Use of Mie theory to analyze experimental data to identify infrared properties of fused quartz containing bubbles

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An improved method used to determine the absorption and scattering characteristics of a weakly absorbing substance containing bubbles is suggested. The identification procedure is based on a combination of directional-hemispherical measurements and predictions of Mie-scattering theory including approximate relations for a medium with polydisperse bubbles. A modified two-flux approximation is suggested for the calculation of directional-hemispherical transmittance and reflectance of a refracting and scattering medium. The complete identification procedure gives not only the spectral radiative properties but also the volume fraction of bubbles and the characteristics of possible impurity of the medium. This procedure is used to obtain new data on near-infrared properties of fused-quartz samples containing bubbles. © 2005 Optical Society of America

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1. Introduction

In many natural phenomena, materials processing, and manufacturing situations, the presence of bubbles affects the thermophysical and radiative properties of the two-phase system and hence the transport phenomena. It is well known that radiation scattering by bubbles in the visible and infrared spectral ranges affects the optical properties of semitransparent substances. One can remember the influence of bubbles on scattering of light in the ocean,[1] the role of vapor bubbles in high-temperature radiative heating of boiling water,[2] and the glass melting process in industrial furnaces where bubbles are generated by chemical reactions.[3] Similar structures with numerous bubbles or hollow microspheres in a semitransparent host medium are considered as advanced thermal insulation materials[4,5]; many aerated foods containing gas bubbles represent the height of culi-

nary art.[6] Following the recent works by Pilon and Viskanta[7] and Baillis *et al.*,[8] the present paper focuses mainly on glass industry applications. At the same time, some methodological and physical results may be interesting in the other previously mentioned fields.

During the past decade, absorption and scattering of infrared radiation in semitransparent disperse media have been intensively studied because of the importance of thermal radiation in many engineering applications. The most popular way to experimentally determine the radiative properties of such media is a formal identification procedure consisting of solving an inverse problem.[9] This technique is based usually on the radiation transfer theory. The coefficients of the radiation transfer equation (RTE)[10] are determined from the measurements of directional-hemispherical and/or bidirectional transmittance and reflectance of semitransparent samples.

Theoretical predictions of the radiative properties of materials containing numerous separate particles or fibers are usually based on Mie theory or similar solutions for particles of different shape and structure.[11] In some cases, solving the inverse problem for the RTE is inappropriate because the radiation transfer theory is not valid such as for relatively dense disperse systems. At the same time, one can use the radiation diffusion approximation, which is treated not as a simplification of the RTE but as a phenomenological approach.[12,13] Similar methods (Kubelka–Munk theory and its modifications,

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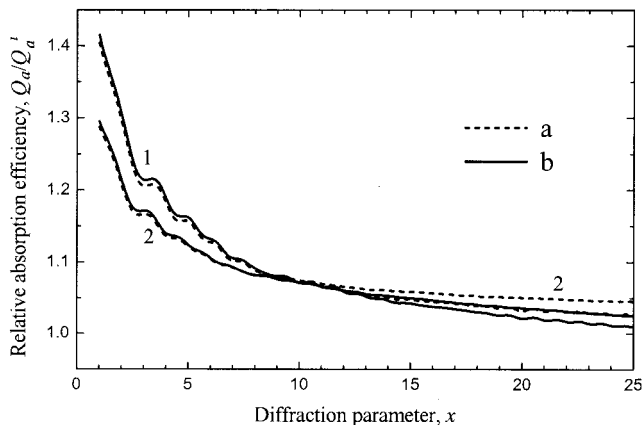
Fig. 1. Effect of the absorbing and refracting medium inside a bubble on its efficiency factor of absorption for $n_0 = 1.4$: a, $\kappa_i = 10^{-4}$; b, $\kappa_i = 10^{-3}$; 1, $n_i = 1.1$; 2, $n_i = 1.2$.
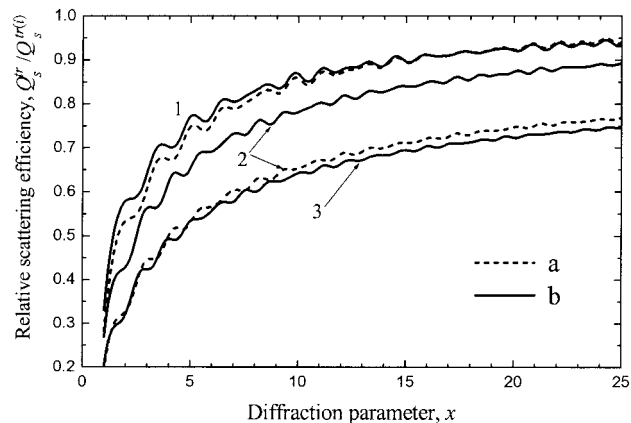

Fig. 2. Effect of refracting medium inside a bubble on its transport efficiency factor of scattering: a, $n_0 = 1.4$; b, $n_0 = 1.5$; 1, $n_i = 1$; 2, $n_i = 1.2$; 3, $n_i = 1.3$.

four-flux model) are employed traditionally to study the optical properties of paints and scattering coatings.[14–17]

It is known that simultaneous identification of several parameters including characteristics of anisotropic scattering by use of an inverse procedure for the RTE may lead to unreliable results due to the insufficient accuracy of the measurements and to the specific nature of the ill-posed inverse problem. To avoid such a problem, one can simplify the radiation transfer model or, if possible, use a procedure combining experimental measurements with theoretical predictions of some radiative properties. Both approaches decrease the number of parameters to be identified, but the latter seems preferable as it gives more detailed information about the medium properties and structure.

Two types of transmittance and reflectance measurement can be used to provide the data for the identification process, namely, directional-hemispherical or directional–directional (bidirectional) measurements.[18] Both measurement methods with normal incidence show advantages and drawbacks. Directional-hemispherical measurements are easily and rapidly acquired, but they enable only the identification of the extinction coefficient and albedo while the scattering (phase) function is assumed to be known. The bidirectional measurements contain much more information but are difficult to use for identification of the scattering function in the case of highly forward-scattering media. Usually, one can find only an additional parameter: the asymmetry factor of scattering.[8]

For the disperse systems considered in the present paper, a combination of a traditional identification procedure and theoretical predictions can be used. Spherical bubbles in a weakly absorbing medium are ideal objects for the application of Mie theory. Recent calculations by Dombrovsky[2] for the most interesting range of parameters showed that scattering properties of polydisperse bubbles do not depend on radiation absorption whereas the absorption is insensitive to the size distribution of bubbles. These results are

used to suggest an improved identification procedure for the directional-hemspherical measurements.

