Original Paper

The Christiansen filter – A centennial retrospective review

Part 2. Application in the characterization of the homogeneity of glass[1])

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The only application of the Christiansen filter which was not foreseen by its inventor – the characterization of glass homogeneity – is reviewed in this part of the paper. First of all Shelyubskii's method for the evaluation of σ_n^2 (the variance of the refractive index of glass) is analyzed on the basis of the theories which were discussed in part 1. Later, the experimental evidence of the correlation between the actual values of σ_n^2 and those determined by Shelyubskii's method or its variations are reviewed, as well as the influence of the experimental parameters of the method on the latter values. Thus, it was verified that both magnitudes are correlated over the usual range of values, but the influence of some of the experimental parameters – particularly the grain size, the washing process and the characteristics of the optical system – remains still unclear. Finally, the applications of this method in glass technology are discussed, arriving at the conclusion that by means of the σ_n^2 values determined by this method it is possible to foresee general trends of the glass homogeneity and in many cases it is also possible to determine ranges of values of σ_n^2 within which one can work without homogeneity problems. But beyond these ranges, the method is of limited utility in order to determine if the inhomogeneities which are present in a glass ware may be harmful because of their intensity and/or distribution.

100 Jahre Christiansenfilter – Eine Übersicht

Teil 2. Anwendung zur Charakterisierung der Glashomogenität

In diesem Teil der Arbeit wird die einzige Anwendung des Christiansenfilters untersucht, die von seinem Erfinder nicht vorausgesehen wurde: die Charakterisierung der Glashomogenität. Zuerst wird der Gültigkeitsbereich der Shelyubskii-Methode für die Bestimmung der Dispersion der Brechzahlverteilung des Glases (σ_n^2) theoretisch festgestellt. Anschließend werden die experimentellen Beweise über die Übereinstimmung zwischen den tatsächlichen und den nach der Shelyubskii-Methode oder ihren Änderungen bestimmten Werten von σ_n^2 besprochen, sowie der Einfluß der experimentellen Parameter der Methode auf die letztgenannten Werte. Es bestätigt sich dabei eine gesetzmäßige Zuordnung beider Größen zueinander, solange die Werte im Normalbereich liegen. Allerdings sollte noch der Einfluß einiger experimenteller Parameter, Reinigungsmethoden der Körner, Eigenschaften des optischen Systems und insbesondere der Korngröße, genauer geklärt werden. Zuletzt werden die Anwendungen dieser Methode in der Glastechnologie besprochen, wobei sich zeigt, daß mittels der mit ihr bestimmten σ_n^2-Werte, die allgemeine Tendenz der Homogenität vorhergesagt werden kann. Es ist auch in einigen Fällen möglich, jenen Bereich der σ_n^2-Werte anzugeben, innerhalb dessen man ohne Homogenitätsprobleme arbeiten kann. Außerhalb dieses Bereiches lassen sich mittels dieser Methode höchstens Andeutungen darüber erhalten, inwieweit Inhomogenitäten in einem Glaserzeugnis wegen ihrer Intensität oder Verteilung schaden können.

1. Introduction

In this part the only application of the Christiansen filter which was not foreseen by its inventor, the characterization of glass homogeneity, will be commented. This application is the most discussed of all and induced the majority of the papers on the Christiansen filter published since 1960. The theories of Christiansen filters with inhomogeneous phases and the experimental evidence that support these theories will be reviewed in section 2., the practical aspects of their application in the characterization of glass homogeneity in section 3., and their uses in glass technology in section 4.

At first, some aspects of homogeneity will be discussed. The term "characterization" instead of "measurement" or "determination" of the homogeneity was used since the homogeneity is not a property in the usual sense of the word, but the result of the distribution of the characteristic quantities of a body. In order to study the homogeneity of such a body, it can be considered to be divided in a series of cells; if each of the mentioned properties has the same value in each cell, it can be said that the body is chemically and structurally homogeneous. If that is not the case the body is inhomogeneous and the problem arises how to differentiate one inhomogeneous body from another. Theoretically, a hypothetical homogeneity tensor may be defined for each property which describes the variations of that property from cell to cell. However, it is very unlikely that such a tensor could be determined experimentally, so it is necessary to resort to methods perhaps not so accurate but applicable in practice.

Before applying one of these methods, it is necessary to determine the size of the cells, since their results depend on that size. The optimum size should be equal as or less than the size of the inhomogeneity.

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[1]) Pt. 1//Fundamental principles and applications as monochromator and polarizer. Glastech. Ber. **60** (1987) no. 3, p. 89–111.

If it is larger, the homogeneity of the body would appear better than it actually is because there is a larger probability that fluctuations of a property are compensated to its mean value. In this case all the cells would show a similar mean value of the property (which is generally the value that one can measure in a cell) and the body would appear as homogeneous. In the case of glasses of normal homogeneity (excluding optical glasses) it is reasonable to take a cell volume of approximately $10^{-3}\,\mathrm{mm}^3$ [136 and 137].

The approximate methods available to describe the homogeneity of a glass were divided in two groups: the "integral" methods and the "differential" methods [137]. With the methods of the first group the sample is generally powdered (thus, the cell size is determined by the grain size of the powder) and the variance or a related quantity of a certain property is determined on the powder. The selected property should be very sensitive to chemical and structural variations, for instance the density [138 and 139] or the refractive index as will be commented here. Such a sort of method gives thus an average of the modulus of the differences between the value of a selected property in each cell and the mean value of that property in the sample, instead of the value of all the properties in each cell as required by the hypothetical method. The other extreme possibility is to determine the position of the most inhomogeneous zones without determining the value of the properties in them; this would be equivalent to a determination of the most inhomogeneous elements of the hypothetic homogeneity tensor without giving their value. This is the basis of the differential methods such as the known methods of cord or striae detection by means of polarized light, deformation of geometric patterns, etc.

There are also methods which cannot be easily classified in one of the cited groups, for instance Löffler's method [140 to 142] for the analysis of striae by etching with different agents and determination of the etching depth by means of an interferometric microscope. This method is similar to the differential ones in the sense that it enables the determination of the position of the striae, which are etched to different depths, but on the other hand it is possible to determine from the etching depth the variation of the chemical composition with respect to its average at many points as in the integral methods. However, it is not possible to measure at so many points (equivaeent here to cells) as in the integral methods, and the determinations are restricted to the surface of the probe. Another method which presents characteristics of the integral and differential methods is the automatic image analysis of the deformation of a pattern of points by the sample [143]. This method is an improvement of the differential methods based on the same principle, as it eliminates the subjective component of them, but also has characteristics of the integral methods because the measurements are performed on a series of cells whose number is the number of points of the pattern and whose size is determined by the area of the points and the thickness of the sample (in the only known application of this method the number of cells was smaller than that usual in integral methods and the cell size slightly larger).

