DETERMINATION OF THE IR REFRACTIVE INDEX AND ABSORPTION COEFFICIENT OF SOLID FUELS

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Measured optical constants are presented for anthracite over the infrared range from 0.8 to 5.5 μm. The spectral absorption and scattering coefficients have been calculated by computer.

The emission from a flame formed by combustion of coal dust is determined by two basic emitters, the triatomic molecules H_2O and CO_2, together with the suspended solid particles of fuel, ash, and partly burned material.

To calculate the radiation energy transport in such a system, one needs to know first of all the radiation properties of the particles, together with the absorption coefficient $k_{\lambda,\ \mathrm{abs}}$ and the scattering coefficient $k_{\lambda,\ \mathrm{scat}}$, together with the scattering indicatrix $\gamma_\lambda(\beta)$.

Available solutions [1-3] show that $\gamma_\lambda(\beta)$, $k_{\lambda,\ \mathrm{abs}}$ and $k_{\lambda,\ \mathrm{scat}}$ are functions of two basic dimensionless parameters: the complex refractive index m and the relative particle size $\rho = \pi x/\lambda$; the first $m = n - i\varkappa$ relates the electro-magnetic and optical properties of the particles; this m is itself dependent on the wavelength.

To calculate the emission from a coal-dust flame, one needs to determine n and $\varkappa$ for the solid particles of fuel, ash, and coke, together with the dispersion in the infrared region. Unfortunately, no such data have yet been published, and for this reason it has not been possible to produce a physically sound method of calculating the emission of such flames. An important step in solving this problem is to examine the optical constants of the condensed solid phase in the flame.

There is no great difficulty in determining n and $\varkappa$ for the absorbing materials; there are various methods, such as prisms, critical angle, interference, and immersion that enable one to determine the refractive index n [4]. In the case of strongly absorbing materials, such as particles of coal and coke, the methods of [4] are unsuitable, because the light interacts with material in very thin layers. One has to use thicknesses comparable with the wavelength of the incident radiation, and the physical properties of such films are very much dependent on methods of preparation, the material of the substrate, and other factors.

Also, n and $\varkappa$ for strongly absorbing materials are very difficult to measure; while n for a transparent or weakly absorbing medium can be measured to 0.1%, one has to accept errors of several per cent for strongly absorbing conditions. Under these conditions, the sole radiation characteristic accessible to measurement [5] is the reflection spectrum. In turn, reflection methods for measuring optical constants of absorbing materials are very varied and a detailed survey has been made in [5].

All solid fuels are strongly absorbing substances, so n and $\varkappa$ are determined by reflection. One measures the reflection at the boundary with an external medium with two different refractive indices n_1 and n_2 for that medium. As one of the media one uses air, while as the other one uses CCl_4. The measurements are made at nearly normal incidence.

In that case, the reflection coefficients R_1 and R_2 may be put in the form

$$R_1 = \frac{(n-n_1)^2+\varkappa^2}{(n+n_1)^2+\varkappa^2}, \tag{1}$$

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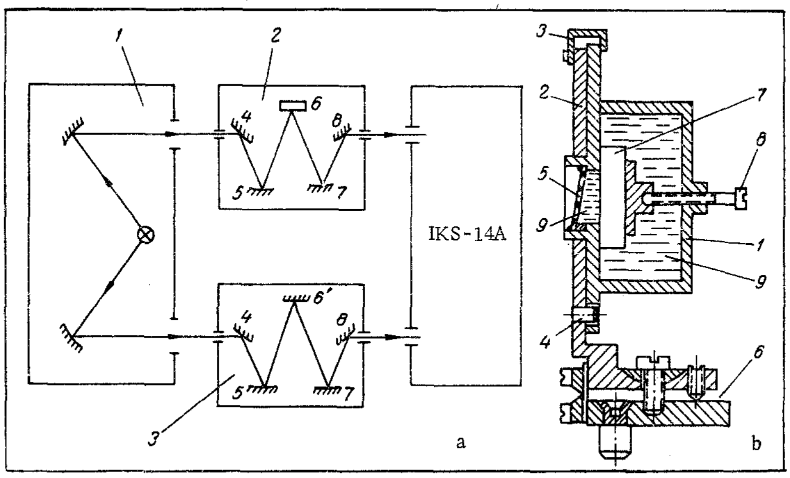

Fig. 1. a) Optical system; b) liquid cell for specimen and standard.

