Harrick, "Internal Reflection Spectroscopy" (Translated into Russian), Izd. Mir, Moscow, 1970.
229. D. Kunath and A. Reklat, Z. Chem., 11, 361 (1971).
230. S. Tanaka, Chem. Ind. (Japan), 21, 928 (1970).
231. N. J. Harrick and A. I. Carlsson, Appl. Optics, 10, 19 (1971).
232. Appl. Spectroscopy, 25, 142 (1971).
233. V. M. Zolotarev, Yu. D. Pushkin, and I. V. Peisakhson, Pribory i Tekh. Eksper., No. 5, 176 (1970).
234. S. L. Grigorovich, V. I. Lygin, and V. A. Fedorova, Kolloid. Zhur., 33, 345 (1971).
235. T. S. Hermann, Appl. Spectroscopy, 23, 473 (1969).
236. T. S. Hermann, Rev. Sci. Instr., 40, 1062 (1969).
237. W. L. Truett, XIII Colloquium Spectroscopicum Internationale, Ottawa, London, 1968, p. 358.
238. N. J. Harrick, Analyt. Chem., 43, 1533 (1971).
239. B. A. Mikhailov and V. M. Zolotarev, Proceedings of the Seventeenth All-Union Congress on Spectroscopy, Minsk, 5 — 9 July 1971, p. 124.
240. V. M. Zolotarev, N. P. Spasskova, L. V. Levsneskaya, G. N. Guseva, and M. S. Vilesova, Zhur. Prikl. Spektrosk., 15, 481 (1971).
241. V. M. Zolotarev and A. F. Perveev, see Ref. 239, p. 101.
242. J. S. Mattson, H. B. Mark, and W. J. Weber, Developments in Appl. Spectr., v. 8, N. Y. — London, 1970, p. 91.
243. G. L. Haller and R. W. Rice, J. Phys. Chem., 74, 4386 (1970).
244. J. P. Devlin, G. Pollard, and R. Frech, J. Chem. Phys., 53, 4147 (1970).
245. M. H. Brooker, J. Chem. Phys., 53, 4100 (1970).
246. M. H. Brooker and J. B. Bates, J. Chem. Phys., 54, 4788 (1971).
247. K. Sato, F. Kurosawa, N. Yamaguchi, and O. Kammori, Kagyo Kagaku Zasshi, 71, 208 (1968).
248. D. Shlits, Ienskoe Obozrenie, 16, 30 (1971).
249. D. Carlsson, T. Supruchuk, and D. M. Wiles, Canad. Textile J., 87, No. 11, 73 (1970).
250. A. Pande, Lab. Practice, 18, 287 (1969).
251. J. M. Wilson, I. Ben-Gera, and A. Bamer, J. Food Sci., 36, 162 (1971).
252. J. S. Mattson, H. B. Mark, and W. J. Weber, Eighth National Meeting of the Society of Applied Spectroscopy, Anaheim, California, 6 — 11 October 1969; Appl. Spectroscopy, 23, 646 (1969).
253. G. F. Trott and E. E. Woodside, J. Colloid Interface Sci., 36, 40 (1971).
254. M. Yamao, S. Nukui, H. Kitazawa, and S. Tanaka, Kogyo Kagaku Zasshi, 74, 2193 (1971).
255. N. P. Spasskova, L. V. Lesnev, G. N. Guseva, L. G. Israilev, M. V. Zolotarev, and M. V. Vilesova, see Ref. 239, p. 22.
256. N. Winograd and T. Kuwana, Abstract of Papers, 158th National Meeting, American Chemical Society, New York, 7 — 12 September 1969.