2. Theoretical Description of Radiative Properties of a Weakly Absorbing Medium with Bubbles

The bubbles in an absorbing and refracting medium are not exactly the same objects as those considered in classical Mie theory,[19,20] which deals with homogeneous spherical particles in vacuum. A composite medium with bubbles consists of two different substances: a refracting and absorbing matrix and the gas phase inside the bubbles. We will assume that bubbles are randomly placed and there is no regular structure or bubble clusters. In the case of relatively small bubble concentration, the later assumptions enable one to consider the bubbles as independent scatterers.[9,11]

The spectral absorption coefficient and the transport scattering coefficient of the polydisperse medium of spherical bubbles of radius a with size distribution $F(a)$ can be calculated as follows[2,11]:
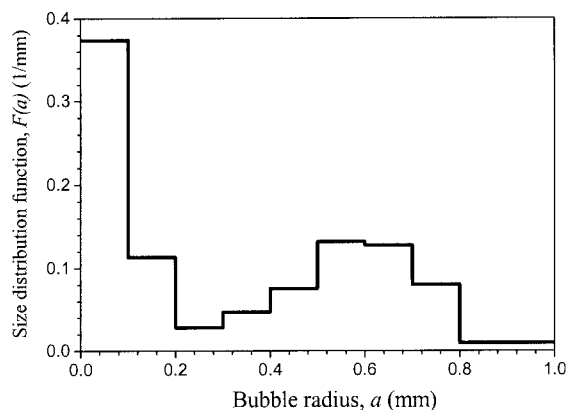

Fig. 3. Normalized size distribution of bubbles in the fused-quartz sample.
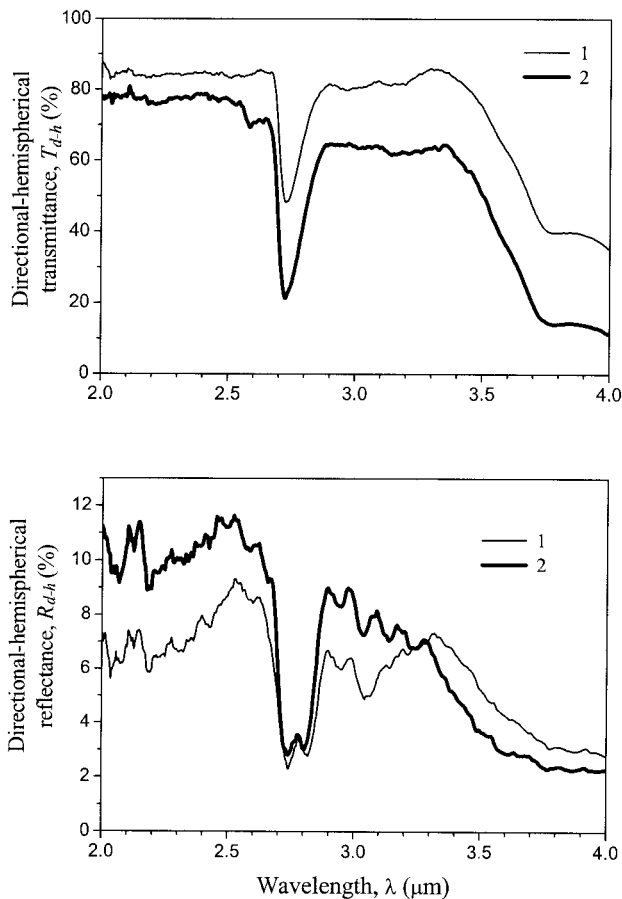
Fig. 4. Directional-hemispherical transmittance and reflectance for two samples of fused quartz containing bubbles: 1, $z_0 = 5$ mm; 2, $z_0 = 10$ mm.

Fig. 5. Comparison of different experimental data for the absorption index of fused quartz: 1, Beder *et al.*[34]; 2, Touloukian and DeWitt[35]; 3, Khashan and Nassif[36]; 4, present paper.

tion in many problems of radiation transfer in disperse systems.[11,21] If necessary, one can use a more detailed description of scattering by using the scattering function $\Phi_\lambda(\mu)$ defined as

$$\Phi_\lambda(\mu)\sigma_\lambda = 0.75 \frac{f_v}{a_{30}} \int_0^\infty Q_s \phi_\lambda(\mu) a^2 F(a) \mathrm{d}a, \qquad (4)$$

where $\phi_\lambda(\mu)$ is the scattering function of a single bubble, $\mu = \cos\theta$ is the director cosine with θ the angle of scattering, and σ_λ is the usual scattering coefficient defined as

$$\sigma_\lambda = 0.75 \frac{f_v}{a_{30}} \int_0^\infty Q_s a^2 F(a) \mathrm{d}a. \qquad (5)$$

Note that the asymmetry factor of scattering of polydisperse bubbles is defined as $\bar{\mu}_p = 1 - \sigma_s^{\mathrm{tr}}/\sigma_s$.

The general scattering problem for particles in a refracting and absorbing medium is considerably more complicated than the classic Mie problem. In several papers, which have considered spherical particles in an absorbing medium,[22–27] two different kinds of optical characteristics of particles have been analyzed: inherent properties calculated near the particle surface (in the near field) and the so-called apparent properties calculated at large distances from the particle (in the far field). Yang *et al.*[26] showed that the apparent properties (and corresponding efficiency factors of absorption and scattering) should be used by calculating the coefficients of the RTE. This conclusion confirms the common practice in radiation transfer calculations in disperse systems.[11]

The Mie solution for a single spherical particle in vacuum is well known and can be found elsewhere.[11,19,20] The independent parameters of this solution (aside from the scattering angle) are the diffraction parameter $x = 2\pi a/\lambda$ and the complex index of refraction of the

$$\alpha_\lambda = \frac{4\pi\kappa_0}{\lambda} + 0.75 \frac{f_v}{a_{30}} \int_0^\infty Q_a a^2 F(a) \mathrm{d}a, \qquad (1)$$

$$\sigma_\lambda^{\mathrm{tr}} = 0.75 \frac{f_v}{a_{30}} \int_0^\infty Q_s^{\mathrm{tr}} a^2 F(a) \mathrm{d}a, \qquad (2)$$

where κ_0 is the absorption index of the matrix, f_v is the volume concentration of bubbles, Q_a and $Q_s^{\mathrm{tr}} = Q_s(1 - \bar{\mu})$ are the efficiency factor of absorption and the transport efficiency factor of scattering, Q_s is the efficiency factor of scattering, $\bar{\mu}$ is the asymmetry factor of scattering,[11] and the parameter a_{30} can be computed from the following definition of a_{ij}:

$$a_{ij} = \int_0^\infty a^i F(a) \mathrm{d}a \Big/ \int_0^\infty a^j F(a) \mathrm{d}a. \qquad (3)$$