$$R_2 = \frac{(n - n_2)^2 + \varkappa^2}{(n + n_2)^2 + \varkappa^2}. \tag{2}$$

From (1) and (2) we determine the refractive index as

$$n = \frac{1}{2} \cdot \frac{(1 - R_1)(1 - R_2)(1 - n_2)(1 + n_2)}{(1 - n_2)(1 - R_1 R_2) - (1 + n_2)(R_2 - R_1)} \tag{3}$$

and the absorption parameter as

$$\varkappa = \sqrt{\frac{R_1 (n + 1)^2 - (n - 1)^2}{1 - R_1}}. \tag{4}$$

This method was first used by Orsel [6]; Kravets [7] used it to determine the optical constants of some absorbing materials by depositing them as films on various types of glass. Further improvements in the method have also been reported [8-11]. The optical constants of germanium have been published [11]. The measurements were made by immersing the specimens in a liquid with a known refractive index. The same method has been used [12, 13] for the optical constants of Co, Ni, Cu, Ag, and Al together with certain ore minerals. In all these studies, the values of n and $\varkappa$ were obtained only for the range from 0.3 to 0.8 μm.

In the present study, the above method was applied to determine the optical constants of coals in the infrared region. The reflection spectra were measured with an LOMO attachment to an IKS-14A spectrophotometer. Figure 1a shows the equipment used, which consisted of the illuminator 1, the IKS-14A infrared spectrometer, and the two attachments 2 and 3, which were placed respectively in the working channel and in the reference channel. The light source was imaged by the plane and spherical mirrors 4 and 5 near the specimen 6 and standard 6' with a magnification of 0.5. Further, the image was transferred to the plane of the IKS-14A photometric wedge by means of mirrors 7 and 8.

Figure 1b shows the liquid cell for holding the specimen and standard; the body 1 is attached to the holder 2 by means of the flat spring 3 and the screws 4. The fluorite window 5 is set at 20° to the axis of the cell. This setting for the window enables one to eliminate reflections from the fluorite—air and fluorite—liquid boundaries. Device 6 is used to adjust the cell. Specimen 7 is pressed by screw 8 on to the carefully polished surface of the cell body. The cavity in the cell is filled with the immersion liquid 9.

In measuring the reflection coefficient at the boundary between the material and the liquid, particular attention was given to obtaining good optical contact between the liquid and the surfaces.

As the standard we used a polished germanium crystal, whose reflection coefficient was fairly close to that of the polished coal surface. One therefore obtains roughly equal energy fluxes in the two channels, which somewhat improve the error of measurement, especially since the optical constants of germanium are known accurately.

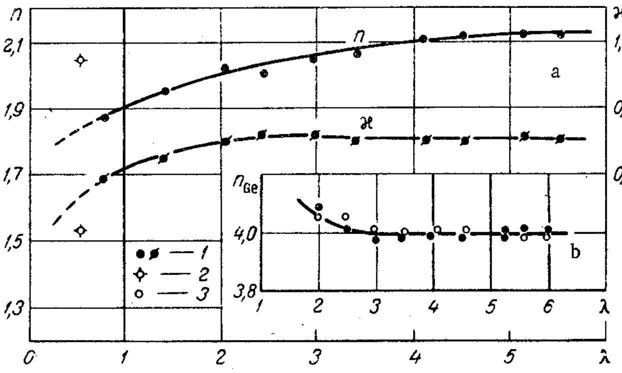

Fig. 2. Dispersion of the optical constants n and ϰ for: a) anthracite; b) germanium: 1) our results; 2) from [21]; 3) from [20]. λ in μm.

The reflectivity of any substance is dependent on the strength of the surface; to determine optical constants by specular reflection one has to eliminate such surface effect. For this purpose, the coal specimens were cut by a diamond saw into plane-parallel plates and were carefully ground and polished. In the treatment, we used the technology used for making plates of silicon and germanium with little surface damage [14-16]. The grinding of the surface and the production of a given plate thickness were provided by abrasive powders grades M10 and M7 using a glass grinding system. The subsequent optical polishing with chromium oxide was done with a silk polishing head to eliminate the traces of the grinding. The polishing was performed with coarse chromium oxide of grain size 0.6-0.8 μm and was completed with fine chromium oxide, which gave a specularly reflecting surface. The quality of the polishing was checked against a test glass.