All these methods are applied in the detection of glassy inhomogeneities, which are generally the most difficult to detect. Gaseous and crystalline inhomogeneities appear usually in smaller amounts than the vitreous ones and are easily detected due to their very different properties with respect to the glass matrix. Also, the only property of those inhomogeneities which is of interest is their chemical composition, which generally enables the determination of their origin; the physical properties are of secondary importance whilst for the vitreous inhomogeneities generally the opposite holds.

As a conclusion to these considerations on glass homogeneity, it can be said that since none of the available methods for the characterization of the glass homogeneity is generally valid, their limitations must be remembered before applying them and perhaps more than one must be used in order to get optimum results. The integral methods can give information on the average variation of some property within a body, but they do not explain if that variation was due to one pronounced inhomogeneity or to many weaker ones and how they were distributed. Thus, these methods would be more useful in cases where the inhomogeneities are uniform in size and regularly distributed, but if they are non-uniform it is necessary to know their size and distribution, and then the differential methods will be more effective.

2. Theories of the Christiansen filter with inhomogeneous dispersed phase

The theories developed in order to predict the transmittance of Christiansen filters whose dispersed phase is an inhomogeneous, isotropic solid and whose dispersing phase is a liquid, will be reviewed here. These theories are the basis of Shelyubskii's method for the characterization of glass homogeneity, an integral method by means of which the variance of the refractive index of a sample (or perhaps a related magnitude, as will be discussed later) is determined from transmittance data of the filter prepared with that sample.

As in section 3., part 1, the employed model, the physical assumptions and mathematical approximations involved in the deduction and the final expression for the transmittance will be collected for each theory. The deduction of the formulas will not be given in detail, as in part 1, yet the experimental evidence will be discussed in detail.

2.1. Theoretical works

The first expression for the transmittance of a Christiansen filter with inhomogenous dispersed phase was deduced by Shelyubskii (equation (1) in table 1) and it is a function of the variance of the refractive index of the dispersed phase (σ_n^2). Shelyubskii proposed the use of σ_n^2 for the characterization of the homogeneity of glasses in a method which now bears his name and was patented in 1956 [144]. Shelyubskii based his deduction [137, 145 and 146] on Raman's equation (see part 1, equation (5) in table 1) which he generalized supposing that each one of the layers had a different value of n_1. Although in the original deduction of Shelyubskii's equation a normal distribution of the refractive index in the dispersed phase was supposed, Hilbig [147] showed later that it was valid for any type of distribution. The underlying problem of the earlier deductions, the artificial arrangement of the dispersed phase, was solved by Imagawa [121], who deduced an equation for the transmittance of a Christiansen filter with randomly distributed inhomogeneous dispersed phase (equation (2) in table 1), also based on Raman's theory. Afghan [93 and 124] questioned Imagawa's deduction, particularly equation (6) in [121], but his criticism is not justified, excepting in respect of the fact that in Imagawa's deduction all the layers have the same value of σ_n^2. In fact, Imagawa's equation (6) in [121] is correct if q_1 and n_1 are statistically independent variables, which is true, and Afghan's equations (3.120 to 3.125) in [93] (which are the basis for his criticism) are incorrect since he did not allow the variations of n_1 and q_1 each in turn maintaining the other variable constant and equal to its mean value. On the other hand, Afghan deduced a new equation (see equation (3) in table 1) by generalization of equation (6), see table 1 in part 1, which is in fact a special case of Imagawa's if the factor β is calculated with the value of k corresponding to equation (3) in table 1, which was deduced without supposing the filter as a succession of layers with the same value of σ_n^2.

Besides these generalizations of Raman's treatment, there were a few other theoretical works on the subject. Vidro and Khorol'skii [148] generalized equation (10), see table 1 in part 1, of Stepanov and Prishivalko; considering a normal distribution of n_1 and the particular case in which $q_1 = 1/2$ they obtained equation (4) in table 1. It can be shown that if $4\pi^2 d^2 \lambda^{-2} \sigma_n^2 \leqq 0.1$, equation (4) is valid for any distribution of n_1.

Hilbig [149] also generalized his equation (equation (14), see table 1 in part 1) in order to consider the inhomogeneity of the dispersed phase, which was artificially arranged. The final result (equation (5) in table 1) is similar to Shelyubskii's, which is not surprising since with the used layer model and supposing equivalent layers, the inhomogeneities were arranged in horizontal layers, similarly as in Shelyubskii's model where they were arranged in vertical layers. Hilbig also deduced Raman's equation again considering that both phases could absorb radiation and that the dispersed phase was inhomogeneous; he used Shelyubskii's model and the resulting expression (equation (6) in table 1) is in fact a generalization of equation (13b), see table 1 in part 1, to the case of an inhomogeneous dispersed phase. There were also some former attempts to obtain an equation for the transmittance of an inhomogeneous, absorbent Christiansen filter [147 and 150] which consisted of the empirical addition of an absorption factor to Shelyubskii's equation.

The last theoretical work on this subject was performed by Afghan [93] and was already commented in part 1. This author attempted to generalize the equations (15 and 16), see table 1 in part 1, in order to consider inhomogeneous dispersed phases. In the first case he arrived at an erroneous result because he complicated the problem unnecessarily by dividing each one of the N cells that constitute the elemental layer of his model (equation (5), see table 1 in part 1) in other N elements and subsequently handled each cell as a homogeneous Christiansen filter, supposing that all the cells had the same value of k (see equation (3.145) in [93]). Such a simplification leads to an equation similar to Shelyubskii's, while it can be shown that this treatment leads to Imagawa's equation if different values of k are considered for each cell. Afghan also showed that an equation similar to Shelyubskii's can be obtained considering that each layer has a different value of σ_n^2, if σ_n^2 of the layer is defined with respect to $\bar{n}_1$ of the assembly of layers. In the case of the second model (equation (16), see table 1 in part 1), Afghan considered the inhomogeneity of the grains using Sogani's expression [98] for σ_θ^2, but the treatment became very complicated and he could not obtain any final equation for the transmittance. A geometrical optics based study of these filters can however be performed by means of computers using Monte Carlo methods, as recently shown by Varshneya et al. [204]. They simulated the tracing of 10 000 rays that were refracted and reflected on particles with a Gaussian distribution of their refractive indices, and determined the fraction of rays which deviates up to half the cut-off angle of the detector at several wavelengths. Using a packing factor as adjustable parameter, they constructed simulated transmission spectra which fitted very closely their experimental spectra, confirming by this way the usefulness of geometrical optics to calculate the fraction of scattered radiation.

As indicated in part 1, the only way to determine accurately the validity range of the above commented equations is by means of experimental work. Thus, the experimental evidence which supports the equations of table 1 will be commented in the following. In order to prove the validity of these equations it is necessary at first to work under conditions where the corresponding equation for the homogeneous case is valid, and then apply the generalized equation to a filter with known σ_n^2. This value of σ_n^2 must be compared with that predicted by the studied equation, which must be evaluated from the transmittance curves. Thus, the methods proposed for the evaluation of σ_n^2 from the experimental data and the equations quoted in table 1 will be discussed at first.