The spectral transport extinction coefficient is defined as $\beta_\lambda^{\mathrm{tr}} = \alpha_\lambda + \sigma_\lambda^{\mathrm{tr}}$. The choice of the so-called transport (or reduced) characteristics of scattering and extinction is based on successful use of the transport approximation for the scattering (phase) func-
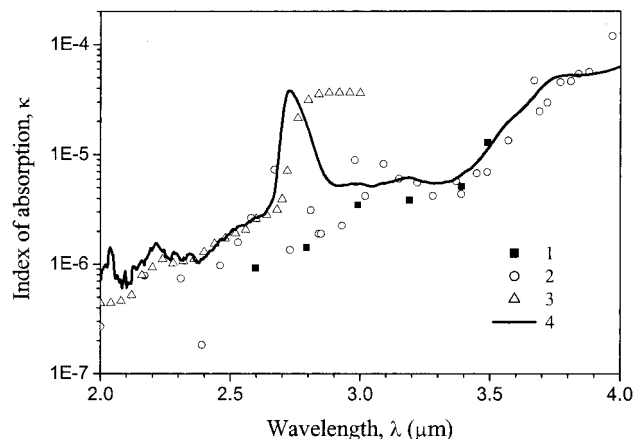
Table 1. Directional-Hemispherical Characteristics for $n_0 = 1.4$

| | $\dfrac{T_{d-h}(\%)}{R_{d-h}(\%)}$ | | | |
| | $\tau_{tr} = 0.2$ | | $\tau_{tr} = 1$ | |
ω_{tr}	MDP_0	CDOM	MDP_0	CDOM
0.2	78.0	78.0	35.9	35.9
	5.1	5.1	4.5	4.5
0.4	78.8	78.8	37.7	37.7
	5.9	5.9	6.6	6.4
0.6	80.0	80.0	40.7	40.6
	7.1	7.1	10.0	9.6
0.8	82.1	82.0	46.6	46.6
	9.2	9.2	16.8	16.0

particle substance $m = n - i\kappa$. Yang et al.[26] showed that the same relations can also be used when the matrix is refracting and absorbing. For an arbitrary value of the complex refractive index of the continuous phase $m_0 = n_0 - i\kappa_0$, it is sufficient to replace the diffraction parameter x by the complex parameter $m_0 x$ and the complex index of refraction m by the corresponding relative value m/m_0. The apparent efficiency factors of absorption and scattering of the particles are obtained by multiplying the resulting values by $\exp(-2\kappa_0 x)/|m_0|^2$. In the present paper, as in recent calculations of radiative properties of hollow glass microspheres in an absorbing polymer matrix,[28] we use slightly modified computer codes from Appendix 3 of the monograph by Dombrovsky.[11]

One of the first theoretical analyses of radiative properties of glass with bubbles has been performed by Fedorov and Viskanta.[29] They considered large gas bubbles (compared with the wavelength of radiation) and used approximate analytical relations for absorption and extinction efficiency factors derived by van de Hulst[19] for the anomalous diffraction regime. The scattering characteristics including the scattering function of bubbles were assumed to be the same as the corresponding characteristics of glass particles. The same approximation was used in the calculations performed by Pilon and Viskanta.[7]

More recently, Dombrovsky[2] calculated the efficiency factor of absorption Q_a and the transport efficiency factor of scattering Q_s^{tr} for spherical gas bubbles ($m = 1$) embedded in an absorbing and refracting medium ($|m_0| > 1$) using Mie theory. The calculations were performed in the range of index of refraction $1.2 \leq n_0 \leq 1.5$ for two values of the absorption index: $\kappa_0 = 10^{-4}$ and 10^{-3}. It was shown that the efficiency factors of large bubbles can be approximated by the following simple asymptotic relations for $x \gg 1$ and $2\kappa_0 x \ll 1$:

$$Q_a = -8\kappa_0 x/3, \quad Q_s^{tr} = 0.9(n_0 - 1). \quad (6)$$

Equations (6) overestimate the absolute values of Q_a and Q_s^{tr} by less than 5% in the range $20 < x$

$\ll 1/(2\kappa_0)$. The resulting approximate expressions for the absorption coefficient and transport scattering coefficients are as follows[2]:

$$\alpha_\lambda = (1 - f_v)\alpha_\lambda^0, \quad \sigma_\lambda^{tr} = 0.675(n_0 - 1)(f_v/a_{32}), \quad (7)$$

where $\alpha_\lambda^0 = 4\pi\kappa_0/\lambda$ is the absorption coefficient of the matrix. It is important that absorption does not depend on the bubbles' size distribution and scattering does not depend on the matrix absorption index. The only parameter related to the bubbles that affects the transport scattering coefficient of the medium is the ratio of the volume fraction of bubbles to their average radius: f_v/a_{32}. Note that the asymmetry factor of scattering is the same for all large bubbles and $\bar{\mu}_p = \bar{\mu}$ where $\bar{\mu}$ is approximated as follows:

$$\bar{\mu} = 1 - 0.45(n_0 - 1). \quad (8)$$

To analyze the effects of possible impurities in the material containing bubbles we also consider the case of an absorbing and refracting substance present inside the bubbles. We assume that this substance has a comparably large absorption index $\kappa_i \gg \kappa_0$ because it is the only case for which a considerable effect on the absorption coefficient of the medium containing bubbles can be observed. Some results of calculations of relative efficiency factors for the simple case of homogeneous particles (when a substance with $m_i = n_i - i\kappa_i$ fills all the bubble volume) are shown in Figs. 1 and 2. We limit our consideration to cases when $n_i < n_0$, $\kappa_i \ll 1$, $2\kappa_i x \ll 1$ and plot the ratios of the efficiency factors to the following values:

$$Q_a^i = 0.9(3\,n_i/n_0 - 1)\kappa_i x,$$

$$Q_s^{tr(i)} = 0.9(n_0/n_i - 1). \quad (9)$$

The latter approximation of Q_s^{tr} is not as exact for $n_i > 1$ as for $n_i = 1$ but it can be used as a first-order approximation. The small-matrix absorption coefficient has no effect on the applicability of the approximate Eqs. (9). In addition, the value of Q_s^{tr} is insensitive to the weak absorption of the particle substance.[11] The approximate expression of Q_a^i in general form is applicable for arbitrary values of $\kappa_i x$ and can be written as follows[30]:

$$Q_a^i = 1 - \exp[0.9(3\,n_i/n_0 - 1)\kappa_i x]. \quad (10)$$

In cases when $2\kappa_i x \ll 1$, the resulting approximate relations for the absorption and transport scattering coefficients of a weakly absorbing media with bubbles can be expressed as

$$\alpha_\lambda = (1 - f_v + f_v^i)\alpha_\lambda^0 + 0.675 f_v^i(3\,n_i/n_0 - 1)\alpha_\lambda^i/2,$$

$$\sigma_\lambda^{tr} = 0.675(n_0/n_i - 1)(f_v/a_{32}), \quad (11)$$

where f_v is the total volume fraction of bubbles, f_v^i is the volume fraction of bubbles filled by an absorbing substance, and $\alpha_\lambda^i = 4\pi\kappa_i/\lambda$ is the absorption coefficient of the filling substance. One can see that the absorption coefficient does not depend on the size distribution of the bubbles but it is important to know the volume fractions of bubbles filled by an absorbing substance. In contrast with the absorption coefficient, the transport scattering coefficient is directly proportional to the total concentration of bubbles and inversely proportional to their average radius. Note that the scattering function does not depend on the volume fraction f_v. The details of the bubble size distribution affect neither the absorption nor the scattering characteristics of the medium.

3. Experimental Data on Volume Fraction and Size Distribution of Bubbles in Fused Quartz

The above analysis showed that size distribution of bubbles is not important but we have to know the total volume fraction of bubbles f_v, the average radius a_{32}, as well as the volume fraction f_v^i of possible bubbles filled by an absorbing substance. Note that one can use the volume-averaged values of f_v, f_v^i, and a_{32} without accounting for their spatial variation because of the small optical thickness of the samples.

The total volume fraction f_v can be evaluated directly by measuring the sample density, but one can
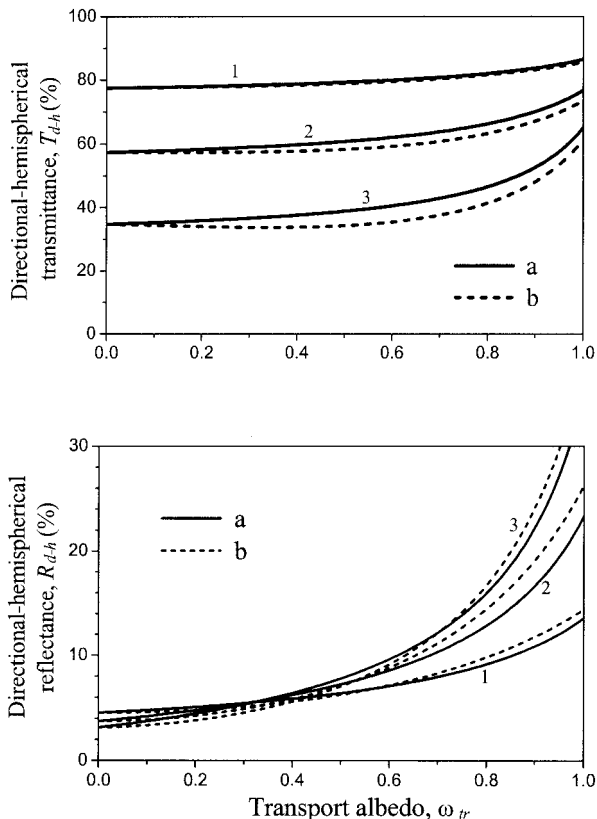

Fig. 6. Effect of the scattering function on the directional-hemispherical transmittance and reflectance. CDOM calculations for $n_0 = 1.4$: a, transport approximation; b, Henyey–Greenstein approximation; 1, $\tau_{tr}^0 = 0.2$; 2, $\tau_{tr}^0 = 0.5$; 3, $\tau_{tr}^0 = 1$.

also use an indirect evaluation of the same value by calculating the surface concentration f_s of bubbles. It is clear that the concentration of bubbles on the sample surfaces (they are looked at as defects of the surface) is proportional to f_v. For a large number of bubbles, the average surface concentration of bubbles f_s for an arbitrary cut of the sample does not depend on the possible order in the spatial distribution of the bubbles. For this reason, we can consider the simplest cubic structure. For samples with uniform volume distribution of polydisperse bubbles, one can write

$$f_v = (4\pi/3)a_{30}/d^3, \qquad (12)$$

where d is the distance between neighboring bubbles (step of the cubic structure). When we cut the sample by planes, which are parallel to one of the sides of the cubic structure, the probability that a bubble is located on the sample surface is $p = 2a_{10}/d$, and the value of the average surface concentration of bubbles is determined by

$$f_s = 2a_{10}/d^3, \qquad (13)$$

Comparison of Eqs. (12) and (13) gives the following relation between the volume fraction and the average surface concentration of bubbles:

$$f_v = (2\pi/3)f_s\, a_{32}a_{21}. \qquad (14)$$

We consider two samples of different thickness: $z_0 = 5$ and 10 mm. The size distribution of bubbles for the thin sample was determined by analyzing high-resolution digital photographs taken with a Sony DSC F-828 camera. The resulting normalized distribution function based on measurements of $N = 212$ bubbles is shown in Fig. 3. Simple calculations give the following values of the average radii of bubbles: $a_{21} = 0.56$ mm and $a_{32} = 0.64$ mm. Note that previous measurements reported by Baillis et al.[8] gave slightly greater values ($a_{21} = 0.70$ mm, $a_{32} = 0.75$ mm) mainly because the significant contribution of small bubbles was ignored. In the case of thin samples, image analysis also enables the direct determination of the volume fraction:

$$f_v = (4\pi/3)Na_{30}/(z_0S), \qquad (15)$$

where S is the sample surface area. The results of the different methods are as follows: $f_v = (4.6 \pm 1.1)\%$ from density measurements, $f_v \approx 3.2\%$ from measurements of surface defects, and $f_v = (4.3 \pm 0.2)\%$ from photographs. The simplest method in which surface defects are used underestimates the volume fraction of bubbles because of the disappearance of small defects after the surfaces of the samples are polished. Both of the other methods give approximately the same results. In the analysis of experimental data for infrared properties of fused-quartz samples containing bubbles, we will use the approximate value of

$a_{32} = 0.64$ mm and the range of volume fraction f_ν = 3.5–5%.