To determine the complex refractive index of coal, one has to measure the reflection from the surface twice: once in air and a second time in an immersion liquid. In the infrared region (1-6 μm), there are very few liquids that pass more than 25% of the incident radiation, and even fewer liquids have been examined from the viewpoint of the refractive index n in this wavelength range. The available published data [17, 18] led us to use CCl_4 as the immersion liquid. These measurements gave n and ϰ from some grades of coal from the USSR; Fig. 2a gives values of n and ϰ for anthracite from the Donets coal basin. It is clear that n and ϰ increase with the wavelength λ; n is more sensitive to λ than is ϰ. The λ dependence of these quantities becomes less as λ increases, and at $\lambda \geq 3$ μm, ϰ is no longer dependent on λ and may be taken as constant at 0.8; It seems likely that constant n is attained for $\lambda > 5$ μm.

The results of Fig. 2a are described satisfactorily by the following formulas:

$$n = 1.72 + 0.19\sqrt{\lambda}, \quad (5)$$

$$\varkappa = 0.59 + 0.13\sqrt{\lambda}. \quad (6)$$

Formula (5) applies for the range of λ from 0.8 to 5 μm, while (6) applies from 0.8 to 3 μm.

Formulas (5) and (6) thus describe the dispersion of the optical constants for anthracite in the infrared spectrum region characteristic of industrial flames.

Figure 2a gives n and ϰ as found in [21] for λ = 0.546 μm; the values differ appreciably from ours for λ = 0.8 μm, but one should bear in mind that our results apply to anthracite containing 93.5% carbon, 1.49% hydrogen, and 2.27% sulfur, where the results of [21] relate to material with C = 94.1%, H = 2.6%, and S = 0.7%.

The error in determining the optical constants is governed in the main by the surface finish (the approach to an optically smooth surface) and also by the perfection in the reference standard.

From (3) and (4) we may write

$$\Delta n = \pm\left\{\left|\frac{\partial n}{\partial R_1}\Delta R_1\right| + \left|\frac{\partial n}{\partial R_2}\Delta R_2\right| + \left|\frac{\partial n}{\partial n_2}\Delta n_2\right|\right\}, \quad (7)$$

$$\Delta\varkappa = \pm\left\{\left|\frac{\partial\varkappa}{\partial R_1}\Delta R_1\right| + \left|\frac{\partial\varkappa}{\partial R_2}\Delta R_2\right| + \left|\frac{\partial\varkappa}{\partial n_2}\Delta n_2\right|\right\}. \quad (8)$$

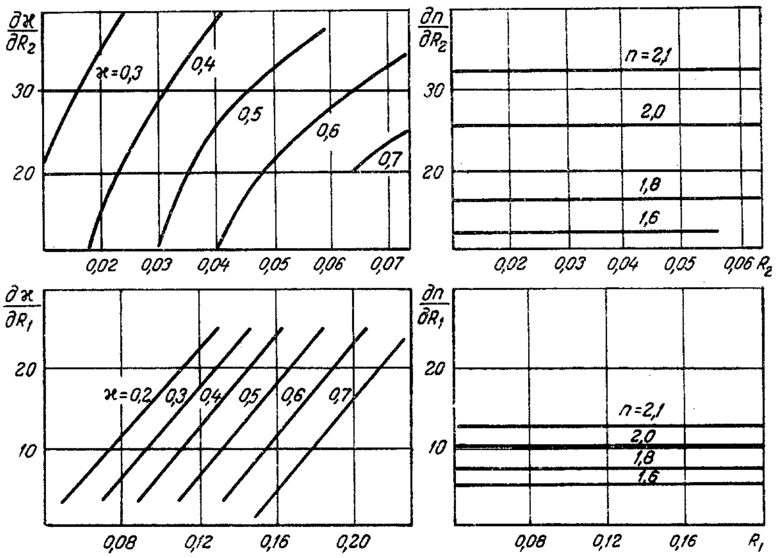

Fig. 3. Determination of the errors of measurement for n and $\varkappa$.

The relative error in measuring R_1 and R_2 is limited by the accuracy of the IKS-14A and is about ± 3%. The value of Δn_2 is close to 0.0005, and its effect can be neglected to a first approximation. Then

$$\Delta n = \pm \left\{ \left| \frac{\partial n}{\partial R_1} \Delta R_1 \right| + \left| \frac{\partial n}{\partial R_2} \Delta R_2 \right| \right\}, \tag{9}$$

$$\Delta \varkappa = \pm \left\{ \left| \frac{\partial \varkappa}{\partial R_1} \Delta R_1 \right| + \left| \frac{\partial \varkappa}{\partial R_2} \Delta R_2 \right| \right\}. \tag{10}$$

Figure 3 shows curves used in determining the error of measurement for n and $\varkappa$; to find $\partial n/\partial R_1$, $\partial n/\partial R_2$, $\partial \varkappa/\partial R_1$, $\partial \varkappa/\partial R_2$ we use the graphical method of [19].