2.2. Methods for the evaluation of σ_n^2

To evaluate σ_n^2 from one of the equations quoted in table 1, excepting the equations (4 and 6), it is necessary to know at least two points of the function $\tau_0(\Delta\bar{n}/\lambda)$. When the Christiansen filters are used as monochromators it is usual to obtain the transmission spectrum, that is the function $\tau_0(\lambda)$, at constant temperature T, so that in order to evaluate σ_n^2 the function $\Delta\bar{n}(\lambda)$ should be known.

Since the dependence of $\Delta\bar{n}$ on λ is complex, it was proposed [144 to 146] to obtain the necessary data from a curve $\tau_0(T)$ at constant λ; that is the opposite process as when the filter is used as monochromator. In this case, n_1 does not vary appreciably with temperature and n_2 varies linearly, a fact which simplifies the calculations. However, it must be considered that if there are temperature gradients in the cell, n_2 would be inhomogeneous too, a fact which was not considered in the deduction of the equations of table 1 and which would increase erroneously the value of σ_n^2. For this reason, the temperature in the cell must be varied very slowly or it must be waited till the temperature homogenizes in the cell before performing each measurement, so that the determination of the curve $\tau_0(T)$ is very time-consuming.

This drawback was avoided by Sakaino et al. [151 and 152], who determined the variation of τ_0 as a function of the pressure P (which was held constant and equal to its atmospheric value in the former experiments) at constant T and λ. Pressure variations cause a linear variation of n_2 and a negligible one of n_1, but with the advantage that there do not arise gradients in the cell and the measurements can be performed quickly. It is also possible to use liquid mixtures as dispersing phase without the risk of composition variations due to selective evaporation of their components (see section 2.1., part 1). The required equipment is however more elaborate, with cells which should withstand pressures up to 50 MPa.

As to the question of the evaluation of σ_n^2, an equation originally derived by Shelyubskii from equation (1) in table 1 may be used if it is desired to use only two points of the $\tau_0(T)$ or $\tau_0(P)$ curves:

$$\sigma_n^2 = \frac{-(\ln \tau_M)\cdot(\Delta T_{1/2})^2\cdot b^2}{4\ln 2}\,. \tag{7}$$

If it is desired to use equation (2) in table 1 the following equation becomes:

$$\sigma_n^2 = \frac{-(\ln \tau_M)\cdot(\Delta T_{1/2})^2\cdot b^2}{4\,\beta\ln 2}\,. \tag{8}$$

In both equations the transmittance τ_M is at the maximum of the curve $\tau_0(T)$, $\Delta T_{1/2}$ is the halfband width of the same curve and $b = \partial n_2/\partial T$. The same expressions can be applied if P is varied instead of T, but the parameters of the $\tau_0(T)$ curve must be replaced by those corresponding to the $\tau_0(P)$ curve. It is to be noted that, although since Shelyubskii's times the habit of using $\Delta T_{1/2}$ was maintained, it is possible to use other bandwidths ΔT_n replacing the ln 2 of equations (7 and 8) by $(-\ln n)$. If it is desired to work under such conditions that equation (1) is still valid, care must be taken of the fact that to the selected bandwidth such a Δn value corresponds that $\xi \leqq 0.1$. On the other hand, if it is desired to consider many points of the $\tau_0(T)$ or $\tau_0(P)$ curves, the parabola method introduced by Hilbig et al. [147] may be used. Replacing in equation (1) of table 1 Δn by $(\bar{n}_1 - a - b\,T)$, these authors obtained:

$$-\ln \tau_0 = A + B\,T + C\,T^2\,, \tag{9}$$

where $A = \alpha\,[(\bar{n}_1 - a)^2 + \sigma_n^2]$; $B = 2\,\alpha\cdot b\cdot(\bar{n}_1 - a)$; $C = \alpha\cdot b^2$ and $\alpha = k\cdot\lambda^{-2}\cdot d\cdot z$. Once the values of A, B and C are obtained which fit the experimental data, σ_n^2 may be evaluated by solving the preceding equations if a and b are known previously. This method can also be applied if P is varied instead of T replacing a and b by the corresponding parameters for the pressure dependence of n_2.

It would be very convenient to have some equations like the previous ones for the case in which the wavelength is varied, because this is the simplest way of varying τ_0, which does not need special devices and which precludes the formation of refractive index gradients in the liquid phase. However, as already said, $\Delta\bar{n}$ does not vary linearly with λ and n_1 also varies in this case, so that if a two-point method is to be utilized, it is necessary to measure previously the value of Δn corresponding to the selected wavelength and later to use equation (1) or equation (2) directly remembering that at τ_M the value of Δn is zero.

An equation similar to equation (9) may be derived taking in account the complex variation of the refractive index with wavelength. Hilbig tried this using three different equations for $n(\lambda)$ [149, 153 and 154]: in the first paper he used $n(\lambda) = c_0 + c_1\,\lambda^{-1} + c_2\,\lambda^{-2}$ and in the second he used Cauchy's formula, according to which $n(\lambda) = c_0' + c_1'\,\lambda^{-2} + c_2'\,\lambda^{-4}$. The equations obtained by replacing $\Delta n(\lambda)$ in equation (1) of table 1 are very complicated and it is only possible to solve them with approximations which generally imply that c_2 and c_2' are neglected. It seems that those equations were not applied in practice and in their last paper, where experimental data were presented, Hilbig and Groll [154] utilize a hybrid method which consists of the determination of $\tau_0(\lambda)$ curves at three different temperatures at least. Such a method is perhaps not so time-consuming as the determination of $\tau_0(T)$, but the operational aspect is more complicated. Supposing that $\bar{n} = c_0'' + c_1'' \lambda + c_2'' \lambda^2$, with $c_0'' = a + b\,T$, it can be deduced from equation (1) of table 1 that:

$$\sigma_\mathrm{n}^2 = (k \cdot d \cdot z)^{-1} \cdot y_\mathrm{min} \,, \tag{10}$$

where $y = -\,\lambda^2 \ln \tau_0 = k \cdot d \cdot z \cdot (c_0'' + c_1'' \lambda + {} + c_2'' \lambda^2)^2 + y_\mathrm{min}$. In order to obtain the value of $k \cdot d \cdot z$ necessary for the evaluation of σ_n^2, a parabola is fitted to the function $z(\lambda) = (y - y_\mathrm{min})^{1/2}$ at at least three different temperatures. The constant term of this parabola is $(k \cdot d \cdot z)^{1/2} \cdot c_0''$, which is plotted as a function of T, where of $k \cdot d \cdot z$ may be obtained if the value of b is known.