The two maxima observed in the bubble size distribution shown in Fig. 3 can be interpreted as a result of strong compression of bubbles of average size before solidification of the quartz melt. The surface tension of the melt leads to a significant increase in gas pressure inside the collapsing bubbles.[3,7] Thus one cannot exclude the possibility that the smallest bubbles contain a condensed substance that absorbs radiation in the near infrared. We will consider this hypothesis by analyzing the experimental results for the spectral absorption coefficient of fused-quartz samples containing bubbles.

4. Directional-Hemispherical Measurements

The samples of fused quartz containing bubbles are illuminated by a normally incident collimated beam. The experimental setup consists of two main parts: a Bio Rad FTS-60A Fourier-transform infrared spectrometer and a gold-coated integrating sphere CSTM-RSA-DI-40D, which collects hemispherically the radiation crossing or is reflected by the sample onto a detector placed on the wall of the sphere. The incident beam is not parallel but is convergent with an angle of 2.25°. The diameter of the sample area subjected to a normally incident beam is ~28 and 16 mm for transmittance and reflectance measurements, respectively. Fused-quartz samples containing bubbles were prepared with special attention to the quality of their surfaces as described by Baillis et al.[8]

The transmittance and reflectance spectrum have been acquired several times for different positions and orientations of the samples. Because of noisy transmittance and reflectance spectra, the data have been smoothed by using the BOXCAR procedure available in the Win-IR Pro software. The parameters of smoothing were chosen to eliminate the numerical noise but not to affect the physical behavior of the spectra. The results of directional-hemispherical measurements in the spectral range $2 < \lambda < 4$ μm are presented in Fig. 4. Note that only the average values are shown. The standard absolute deviation is 3–8% for transmittance and 8–15% for reflectance. The analysis of the experimental results is based mainly on the more reliable transmittance measurements whereas the reflectance data are used only to evaluate the volume fraction of bubbles.

Similar measurements were performed to determine the index of absorption κ_0 of fused-quartz samples without bubbles cut from the same piece as that used for the samples containing bubbles. The absorption index was calculated from the transmittance data. The three-term dispersion relation suggested by Malitson[31] for the index of refraction of fused quartz is used instead of the measurements of reflectance, which are too noisy. The standard absolute deviation of transmittance from the average values was less than 5%. Note that applicability of Malitson's dispersion relation has been confirmed in more recent papers.[32,33] One can see in Fig. 5 that the

values of the absorption index of fused quartz determined in the present study are in a good agreement with published data.[34–36]

5. Inverse Problem Solution

Because of the small volume fraction of randomly placed bubbles, the radiation transfer theory can be used to calculate the reflection and transmission of infrared radiation in glass with bubbles. Consider the problem of radiation transfer in a plane-parallel slab of an absorbing, refracting, and anisotropically scattering medium. We will limit our consideration to one-dimensional azimuthally symmetric problems when the front surface of the slab is uniformly illuminated along the normal direction by randomly polarized radiation. In the case of a homogeneous isotropic medium, the RTE and the associated boundary conditions can be written as follows[10]:

$$\mu \frac{\partial \bar{I}}{\partial \tau} + \bar{I} = \frac{\omega}{4\pi} \int_{-1}^{1} \bar{I}(\tau, \mu') \left[\int_{0}^{2\pi} \Phi(\mu_0) d\psi' \right] d\mu', \quad (16)$$

$$\bar{I}(0, \mu) = R\bar{I}(0, -\mu) + (1 - R)\delta(1 - \mu),$$

$$\bar{I}(\tau_0, -\mu) = R\bar{I}(\tau_0, \mu) \quad \text{for} \quad \mu > 0, \quad (17)$$

where

$$\bar{I} = I_\lambda / (n_0^2 I_\lambda^e), \quad \omega = \sigma_\lambda / \beta_\lambda, \quad \tau = \beta_\lambda z, \quad (18)$$

$$\mu_0 = \mu\mu' + (1 - \mu^2)^{1/2}(1 - \mu'^2)^{1/2} \cos(\psi - \psi'). \quad (19)$$

Here $\mu = \cos \vartheta$, where the angle ϑ is measured from the normal directed into the medium; I_λ^e is the incident spectral radiation intensity, and $R(\mu)$ is the Fresnel reflection coefficient.[10,37] Note that the integral term on the right-hand side of the RTE does not depend on the azimuthal angle ψ and one can set $\psi = 0$ in Eq. (19).

The well-known difficulty in the numerical solution of the RTE is related to the complex scattering functions: One needs a very fine angular discretization to take into account all the details of the angular dependency of $\Phi(\mu_0)$. Various approximations of scattering functions are usually considered to simplify the calculations.[38,39] In the case of large particles, which are characterized by the forward-scattering peak, the simplest approach is the transport approximation[11]:

$$\Phi(\mu_0) = 1 - \bar{\mu} + 2 \bar{\mu}\delta(1 - \mu_0), \quad (20)$$

which enables one to reduce the problem into a form similar to that valid for isotropic scattering media:

$$\mu\frac{\partial \bar{I}}{\partial \tau_{\mathrm{tr}}} + \bar{I} = \frac{\omega_{\mathrm{tr}}}{2}\int_{-1}^{1}\bar{I}\,d\mu, \qquad (21)$$

$$\bar{I}(0,\ \mu) = R\bar{I}(0,\ -\mu) + (1-R)\delta(1-\mu),$$

$$\bar{I}(\tau_{\mathrm{tr}}^{0},\ -\mu) = R\bar{I}(\tau_{\mathrm{tr}}^{0},\ \mu),\quad \mu>0, \qquad (22)$$

where $\omega_{\mathrm{tr}} = \sigma_\lambda{}^{\mathrm{tr}}/\beta_\lambda{}^{\mathrm{tr}}$, $\tau_{\mathrm{tr}} = \beta_\lambda{}^{\mathrm{tr}}z$, $\tau_{\mathrm{tr}}^{0} = \beta_\lambda{}^{\mathrm{tr}}z_0$. We will compare results obtained from the complete calculations with those based on the transport approximation applied to our problem. But all the subsequent relations are written for the problem stated in Eqs. (21) and (22).