The coefficient of variation for the refractive index on average was 6%, as against 15% for the absorption parameter; note that Δn and $\Delta \varkappa$ are dependent not only on the condition of experiment but also on the absolute values of the quantities.

To check the method we performed measurements on a standard germanium specimen; the results for R and n were compared with published values [20]. Table 1 gives the spectral reflection coefficients for germanium in contact with air R_1 and carbon tetrachloride R_2. Our results agree well with published values. The maximum value for the coefficient of variation in the reflection coefficient is 2.5% for germanium.

Figure 2b gives the dispersion of n for germanium; it is clear that our values for n agree well with the published values of [20] over the entire relevant wavelength range. The maximum coefficient of variation in determining n was 2.5%.

These results for n and $\varkappa$ were used to determine the spectral coefficient for absorption $k_{\lambda,\mathrm{abs}}$ and scattering $k_{\lambda,\mathrm{scat}}$ for anthracite particles [1-3]. We found that these two coefficients were dependent on the wavelength and on the particle size x.

In examining the effect of wavelength on these parameters, we first have to establish the effects arising from the dispersion $n(\lambda)$ and $\varkappa(\lambda)$; for this purpose, Figs. 4a and b give our results for the absorption and scattering parameters as functions of wavelength for various constant numerical values for the relative particle size ρ; the ρ used in the analysis cover fairly well the characteristic range used in boilers for fuel particle size x and radiation wavelength λ.

It is clear that the dispersion of the optical constants of anthracite has a certain effect on the scattering and absorption parameters of the particles, especially for λ small; here the variation in the spectral absorption coefficient is due in the main to dispersion in the absorption parameters, as is most clearly seen in the range $0.8 \le \lambda \le 3\,\mu$m, in which there is appreciable dispersion in $\varkappa$. In this range, with $1 \ge \rho \ge 0.5$, the variation as a function of ρ and λ is described satisfactorily by

TABLE 1. Reflectivity of Ge

λ, μm	Interface with air		Interface with CCl_4	
	R_1, %		R_2, %	
	our results	[21]	our results	[21]
2,07	37,2	37,1	23,2	23,0
2,42	36,4	36,8	23,0	22,8
2,98	35,8	36,5	23,0	22,5
3,41	36,0	36,4	22,8	22,4
4,12	36,0	36,2	22,3	22,3
4,51	35,4	36,2	22,3	22,3
5,14	35,8	36,2	22,3	22,3
5,53	36,0	36,2	22,3	22,3
5,97	36,4	36,2	22,3	22,4

$$k_{\lambda,\mathrm{abs}} = (1.68\,\rho - 0.24)\,\lambda^{0.06}. \tag{11}$$

The variation in the spectral scattering coefficient is due in the main to dispersion in n, and makes itself felt over the wider wavelength range ($0.8 \le \lambda \le 5\,\mu m$), i.e., where there is appreciable dispersion in n. For this range in λ and for $1 \ge \rho \ge 0.5$, the variation as a function of ρ and λ is described satisfactorily by

$$k_{\lambda,\mathrm{scat}} = 0.7\,\rho^3\lambda^{0.2}. \tag{12}$$

The difference in the dispersions of n and ϰ has different effects on the two parameters as functions of λ; if ρ is greater than 1, the effects of the dispersion in the optical constants is less, and above $\lambda = 3\,\mu m$, the spectral coefficients for each ρ are practically independent of λ.

There is a turning-point relationship to particle size for the scattering and absorption parameters; the maximum value for the absorption coefficient occurs in the range $1 \le \rho \le 2$, while the maximum scattering coefficient occurs for $\rho \approx 2$. Here a variation in wavelength from 1 to 5.5 μm has practically no effect on the scattering peak position, but it does appreciably affect the position of the absorption peak. While for $\lambda = 1\,\mu m$ we get the maximum value of the absorption coefficient at $\rho = 1.1$, for $\lambda = 5.5\,\mu m$ we get the same for $\rho = 1.9$. This change in the position of the absorption in relation to λ is entirely due to the dispersion in the optical constant.

In (11) and (12), the effects of the dispersion in the optical constants take into account the dependence of the two constants on λ; The resulting λ dependence of the constants is due to the dispersion in the optical constants to the relative particle size.