The following methods were suggested for the case of absorbing phases. Budd and Blanchard [150] multiplied equation (1) of table 1 by an absorption factor independent of wavelength, which was called "dust factor". In order to determine σ_n^2 using the resulting empirical equation, it is necessary to know the $\tau_0(T)$ curves at at least two different wavelengths, resulting in:

$$\sigma_\mathrm{n}^2 = \frac{\ln \tau_\mathrm{M}(\lambda_2) - \ln \tau_\mathrm{M}(\lambda_1)}{k \cdot d \cdot z \cdot (\lambda_1^{-2} - \lambda_2^{-2})} \,, \tag{11}$$

where $k \cdot d \cdot z$ may be obtained from the slope of any of the $\ln \tau_0$ vs. $(T - T_\mathrm{M})^2$ plots corresponding to the selected wavelengths.

The fact that the values of $k \cdot d \cdot z$ obtained from each plot were generally different and that if three different wavelengths were selected, the values of σ_n^2 calculated by means of equation (11) using the different possible pairs did not coincide [155], promoted the development of two alternative methods. In one of them, which is empirical, equation (8) was used at two different wavelengths with transmission data obtained by means of a spectrophotometer with a glass plate inserted in the path of its reference beam. The glass was the same as the tested one and its thickness was such that the values of σ_n^2 obtained at both wavelengths coincided [155]. The other method [106] was based on equation (6) of table 1, from which σ_n^2 may be calculated by means of the parabola method if α is replaced by $\alpha' = k \cdot d \cdot z \cdot \lambda^{-2} [1 - {}^1\!/_2\, (a_1 - a_2)\, d]$ and a term $\bar{a} \cdot z$ is added to A in equation (9).

The methods based on equation (4) in table 1 will now be considered in order to finalize this review of methods for the evaluation of σ_n^2. Since it is very complicated to evaluate σ_n^2 using equation (4) of table 1, Vidro and Khorol'skii obtained expressions for $\tau(\lambda_\mathrm{Chr})$ and $\Delta\lambda_{1/2}$ as functions of σ_n^2 (the last of them being valid if Δn varies linearly with λ and if $\xi \leqq 0.5$). These expressions indicate that, for the usual dispersed and dispersing phases, $\tau(\lambda_\mathrm{Chr})$ is more sensitive to variations of σ_n^2 if $\sigma_\mathrm{n}^2 \lesseqqgtr 10^{-7}$ and that if σ_n^2 is smaller, the most sensitive parameter is $\Delta\lambda_{1/2}$. For this reason, the just cited authors suggested that $\Delta\lambda_{1/2}$ could be used to characterize the homogeneity of technical glasses and $\tau(\lambda_\mathrm{Chr})$ to characterize that of optical glasses [148 and 156], bearing in mind that if different glasses are compared, the same liquid must be used and the temperature must be adjusted in such a way that the value of λ_Chr is always the same, if that is not the case the observed variations of $\Delta\lambda_{1/2}$ could be due not only to the different values of σ_n^2 but also to the different values of Δn.

2.3. Experimental evidence

The experimental verification of the equations listed in table 1 has an additional difficulty with respect to those of part 1, which is the result of a dispersed phase of known σ_n^2. Mixtures of optical glasses were generally used, for which:

$$\sigma_\mathrm{n}^2 = \sum_i q_i \left[(\bar{n}_i - \bar{n}) + \sigma_{\mathrm{n}i}^2 \right] , \tag{12}$$

where $\bar{n} = \sum_i q_i \, \bar{n}_i$, and the subindex i refers to the different glasses of the mixture. The problem here is to know the value of $\sigma_{\mathrm{n}i}^2$. In the case of the most homogenous optical glasses, the manufacturers guarantee variations of the refractive index equal as or less than $1 \cdot 10^{-6}$ with respect to the mean value; in normal optical glasses these variations can be in the order of 10^{-5}. Thus, if in all the tested samples the observed variation reached the allowed maximum, $\sigma_{\mathrm{n}i}^2$ would range from 10^{-10} to 10^{-12} in this worst case. But it must be remembered that the control measurements of the refractive index of optical glasses are performed on samples larger than the grains of the dispersed phase of a Christiansen filter, so that in the last case $\sigma_{\mathrm{n}i}^2$ can be larger than the quoted values for reasons discussed in the introduction. This fact is also confirmed by computer simulations recently carried out [202] on models constructed by piling up glass cubes with $d = 0.15$ mm, sampled at random from a population of known σ_n^2, with the purpose of studying the relation between σ_n^2 and the maximum difference in optical path length (which corresponds roughly to the range of refractive index within a glass slab 1 cm thick). The calculated values of this last property were always about one order of magnitude lower than those of $\sqrt{\sigma_\mathrm{n}^2}$. The way in which this problem was faced by different authors will be indicated when commenting their experimental work. The values of σ_n^2 obtained from equation (12) will be designated from now on as "calculated" ones, and those evaluated from the transmission data of a Christiansen filter by one of the methods discussed in section 2.2. as "experimental" values.

Although since the first works on the subject by Shelyubskii, optical glasses and mixtures of them have been used to illustrate the sensitivity of the method to small variations of homogeneity due to the addition of a small fraction of an optical glass to another, the experiments have only been qualitative and the experimental and calculated values of σ_n^2 have not been obtained and compared. The first in proposing such a comparison was Imagawa [121], who used however the experimental data of Shelyubskii [146] probably with an assumed value of $\Delta T_{1/2}$, since this value is not given in Shelyubskii's work.

The first experimental work where such a comparison was performed with original data was that of Sakaino et al. [151 and 152]. They used mixtures of two optical glasses whose difference of refractive indices was $\Delta\bar{n}_1 = 8 \cdot 10^{-4}$. The technique of the variation of P at constant T and λ (591 nm) was employed and for the evaluation of the experimental data equation (8) with $\beta = 5$ was used. The characteristic parameters of their filter had the following values: $\xi \leqq 1.2$; $z/d = 87$; $\theta_c = 4 \cdot 10^{-3}$ and $\lambda/d = 5 \cdot 10^{-3}$, so that the conditions of validity of equation (2) in table 1 were not entirely fulfilled (see table 1). The values of σ_{ni}^2 necessary for the application of equation (12) were obtained from Christiansen filters made with grains of one optical glass alone, using equation (8). Such a procedure is valid if it is confirmed later that equation (2) of table 1, and thus equation (8), are valid. Proceeding in such a way, a satisfactory coincidence was verified between experimental and calculated values of σ_n^2 in four mixtures of optical glasses with $\sigma_n^2 \leqq 1.7 \cdot 10^{-7}$; for larger values of σ_n^2 the coincidence was not so good (they tested mixtures with calculated values of σ_n^2 of up to $2.3 \cdot 10^{-7}$). The value of $\beta = 5$ used in this work was considered too high by Cable and Walters [157], since if the grains were spherical and $q_1 = 0.5$ it would be 3 (see equation (2b) in table 1), but it must be remembered that $q_1 = 0.5$ is a usual value in conventional Christiansen filters and Sakaino et al. worked at high pressures, which could cause a closer packing of the grains and thus justify larger values of β. Cable and Walters also pointed out that the mixtures for which experimental and calculated values of σ_n^2 show a better agreement are those where the terms depending on σ_{ni}^2 in equation (12) have the largest weight (45 to 83 %) and, as the values of σ_{ni}^2 were obtained from the same equation to be tested, this is not a truly independent test of that equation.