The usual technique[10,11] expresses the radiation intensity $\bar{I}$ as a sum of a diffusion component $\bar{J}$ and a term corresponding to the collimated external radiation:

$$\bar{I} = \bar{J} + \frac{1-R_1}{1-R_1 C}[\exp(-\tau_{\mathrm{tr}})\delta(1-\mu)$$
$$+ C\exp(\tau_{\mathrm{tr}})\delta(1+\mu)], \qquad (23)$$

where $C = R_1\exp(-2\tau_{\mathrm{tr}}^{0})$ and $R_1 = R(1) = (n_0 - 1)^2/(n_0 + 1)^2$. The mathematical problem statement for the diffuse component can be stated as follows:

$$\mu\frac{\partial \bar{J}}{\partial \tau_{\mathrm{tr}}} + \bar{J} = \frac{\omega_{\mathrm{tr}}}{2}\left\{\int_{-1}^{1}\bar{J}\,d\mu + \frac{1-R_1}{1-R_1 C}\right.$$
$$\left. \times [\exp(-\tau_{\mathrm{tr}}) + C\exp(\tau_{\mathrm{tr}})]\right\}, \qquad (24)$$

$$\bar{J}(0,\ \mu) = R(\mu)\bar{J}(0,\ -\mu),$$

$$\bar{J}(\tau_{\mathrm{tr}}^{0},\ -\mu) = R(\mu)\bar{J}(\tau_{\mathrm{tr}}^{0},\ \mu)\quad \text{for}\quad \mu>0. \qquad (25)$$

The directional-hemispherical reflectance and transmittance can also be expressed as a function of the diffuse component of the radiation intensity:

$$R_{d-h} = R_{d-h}{}^{0} + \int_{0}^{1}[1-R(\mu)]\,\bar{J}(0,\ -\mu)\mu\,d\mu,$$

$$T_{d-h} = T_{d-h}{}^{0} + \int_{0}^{1}[1-R(\mu)]\,\bar{J}(\tau_{\mathrm{tr}}^{0},\ \mu)\mu\,d\mu, \qquad (26)$$

where the first terms are given by the well-known equations[10]

$$R_{d-h}{}^{0} = \frac{R_1 + (1-R_1)^2 C}{1-R_1 C}, \quad T_{d-h}{}^{0} = \frac{(1-R_1)^2}{1-R_1 C}\exp(-\tau_{\mathrm{tr}}^{0}). \qquad (27)$$

A. Alternative Models for Radiation Transfer

We consider two alternative models to calculate the diffuse component of the radiation intensity: (1) the numerical solution by using the discrete ordinates method (DOM)[10] and (2) the analytical solution based on the modified two-flux approximation MDP$_0$ (modified double spherical harmonics method, where subscript zero denotes the zero approximation of this method), similar to that suggested by Dombrovsky[40,41] for spherically symmetric problems in nonscattering media. In the first case, two approximations of the scattering function are considered: the transport approximation given by Eq. (20) and the Henyey–Greenstein approximation[10] expressed as

$$\Phi(\mu_0) = (1-\bar{\mu}^2)/(1+\bar{\mu}^2 - 2\bar{\mu}\mu_0)^{3/2}. \qquad (28)$$

The approximate MDP$_0$ solution is given only for the transport approximation. It will be shown that it is sufficient for the correct calculation of the hemispherical characteristics of optically thin samples considered in the present paper.

By use of the DOM, the Fresnel reflection may cause the so-called ray effect associated with insufficiently fine angular discretization of the radiation intensity field.[42] Ray effects may be mitigated by refining the angular discretization or by using the modifications of the DOM. In our case, an adequate account of the angular dependence can be reached thanks to the composite DOM (CDOM) in which the integral over all directions is split into the integrals over three subintervals $-1 < \mu < -\mu_c$, $-\mu_c < \mu < \mu_c$, and $\mu_c < \mu < 1$ defined using the critical angle. Finally, each subinterval uses its own set of quadrature points.[43]

The numerical procedure based on the DOM code is general and can be applied to rather complicated problems. But in our case, the angular dependencies of the diffuse radiation component are expected to be relatively simple. For this reason, we consider also an alternative approach, which is a modification of the well-known two-flux approximation. Taking into account the effect of total internal reflection occurring at both interfaces of the slab, we suggest the following approximation[40,41]:

$$\bar{J}(\tau_{\mathrm{tr}},\ \mu) = \begin{cases} \varphi_0{}^{-}(\tau_{\mathrm{tr}}), & -1 \le \mu < -\mu_c \\ \psi_0(\tau_{\mathrm{tr}}), & -\mu_c < \mu < \mu_c \quad \text{with}\quad \mu_c = (1-1/n_0{}^2)^{1/2}. \\ \varphi_0{}^{+}(\tau_{\mathrm{tr}}), & \mu_c < \mu \le 1 \end{cases} \qquad (29)$$

Note that the case $\mu_c = 0$ corresponds to the usual two-flux model. The intermediate angle interval $-\mu_c < \mu < \mu_c$ gives no contribution to the radiation flux and the words two-flux are also applicable to the modified approximation. It is clear that Eq. (28) is just the same as in a CDOM of zero-order quadrature.

Integrating Eq. (24) separately over the above three intervals and after simple transformations, one can obtain the following boundary-value problem for the function $g_0 = \varphi_0{}^- + \varphi_0{}^+$:

$$-g_0'' + \beta^2 g_0 = \beta^2 \chi[\exp(-\tau_{\text{tr}}) + C \exp(\tau_{\text{tr}})],$$

$$(1 + \mu_c)g_0'(0) = 2\gamma\, g_0(0),$$

$$(1 + \mu_c)g_0'(\tau_{\text{tr}}{}^0) = -2\gamma\, g_0(\tau_{\text{tr}}{}^0), \qquad (30)$$

where

$$\beta^2 = \frac{4}{(1 + \mu_c)^2} \frac{1 - \omega_{\text{tr}}}{1 - \omega_{\text{tr}}\mu_c},$$

$$\gamma = (1 - R_1)/(1 + R_1),$$

$$\chi = \frac{\omega_{\text{tr}}}{1 - \omega_{\text{tr}}} \frac{1 - R_1}{1 - R_1 C}. \qquad (31)$$

Thus the approximate equations for the directional-hemispherical reflectance and transmittance of the medium simplify as follows:

$$R_{d-h} = R_{d-h}{}^0 + \gamma(1 - \mu_c{}^2)g_0(0)/2,$$

$$T_{d-h} = T_{d-h}{}^0 + \gamma(1 - \mu_c{}^2)g_0(\tau_{\text{tr}}{}^0)/2. \qquad (32)$$