257. N. Winograd and T. Kuwana, Analyt. Chem., 42, 252 (1971).
258. H. N. Blount, N. Winograd, and T. Kuwana, J. Phys. Chem., 74, 3231 (1970).
259. N. Winograd and T. Kuwana, J. Amer. Chem. Soc., 92, 224 (1970).
260. N. Winograd and T. Kuwana, J. Amer. Chem. Soc., 93, 4343 (1971).

261. E. L. Saier, H. F. Acevedo, and B. M. Dick, Analyt. Biochem., 37, 345 (1970).
262. S. C. Mutha, J. Pharm. Sci., 60, 1264 (1971).
263. J. E. Atkinson, J. Pharm. Pharmacol., 23, 781 (1971).
264. D. Edwards, J. Pharm. Pharmacol., 23, 957 (1971).
265. D. J. Carlsson and D. M. Wiles, Macromolecules, 4, 179 (1971).
266. D. J. Carlsson and D. M. Wiles, Macromolecules, 4, 174 (1971).
267. D. J. Carlsson and D. M. Wiles, Abstracts of Papers, 160th National Meeting, American Chemical Society, Chicago, 14 — 18 September 1970 (Division of Polymer Chemistry, No. 71).
268. D. J. Carlsson and D. M. Wiles, Abstracts of Papers, 160th National Meeting, American Chemical Society, Chicago, 14 — 18 September 1970 (Division of Polymer Chemistry, No. 10).
269. Yu. A. Pentin, B. N. Tarasevich, and B. S. El'tsefon, Proceedings of the All-Union Conference on Physical Methods of Studying the Structure of Organic Compounds, Kazan', 1971, p. 396.
270. Yu. A. Pentin, B. N. Tarasevich, and B. S. El'tsefon, see Ref. 239, p. 192.
271. J. P. Luongo, and R. Salovey, J. Polymer Sci., Part 2, 4, 997 (1966).
272. J. P. Luongo and H. Schonhorn, J. Polymer Sci., Part 2, 6, 1649 (1968).
273. S. Tanaka and T. Matsui, Bunsek Kagaku, 20, 1128 (1971).
274. D. Kunath, A. Reklat, and H. Jost, Plaste Kaut., 17, 899 (1970).
275. N. J. Harrick, Surface Sci., 13, 134 (1969).
276. T. I. Kovalevskii, S. N. Nesterova, A. V. Rzhanov, and K. K. Svitashev, FTP, 5, 1720 (1971).
277. A. V. Rzhanov and M. P. Sinyukov, FTP, 2, 504 (1968).
278. A. V. Rzhanov and M. P. Sinyukov, FTP, 2, 514 (1968).
279. A. V. Rzhanov and M. P. Sinyukov, FTP, 3, 52 (1969).
280. S. Thibaut and J. Talbot, Compt. rend., Ser. C, 272, 805 (1971).
281. K. V. Nel'son and N. V. Ionina, see Ref. 239, p. 183.
282. D. S. Bulatov, Biofizika, 16, 977 (1971).
283. G. J. Loeb, J. Colloid Interface Sci., 27, 38 (1968).
284. H. Müller and S. Friberg, Acta Chem. Scand., 23, 515 (1969).
285. D. F. Burow and J. J. Lagowski, J. Phys. Chem., 72, 169 (1968).
286. R. N. O'Brien and K. J. Hartmann, J. Polymer Sci., Part C, Polymer Symposium 1971, No. 34, p. 293.
287. R. N. O'Brien and K. J. Hartmann, Abstracts of Papers, 160th National Meeting of the American Chemical Society, Chicago, 14 — 18 September 1970 (Division of Colloid and Surface Science, No. 13).
288. V. A. Bershtein, Yu. D. Varfolomeev, and V. V. Nikitin, Fiz. Tverdogo Tela, 13, 693 (1971).
289. V. M. Zolotarev, V. A. Veremei, and T. A. Gorbunova, Optika i Spektrosk., 31, 77 (1971).
290. R. J. McGowak, Analyt. Chem., 41, 2074 (1969).
291. "Infrared Spectroscopy, Its Use in the Coating Industry", Philadelphia, 1969.
292. T. Fujiyama and B. Crawford, J. Phys. Chem., 72, 2174 (1968).
293. C. E. Pavelukes, A. A. Clifford, and B. Crawford, J. Phys. Chem., 72, 962 (1968).
294. V. M. Zolotarev, Optika i Spektrosk., 29, 66 (1970).
295. K. Tsuji and H. Yamada, Bull. Chem. Soc. Japan, 41, 1975 (1968).
296. R. P. Young and R. N. Jones, Chem. Rev., 71, 219 (1971).
297. J. Chamberlain, Phys. Bull., 22, 333 (1971).