The following work on the subject was performed by the already cited Imagawa [135], who worked in the range of validity of equation (2), since in his experiments: $\Delta\bar{n}_1 = 2.6 \cdot 10^{-4}$ (in two cases this value was higher: $4.0 \cdot 10^{-4}$ and $6.8 \cdot 10^{-4}$ respectively); $\xi \leqq 0.4$; $z/d = 112$; $\theta_c = 1 \cdot 10^{-3}$ and $\lambda/d = 6 \cdot 10^{-3}$. The experiments were performed varying T at constant P and λ (546.1 nm), σ_n^2 was evaluated by means of the parabola method and the values of σ_{ni}^2 were neglected in equation (12). Imagawa verified in this way a correlation between $\ln \tau_0$ and $(\Delta\bar{n})^2$, as required by equation (2) of table 1 and similar ones; he also verified a linear correlation between $(-\ln \tau_M)$ and the calculated values of σ_n^2. According to equation (2) the slope of that straight line should be $\alpha \cdot \beta$ and the ordinate at the origin zero. In this work the slope was equal to the value of α (which was obtained from the $\ln \tau_0$ vs. $(\Delta\bar{n})$ curve) multiplied by 4.3, a reasonable value for β which is in the range of theoretical values that can be calculated by means of equation (2b) of table 1 considering that in this work $q_1 = 0.54 \pm 0.04$. The ordinate at the origin however was not zero, a fact which was attributed by Imagawa to a "parasitic scattering" due to other causes than the variations of refractive index (it may be thought in small effects such as acceptance of a small fraction of scattered radiation by the detector, divergence of the beam (see section 3.7.), slight impurifications of the glass grains (see section 3.4.) and a small contribution of the neglected values of σ_{ni}^2 as possible causes). Thus, it can be accepted that this set of experimental data supports the validity of equation (2) in table 1 in respect of its functional dependence on $\Delta\bar{n}$ and σ_n^2 in the investigated range of values of $\Delta\bar{n}$ ($\Delta\bar{n} \leqq \leqq 5 \cdot 10^{-4}$) and σ_n^2 (6 mixtures with $\sigma_n^2 \leqq 4.5 \cdot 10^{-8}$) and for $\tau_0 \geqq 0.5\,\tau_M$.

As can be seen in the preceding works, the range of values of σ_n^2 for which equation (2) of table 1 or similar ones are theoretically valid is very narrow. Since in practice larger values of σ_n^2 are also of interest, the relation between the calculated values of σ_n^2 and those obtained using equation (2) or similar ones beyond their range of validity was studied. In these cases, the contribution of σ_{ni}^2 in equation (12) is generally negligible, so that the problem of its determination does not arise.

The first work of this kind was that of Cable and Walters [157], who scanned the range $4.9 \cdot 10^{-7} \leqq \sigma_n^2 \leqq 1.1 \cdot 10^{-5}$ by means of mixtures of two or three optical glasses. The experimental parameters were: $\Delta\bar{n}_1 = 6.8 \cdot 10^{-3}$ (and in some cases up to $1.47 \cdot 10^{-2}$); $z/d = 45$; $\theta_c = 0.03$ and $\lambda/d = 3 \cdot 10^{-3}$; the experiments were performed varying the wavelength at constant T (37 °C) and P. These authors verified a good correlation between the calculated values of σ_n^2 and those obtained from transmission data evaluated by means of equation (2) of table 1 with $\beta = 3$ and neglecting the variation of α with the wavelength. The experimental values were always smaller than the calculated ones and the correlation was not linear. The experimental values of α varied with σ_n^2 (in one set of experiments a linear relation was verified between α and $(\sigma_n^2)^{-0.46}$), which is in contradiction with equation (2) of table 1 that predicts a constant value of α. Imagawa [135] also observed a slight diminution of α with increasing σ_n^2.

In the other available work, Inoue et al. [158] studied the range $5 \cdot 10^{-9} \leqq \sigma_n^2 \leqq 4.4 \cdot 10^{-6}$ using 27 mixtures of two to seven optical or experimental glasses. The technique used by these authors was the same as in their first paper [152] and the experimental data were evaluated by means of equation (8) with $\beta = 4$. The values of σ_{ni}^2 were considered negligible in the case of optical glasses and were determined by the method to be tested in the case of the experimental glasses which were melted in laboratory scale. The value of $\Delta\bar{n}_1$ was in the range $1 \cdot 10^{-4}$ to $5.7 \cdot 10^{-3}$, but in the majority of the mixtures $\Delta\bar{n}_1 \geqq 9 \cdot 10^{-4}$. A non-linear correlation between the calculated and experimental values of σ_n^2 was shown, the experimental values being four to eight times larger than the calculated ones. It was also shown that in the case of mixtures with equal proportions of two optical glasses with $\Delta\bar{n}_1 = 3.3 \cdot 10^{-3}$, it is necessary to use filters with $z/d \geqq 13$ because for smaller values of that parameter the $\tau_0(P)$ curve shows two maxima and it is impossible to evaluate σ_n^2. This is probably due to the fact that in cells with small values of z/d, the glass grains are not distributed at random and the radiation traverses mainly grains of one of the glasses, and the filter acts as two superposed filters of homogeneous grains with even smaller values of z/d and thus poor efficiency. The treshold value of z/d and the explanation given by Inoue et al. seem to be valid under other conditions, since in independent experiments Lenhart [159] did not observe the two maxima in mixtures with similar proportions of glasses whose refractive indices differed by $3 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ using filters with $z/d = 23$.

Another experiment of this kind was recently performed by Varshneya et al. [204], who used 5 mixtures of 2 borosilicate glasses which scanned the range $3.18 \cdot 10^{-6} = \sigma_n^2 = 8.41 \cdot 10^{-6}$. They employed the technique of variation of λ at constant temperature (34 °C) and pressure; the experimental parameters were: $\Delta\bar{n}_1 = 5.7 \cdot 10^{-3}$; $z/d = 22$; $\theta_c = 0.03$ and $\lambda/d = 3 \cdot 10^{-3}$. σ_n^2 was evaluated by the parabola method and a correlation between the experimental and calculated values of σ_n^2 was verified, the former values being always smaller than the latter ones.