The boundary-value problem formulated in Eqs. (30) can be solved analytically. The resulting expressions for R_{d-h} and T_{d-h} can be written as

$$R_{d-h} = R_{d-h}{}^0 + D(1 + B/\beta + C)/2,$$

$$T_{d-h} = T_{d-h}{}^0 + D\big[(1 + R_1)\exp(-\tau_{\text{tr}}{}^0) + A/\beta\big]/2, \qquad (33)$$

where

$$D = \gamma(1 - \mu_c{}^2)\chi\beta^2/(\beta^2 - 1), \qquad (34)$$

$$A = \frac{(\gamma_1 - \gamma_2 R_1)(\varphi s + c)\exp(-\tau_{\text{tr}}{}^0) - (\gamma_2 - \gamma_1 C)}{(1 + \varphi^2)s + 2\varphi c},$$

$$B = \frac{(\gamma_1 - \gamma_2 R_1)\exp(-\tau_{\text{tr}}{}^0) - (\gamma_2 - \gamma_1 C)(\varphi s + c)}{(1 + \varphi^2)s + 2\varphi c},$$

$$\gamma_1 = 1 - 2\bar\gamma, \quad \gamma_2 = 1 + 2\bar\gamma, \quad \varphi = 2\bar\gamma/\beta,$$

$$\bar\gamma = \gamma/(1 + \mu_c), \quad s = \sinh(\beta\tau_{\text{tr}}{}^0), \quad c = \cosh(\beta\tau_{\text{tr}}{}^0).$$

A comparison between the analytical solution given by Eqs. (33) and (34) in MDP_0 and the numerical results obtained using the high-order CDOM for the transport approximation of the scattering function is given in Table 1. We limit our consideration to the range of albedo and optical thickness typical of the present problem. One can see that the modified two-flux approximation gives rather accurate predictions. The error of this approximation is less than 0.3% for the hemispherical transmittance and 5% for the hemispherical reflectance.

The effect of the scattering function on the hemispherical characteristics is illustrated by the CDOM calculations shown in Fig. 6. The error of the transport approximation increases with optical thickness but it is insignificant in the range of weak extinction, which is the most important for the problem under consideration in this paper. Good agreement between calculations by use of the Henyey–Greenstein and the transport approximation shows that a separate determination of the scattering coefficient and of the asymmetry factor using hemispherical measurements is practically impossible. Fortunately, one does not need these data in the usual radiation heat transfer calculations.[11,21]

The above analysis showed that the modified two-flux approximation (and the corresponding analytical solution) can be used to analyze the experimental data for the directional-hemispherical transmittance and reflectance of fused-quartz samples containing bubbles.

B. Identification Procedure and Results of Calculations

It was shown previously that the scattering characteristics of a weakly absorbing medium containing bubbles do not depend on the absorption characteristics of the continuous or dispersed phases [see Eqs. (7)]. This is important because small impurities in either phase can affect the absorption coefficient in the semitransparency region of the spectrum, and one cannot be sure of the theoretical predictions based on the absorption properties of the medium components. For this reason, it is suggested that only the predictions be used for the scattering characteristics but not for the absorption in the identification procedure.

Let us assume that the scattering characteristics of the heterogeneous medium can be determined from the approximate relations suggested above. Three values of the volume fraction of bubbles are considered: $f_v = 3.5\%$, 4%, and 4.5% and a fixed value of $a_{32} = 0.64\ \mu\text{m}$. It is also assumed that $f_v{}^i = 0$. The choice of f_v is based on the estimates that give the best curve fit for the measured reflectance spectra. The averaged experimental values of the directional-hemispherical transmittance at each wavelength are considered to be exact. The spectral dependency of $T_{d-h}(\lambda)$ is used to determine the transport albedo and the absorption coefficient of the heterogeneous medium. It should be noted that this procedure does not require us to solve the ill-posed inverse problem as in
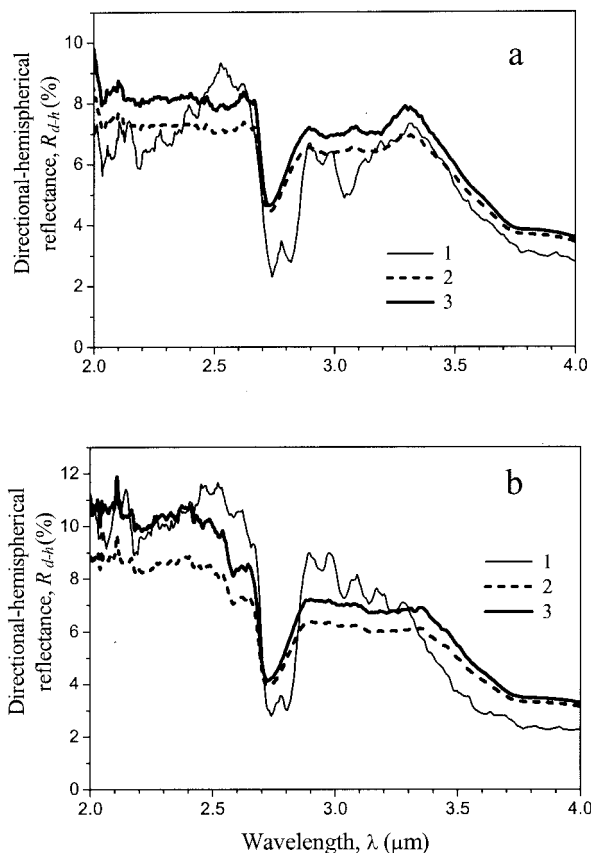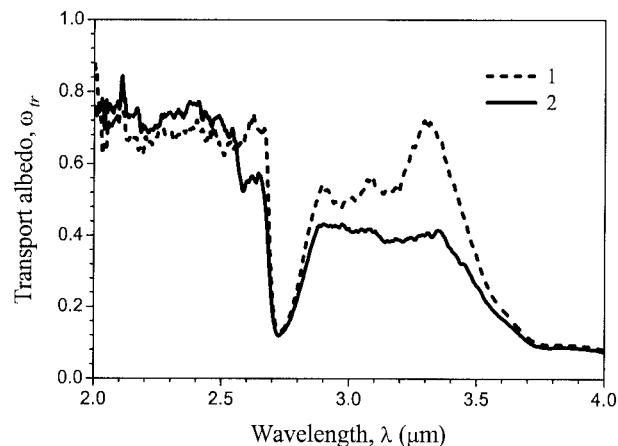
Fig. 8. Transport albedo of fused quartz containing bubbles (f_v = 4%): 1, z_0 = 5 mm; 2, 10 mm.

medium containing bubbles. Assuming the presence of an absorbing medium inside the bubbles, one can obtain from Eqs. (11) the following approximate relation:

$$\Delta\alpha_\lambda = 4f_v{}^i\kappa_i(3n_i/n_0 - 1)/\lambda. \qquad (35)$$

Fig. 7. Directional-hemispherical reflectance for two samples of fused quartz containing bubbles: a, z_0 = 5 mm; b, 10 mm; 1, measurement; 2, calculation for f_v = 3.5%; 3, f_v = 4.5%.

the case of several unknown optical parameters.[8] All the calculations are performed using the analytical solution of the MDP$_0$ approximation.