Fig. 4c shows how the spectral attenuation coefficient $k_\lambda = k_{\lambda,\ \mathrm{abs}} + k_{\lambda,\ \mathrm{scat}}$ varies directly with the particle size x and wavelength λ; the hatched circles show the results for k_λ as calculated from our measured optical constants. The open circles represent the k_λ calculated for $\lambda = 0.546\,\mu m$ [21].

It is clear that there is a turning-point relationship of k_λ to x; the position of the peak in k_λ is dependent on the wavelength, the peak shifting towards larger particles sizes as λ increases.

The effects of wavelength of k_λ are in turn dependent on x; in the relevant range of λ, increase in wavelength results in reduction in k_λ for $x < 0.5\,\mu m$; conversely, for $x > 3\,\mu m$ we find that k_λ is an increasing function of wavelength. There is a more complex variation of k_λ as a function of λ in the range $0.5 < x < 3$ μm, in which one usually finds the maximum attenuation.

As x increases, the effect of wavelengths of k_λ become appreciably less, as do those of x itself. However, a difference from other fuels is that the emission of anthracite is selected even for quite large particle sizes. Figure 4c shows that k_λ is still dependent on λ even for particles of size 200-300 μm. In the limit $x \to \infty$, the asymptotic value of k_λ is found to be 2, as will be expected, and the particles can be considered as gray radiation sources.

In the range of thermal radiation wavelengths of interest, only particles with $x > 500\,\mu m$ act as gray in the case of anthracite; under practical firing conditions with powdered fuel, such particles are absent from the flames, and the limiting value for particle size for anthracite is about 300 μm. Then the anthracite particles in a powder flame cannot be considered as gray emitters, and one has to use the emissivity as a function of wavelength in calculations.

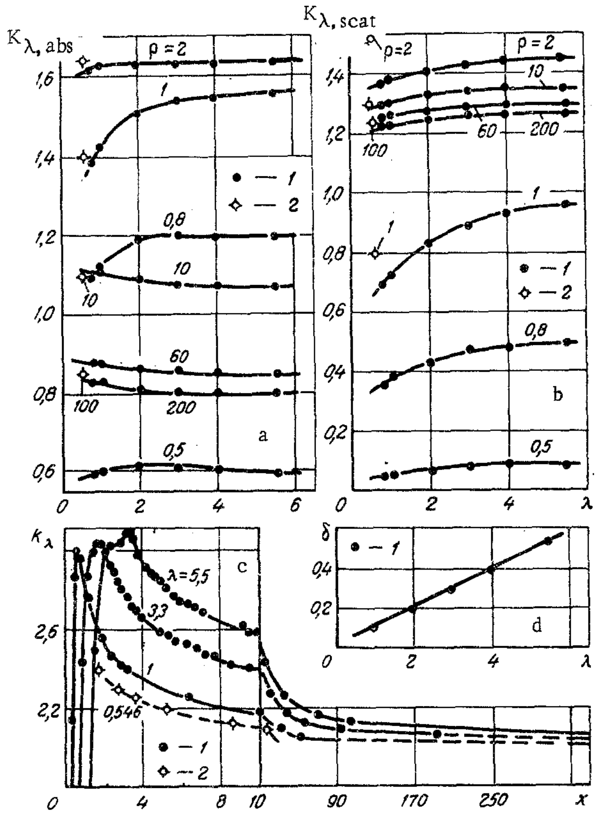

Fig. 4. Radiation behavior of anthracite particles: a-c) spectral coefficients for absorption, scattering, and attenuation respectively; d) radiation penetration depth: 1) our results; 2) from [21]; $\varkappa$, λ, and δ in μm.

In examining the interaction of radiation with matter, it is often necessary to know the penetration depth of the radiation as a function of λ. Fig. 4d shows how the penetration depth $\delta = (1/4\pi\varkappa)\lambda$ varies with λ for anthracite having the above dispersion in $\varkappa$. As regards this depth, anthracite falls between an insulator and a metal.

NOTATION

$k_{\lambda,\ abs}$, $k_{\lambda,\ scatt}$, k_λ	are the spectral coefficients for absorption;
$\gamma_\lambda(\beta)$	is the scattering indicatrix;
ρ	is the relative particle size;
x	is the particle size, μm;
λ	is the wavelength, μm;
n	is the refractive index;
$\varkappa$	is the absorption index;
R_1	is the reflectivity in air;
R_2	is the reflectivity in CCl_4;
n_2	is the refractive index of CCl_4.

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