2.4. Final remarks on the theories of the Christiansen filter with inhomogeneous dispersed phase

All the available expressions are based on wave optics. The majority of them which are derived from Raman's treatment (see equation (5), see table 1 in part 1) and equation (4) in table 1, which is the only one not directly derived from Raman's equation, can be reduced to equation (2b) in table 1 if $\sigma_n^2 \leqq 0.4\,\pi^2\,\lambda^{-2}\,d^2$. Thus, if the validity of equations (1 or 2) can be proved experimentally, the validity of all the other available equations would be shown, so that it is not surprising that all the experimental works were concentrated on those equations.

The available data demonstrate the dependence of equation (2) in table 1 on $(\Delta\bar{n})^2$ and σ_n^2 in conditions similar to those theoretically predictable. The other variables were held constant in all the experiments and thus there is no evidence on the dependence of equation (2) of them. In fact, Imagawa [135] observed a small variation of the parameter α, which includes those variables, with $\ln \tau_M$ (and thus with σ_n^2). Although it might be suspected that this variation is due to an incorrect dependence of equation (2) in table 1 on those variables, it can be seen that it may also be explained without considering that hypothesis. The fact that α decreases as σ_n^2 increases suggests that this variation of α is due to an increase of the band-width (the experimental value of α is inversely proportional to it), which is in turn due to the sensing of scattered radiation by the detector, since the proportion of scattered radiation that may reach it increases with Δn and thus with σ_n^2. The values of α obtained by other authors [157], who worked under such experimental conditions that equation (2) is not expected to be valid, showed the same trend, a fact which is coherent with the preceding explanation (see also section 3.7.). This fact could be cleared up by means of Monte Carlo simulations of ray tracing, such as those recently performed by Varshneya et al. [204].

The values of σ_n^2 predicted by equation (2) in table 1 still remain correlated with the calculated ones outside the range of validity of that equation, where the values of σ_n^2 usual in commercial glasses may lie. In one case the experimental values were found to be smaller than the calculated ones [157 and 204] and in other cases they were always larger [152 and 158].

Thus, it can be concluded that the experimental values of σ_n^2, evaluated with the equations (1 and 2), are correlated with the calculated ones within the whole range of usual values. The parameters of that correlation can be predicted theoretically only in the range of validity of the equations (1 and 2) of table 1, where both values are equal. Outside that validity range the correlation parameters depend on the experimental conditions in a way which remains still unexplained. Therefore, the experimental conditions which assure an optimum correlation must be determined empirically and the conditions used by different authors will be reviewed in the next section in order to find those for which the reproducibility is better, analyzing the causes of the differences observed between the results of different authors.

3. Experimental aspects of the application of Shelyubskii's method and its variations

The preparation of a Christiansen filter implies the selection of an appropriate immersion liquid (dispersing phase) and the preparation of the grains of the glass to be tested. The grain preparation involves the following steps in turn: crushing, sieving, washing, drying and eventually annealing. Powder and liquid (liquid-glass filters are the only ones used in the characterization of glass homogeneity) are subsequently mixed in a cell of length z in such a way that a reproducible distribution is attained. Finally, the cell is irradiated scanning a range of wavelengths at constant T and P or varying T or P at constant λ, and its transmittance is measured by means of a detector with cut-off angle θ_c.

All these experimental steps will be considered in the next paragraphs, paying attention to their influence on the measured values of σ_n^2.

3.1. Immersion liquid

There were no difficulties for finding appropriate liquids for testing glasses or other dispersed phases with $1.458 \leqq n_D^{20} \leqq 1.645$, using the method of variation of temperature. In that range, pure liquids are available which are more suitable than the liquid mixtures since their refractive index can not vary by volatilization of one of their components. Many authors gave tables with the variation of the refractive index of various liquids with the temperature [150, 160, 161, 163 and 164], which can be used as a guide for the selection of an appropiate liquid for the glass to be tested. These collected values can be introduced in the equations (7 to 9) for the calculation of σ_n^2 if a series of comparative measurements is performed, but if precise measurements are desired, it would be advisable to measure previously the coefficient of variation of the refractive index of the selected liquid with temperature since the collected values can vary within a wide range. For example, the collected values of b for one of the most commonly used liquids, the chlorobenzene, range from $5.0 \cdot 10^{-4}\ \mathrm{K}^{-1}$ to $5.5 \cdot 10^{-4}\ \mathrm{K}^{-1}$, and if the extreme values were introduced in equation (7), the obtained values of σ_n^2 would differ by 18 % only for that reason. With respect to the variation of the refractive index with pressure, there are data in [152 and 153], where the technique of variation of P at constant T and λ was applied. Only glasses with $1.514 \leqq n_D \leqq 1.527$ were tested using this technique.

The data of the variation of n_1 and n_2 with λ, necessary if the original version of the Christiansen filter is used, are scarce and generally they must be determined previously.

3.2. Crushing

The majority of the authors who used this method did not give details of the method adopted for crushing their sample. Since this step determines the shape of the grains and thus the value of k in equations (1 and 2) of table 1, it would be worthy to study it in detail.

Mortars of porcelain, steel and agate as well as agate ball mills were used to crush the samples. When a percussion mortar (generally of steel) is used, it is recommended to put only one layer of glass fragments and strike once in order to avoid producing aggregates of fine particles [125] and excessive abrasion, following the technique of preparation of grains for the determination of glass durability developed by Sykes [165]. On the other hand, Paoletti [161] indicates that the use of ball mills allows to obtain nearly spherical particles, which would result in an improved reproducibility, but more experimental evidence is needed to support this hypothesis.

3.3. Particle size of the glass

Particle sizes ranging from 0.053 to 0.40 mm were used in the preparation of Christiansen filters for the determination of σ_n^2. These are average values, since actually a range of particle sizes determined by the used sieves is present in the filter. This range was in the order of 15 to 80 % of the largest particle size present in the fraction, but in the majority of the cases it was between 15 and 25 %.

The optimum grain size should be very small if it is desired to work under such conditions that the equations (1 and 2) of table 1 are valid. However, as can be seen in table 1, even in the case of very fine particles, σ_n^2 should be smaller as it is in commercial glasses (for instance, $\sigma_n^2 \leqq 9 \cdot 10^{-8}$ if $d = 0.057$ mm) so that the just cited equations are valid. Thus, it is not advisable to work with such particle sizes, which are experimentally difficult to obtain and which can impair the reproducibility of the results, as will be seen later. On the other hand, and remembering the discussion about the effect of the sample size on the measured homogeneity of a body (see section 1.), it is to be expected that σ_n^2 increases with decreasing particle size or, if the initial grain size is smaller or much larger than that of the inhomogeneities that σ_n^2 remains constant with decreasing particle size.