Comparison between the calculated reflectance and the experimental measurements shown in Fig. 7. enables the evaluation of the bubble volume fraction: It is of the order of 4% for both samples. Note that it is difficult to curve fit $R_{d-h}(\lambda)$ by choosing the value of f_v. But one should have in mind that the experimental error associated with the reflectance measurements is much greater than that for the transmittance. Therefore the reflectance measurements were used to evaluate only the volume fraction of bubbles f_v. It is important that this value be in good agreement with independent estimations based on density measurements and on image analysis of high-resolution photographs of the thin sample.

The values of the transport albedo and of the absorption coefficient determined by the identification procedure for f_v = 4% are presented in Figs. 8 and 9. In the latter, the theoretical value of the absorption coefficient predicted by Eqs. (7) is also shown. One can see that the difference between experimental and theoretical values of the absorption coefficient $\Delta\alpha_\lambda$ is relatively small except around the narrow absorption peak near λ = 2.7 μm. This result can provide an estimate of the maximum value of the integral parameters in the event impurities are present in the
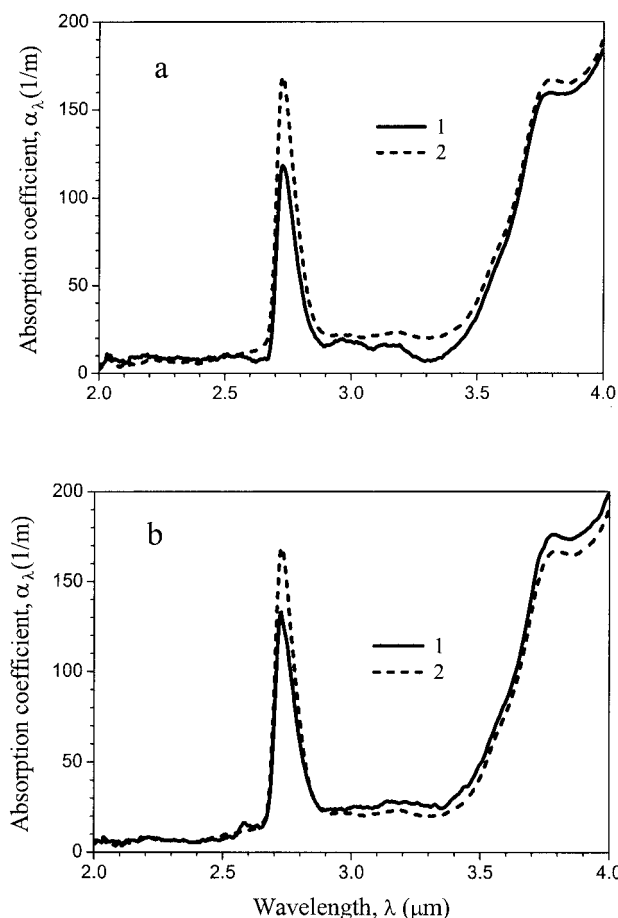
Fig. 9. Absorption coefficient of fused quartz containing bubbles (f_v = 4%): a, z_0 = 5 mm; b, z_0 = 10 mm; 1, experiment; 2, theoretical prediction.

It should be noted that even the presence of molecular water impurity in the fused quartz should be accounted for in the absorption spectrum of glass.[44–46] To obtain some quantitative estimates, consider water as a model condensed substance inside some part of small bubbles. Using the data by Hale and Querry[47] ($n_i = 1.3$, $\kappa_i = 10^{-3}$ at $\lambda = 2$ μm and $n_i = 1.2$, $\kappa_i = 0.02$ at $\lambda = 2.7$ μm) and assuming $f_\nu^i = 0.4\%$, we find $\Delta\alpha_\lambda \sim 1$ m^{-1} at $\lambda = 2$ μm and $\Delta\alpha_\lambda \sim 30$ m^{-1} at $\lambda = 2.7$ μm. These evaluations correlate rather well with the level of differences between the experimental data for fused quartz containing bubbles and the theoretical predictions based on the assumption of $f_\nu^i = 0$. This suggests that the experimental data for the absorption coefficient of fused-quartz samples containing bubbles do not exclude the presence of some radiation-absorbing impurities entrapped in the bubbles.

6. Conclusions

The research of absorption and scattering of near-infrared radiation by fused quartz containing bubbles is based on a combination of experimental measurements and theoretical analysis using Mie theory. Mie calculations over a wide range of parameters enable the formulation of approximate relations for the main radiative characteristics of semitransparent media containing large polydisperse bubbles, including those filled with an absorbing and refracting substance. It is shown that radiation scattering by bubbles is independent of the weak absorption by the matrix and the potential absorbing substance inside the bubbles. Use of theoretically predicted scattering characteristics of the heterogeneous medium makes it possible to avoid large errors in the identification procedure caused by noisy experimental data for the small values of reflectance.

A modified two-flux approximation that takes into account the total internal reflection of radiation at both interfaces of the plane-parallel slab samples is suggested for radiation transfer calculations. The corresponding analytical solution for directional-hemispherical transmittance and reflectance is derived. In the transport approximation, comparison with exact numerical calculations based on the composite discrete ordinate method showed that the error of the modified two-flux approximation is less that 5% in the most important range of the problem parameters. It is shown also that the transport approximation is sufficiently accurate in the case of small optical thickness of the sample and it is not necessary to use the more complex Henyey–Greenstein approximation for the scattering function.

Application of the suggested identification procedure used to study, the near-infrared properties of fused-quartz samples containing bubbles provides new data on spectral single-scattering albedo and for the absorption coefficient of the heterogeneous medium in the spectral range from 2 to 4 μm. The volume fraction of bubbles obtained from directional-hemispherical reflectance of fused-quartz samples is in good agreement with both density measurements and image analysis of high-resolution photographs of the thin sample. Comparison between experimentally determined and predicted values of the absorption coefficient of fused quartz containing bubbles enables the evaluation of the integral characteristic of possible impurities that are treated as an absorbing substance entrapped inside the bubbles.

The suggested procedure combining experimental measurements and theoretical analysis of infrared radiative properties of semitransparent substances containing bubbles can be used to both control the optical purity of the medium and to estimate the volume fraction of polydisperse bubbles in various applications.

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