There are some data on the dependence of σ_n^2 on d, although contradictory. Schilling and Weiss [160] did not observe variations of σ_n^2 with particle sizes ranging from 0.06 to 0.50 mm, in experiments performed presumably on optical glass. La Due [166] and Rykiert [163] noted a slight increase of σ_n^2 as d was decreased from 0.14 to 0.07 mm in container glass or from 0.12 to 0.10 mm in flat glass, respectively. Paoletti [161] reports a similar trend, although without giving the experimental data. All these results are in accordance with the former statements, but for particle sizes larger than those recently mentioned, an anomalous increase in σ_n^2 with increasing d was noticed by the just cited La Due [166] between 0.21 and 0.59 mm and by Šultéty [164] between 0.18 and 0.63 mm. The data recently obtained by Inoue et al. [202] show a similar trend: σ_n^2 decreases as d increases up to 0.25 mm, while for larger grain sizes (up to 0.42 mm) σ_n^2 does not show a clear relation with d. Since all these determinations were performed at constant cell length, the number of grains traversed by the radiation (which is proportional to z/d) decreases as d increases, a fact which introduces two problems. First, if only a few grains are traversed by the radiation, the sample may not be representative and second, in this case the separation of the scattered and directly transmitted radiation is very poor. Škultéty verified a linear relation between σ_n^2 and d and therefore it is not probable that this behaviour is due to a lack of representativeness of the sample, which would cause a random relation between both variables. Thus, the second explanation remains, which is reasonable since if scattered radiation reaches the detector in increasing proportion as d increases, the bandwidth will increase more than predicted by equation (1) (see section 2.4.) and with it the measured values of σ_n^2 (see equation (7)). It must also be remembered that a correlation between the measured and calculated values of σ_n^2 was only verified for dispersed phases with grain sizes between 0.15 and 0.22 mm and $z/d > 13$ (see section 2.3.). In other conditions, this correlation can fail and thus the variations of the experimental value of σ_n^2 will not necessarily reflect those of the actual value. Inoue et al. [202] obtained their values of σ_n^2 by extrapolating τ_M and ΔP to $\theta_c = 0$; for this reason the scattered radiation should not be a source of errors, but probably the extrapolation does not eliminate the scattering contribution if d is large (section 3.7.).

The experimental problems mentioned above, which arise when working with small grains, are due mainly to the difficulty of separating those grains from the smaller ones (the "dust"). If the dust is not eliminated, it is to be expected that values of σ_n^2 larger than the actual ones will be measured due to the smaller sample size that it represents and to the contaminants that it can include. This supposition is supported by experimental data of Rykiert [162] who observed an increase of 6 % in σ_n^2 when 5 % of dust were added to a clean fraction of grains of 0.10 to 0.12 mm size. It is thus evident that the values of σ_n^2 obtained using fine grains will depend strongly on the efficiency of the washing procedure since it must eliminate the dust and the contaminants arising from the prolonged crushing needed to obtain those grains. La Due verified [165] differences of 600 % between values of σ_n^2 measured on grain fractions with $d < 0.07$ mm washed and without washing, while for larger particle sizes these differences decreased to 60 %. It was also verified that if the dust is not eliminated, the transmittance of the filter varies with time, impairing the reproducibility of the measurements.

3.4. Washing, drying and annealing

This step is very important because it should remove all the inhomogeneities introduced during the crushing and sieving of the glass and also the "dust" which could adhere to the glass grains (see section 3.3.). The importance of this step was recognized since the early times of the application of the Christiansen filter as monochromator and is one of the most thoroughly studied aspects of the preparation of these filters.

The most efficient way to eliminate the adhered dust is the rinsing and decanting with organic solvents, as showed in the studies on sample preparation for glass durability tests [165]. This procedure was used by all who worked with Christiansen filters after Weigert and Staude [13], using mainly acetone, although methanol and ethanol were also used. The original method of Sykes [165] for the preparation of samples for glass durability tests includes also scouring in ethyl ether in order to remove agglomerates of fine grains. However, Afghan [93] showed that these agglomerates did not have any appreciable effect on the transmission spectrum of the filter if the glass was properly crushed (see section 3.2.) and since the scouring can introduce polyethylene particles (it is performed in a polyethylene beaker with a polyethylene spatula) which do not affect the durability test but can impair the determination of σ_n^2, it was concluded that ether scouring did not have any appreciable advantage in this case.

If the crushing is performed in a metallic percussion mortar, as usual, the grains can be contaminated with metal particles, which can also arise from the sieves, generally with metallic meshes. In the just cited method of Sykes these impurities are removed magnetically, but in the preparation of Christiansen filters a more effective process should be used, since these impurities are here more critical than in durability tests. Thus, it was suggested to treat the grains with diluted acids. Weigert and Staude [13] were the firsts to do this, using HCl, and later almost all the authors who crushed in metallic mortars included washings with that acid or HNO_3 in the preparation of the filter. A complete research on the efficiency of washings with organic solvents and/or diluted acids was carried out by Moore [166] who, based on determinations of the transmittance of the filter and scanning electron micrographs of the surface of the grains, concluded that the cleanest grains were obtained washing with 3N HCl for 5 min at room temperature, decanting the acid, rinsing three times with deionized water and finally rinsing and decanting three times with acetone.

It is important that before washing the grains in such a way, their chemical durability is verified, since otherwise important mistakes may arise, as can be inferred from an experiment performed by Paoletti [162]. He carried out a previous hydrolytic attack on the grains which were subsequently used for the determination of σ_n^2 and found that while the values of σ_n^2 for grains of borosilicate glass did not vary after treatments of up to 2 h, the same treatment could increase the value of σ_n^2 by 400 % in less durable glasses. In such glasses, different values of σ_n^2 were obtained with grains which were exposed different times to air before the measurement. This fact must be considered in the drying steps of such grains after their washing, which should be carried out in vacuum.

With respect to the possible impurifications introduced by the crushing in non-metallic mortars or mills, there is no information available on the extent of such impurification and its possible effects.

In almost all the cases the grains were dried at temperatures between 105 and 150 °C for 0.5 to 1 h, in some cases under vacuum. Only in two cases where the glass grains were washed with methanol, it was dried at 50 °C and 80 °C [154 and 166].

All the washing procedures just described can remove inhomogeneities due to strange particles which contaminate the glass grains, but since the early times of the utilization of Christiansen filters it was thought that the crushing could introduce a thin stressed layer in the grain surface, which would also cause spurious inhomogeneities of the refractive index. For this reason it was recommended to anneal the glass grains at temperatures between 190 and 300 °C during some days [13 and 21]. However, an annealing at 190 °C during 3 d had no appreciable effect on $\tau(\lambda_{\mathrm{Chr}})$ and the bandwidth of the filter according to Denmark and Cady [21]. Later, Afghan [93] annealed optical glass grains 30 min at 560 °C, cooling them thereafter at rates of -0.1 or -1 K/min. He observed a variation of $\bar{n}_1$ (as expected, the largest value corresponded to the fraction cooled at the slowest rate) and slight variations of $\tau(\lambda_{\mathrm{Chr}})$ (an increase of 0.8 % and a decrease of 1.3 % with respect to the value corresponding to unannealed grains). Since the decrease in transmittance was observed in the fraction which was cooled more slowly and therefore should be less stressed, it is probable that it is due to other factors than the annealing, whose effect would thus be negligible.

On the basis of a paper by Debye and van Beek [168], it was suggested [93 and 125] that another impurification factor could be the presence of a thin adsorbed film of water on the grains. In the just cited paper by Debye and van Beek, an expression is derived for the transmittance of spheres immersed in a liquid of the same refractive index and with a thin adhering layer of different refractive index. This was done by resolution of Maxwell's equations for the case of radiations that occur at different angles on a thin layer, without considering multiple scattering. In order to verify their expression, those authors prepared Christiansen filters with glass grains obtained from standard flint glass rods, which were immersed in a benzene-bromobenzene mixture without washing or washed with water and dried at 100 or 500 °C (washing and drying procedures and times were not specified). At a drying temperature of 500 °C a weight reduction was verified, which was assumed to be due to the elimination of the adsorbed water film and on that basis a film thickness was calculated, which was 27 to 45 % higher than the theoretically predicted thickness. The difference was attributed to the irregular shape of the grains. Two aspects of the experiments carried out by Debye and van Beek are surprising when compared with the subsequent experimental work on the Christiansen filter. First, the difference of 190 nm between the values of λ_{Chr} of a filter prepared with grains without washing and another with grains washed with water and dried at 100 °C is large when compared with the shifts which were reported to be less than 1 nm after a washing procedure with water and acetone and drying at 150 °C [167]. Second, a value of $\tau(\lambda_{\mathrm{Chr}}) = 1$ was reported for filters prepared with grains dried at 500 °C, while other authors did not reach such a high transmittance in filters carefully prepared with more homogeneous optical glasses and similar thermal treatments and equipment. Thus, it would be desirable to carry out carefully planned experiments in order to clarify these facts and prove the existence of the adsorbed water layer.

It is probable however that the two just commented surface effects would only be of importance if very homogeneous glasses are tested and it is desired to obtain values of σ_n^2 approaching those predictable from macroscopic determinations (see section 2.3.). As can be seen in table 2, the values of σ_n^2 obtained by different authors for different optical glasses remained larger than 10^{-8} until the cut-off angle of the detector was substantially reduced (this aspect will be commented in detail in section 3.7.). Under the determinations performed with small cut-off angle detectors, the lowest value of σ_n^2 was obtained etching the grains with a 1 % HF – 5 % H_2SO_4 solution. Even if new measurements would confirm the efficacy of this washing procedure, it should be applied with care and preferably only on optical glasses. This is because in optical glasses the inhomogeneities are weak and regularly distributed, so that the etching will be even and variations of the surface composition will not appear (as showed in [169] by means of ion microanalysis). In more inhomogeneous glasses different parts of the sample may be etched to a different extent, which is in fact the basis of the already commented etching technique of Löffler (1 % HF during 6 min) [140]. When this etching procedure is applied to other optical glasses or grain sizes than those tested in [169], the optimal etching parameters should be determined again, since otherwise its effects can be contrary to the desired ones, as can be seen from the experimental data

Table 1. Equations for the transmittance of Christiansen filters with inhomogeneous dispersed phase

equation, author and reference	filter model	physical assumptions and mathematical approximations	final expression
equation (1), Shelyubskii [137, 145 and 146]	The same as in equation (5), see table 1 in part 1, but the different layers which constitute the filter have different n_1 values.	The same as in equation (5), see table 1 in part 1 (reflection was neglected, $\xi \cdot (q_{1r} - q_{1s}) \leqq 0.1$ and z/d large).	$\tau_0 = \exp\{- k \cdot \lambda^{-2} \cdot d \cdot z \cdot [(\Delta\bar{n})^2 + \sigma_{\mathrm{n}}^2]\}$, where k was defined in equation (5), see table 1 in part 1.
equation (2), Imagawa [121]	The same as in equation (5), see table 1 in part 1, but the dispersed phase is now inhomogeneous and randomly distributed in each layer.	The same as in equation (1) of this table and it is also supposed that each layer has the same value of σ_{n}^2 (see equation (7) in [121]) and $2\pi \cdot \lambda^{-1} \cdot d \cdot q_{1s} \cdot \mid n_{1r} - n_{1s} \mid \leqq 0.1 - \xi \cdot (q_{1r} - q_{1s})$ or $\mid n_{1r} - n_{1s} \mid \lessapprox 0.03 \cdot \lambda \cdot d^{-1}$ (see equation (5), table 1 in part 1 and equations (17, A5 and A8) in [121]).	$\tau_0 = \exp\{- k \cdot \lambda^{-2} \cdot d \cdot z \cdot [(\Delta\bar{n})^2 + \beta \cdot \sigma_{\mathrm{n}}^2]\}$, where k is the same as in equation (5), see table 1 in part 1 and a) $\beta = q_2^{-1}$ in the case of equation (5a), see table 1 in part 1; b) $\beta = \left(1 - \frac{4}{3} q_1\right)^{-1}$ in the case of equation (5b), see table 1 in part 1.
equation (3), Afghan [93]	The same as in equation (6), see table 1 in part 1, but each solid cubical block can have a different refractive index value.	Equation (A18) in [93] is valid if $2\pi^2 \cdot \lambda^{-2} \cdot d \cdot q_1 \cdot q_2 \cdot [(\Delta\bar{n})^2 + q_2^{-1} \cdot \sigma_{\mathrm{n}}^2]$ is small and z/d large (for instance, if the first quantity is $2 \cdot 10^{-3}$, z/d should be 200). Reflection was not considered (see equation (6), table 1 in part 1).	$\tau_0 = \exp\{- 4\pi^2 \cdot q_1 \cdot q_2 \cdot \lambda^{-2} \cdot d \cdot z \cdot [(\Delta\bar{n})^2 + q_2^{-1} \cdot \sigma_{\mathrm{n}}^2]\}$
equation (4), Vidro and Khorol'skii [148]	The same as in equation (10a), see table 1 in part 1, but each solid block has a different refractive index value.	The case $q_1 = 1/2$ is considered only. The glass refractive index should have a normal distribution with the same value of σ_{n}^2 for each layer. Reflection was not considered (see equation (10), table 1 in part 1).	$\tau_0 = \left\{\frac{1}{4} [1 + \exp(- 4\pi^2 \cdot \lambda^{-2} \cdot d^2 \cdot \sigma_{\mathrm{n}}^2) + {} + 2 \exp(-2\pi^2 \cdot \lambda^{-2} \cdot d^2 \cdot \sigma_{\mathrm{n}}^2) \cdot \cos (2\pi \cdot \Delta\bar{n} \cdot \lambda^{-1} \cdot d)]\right\}^{z/d}$
equation (5), Hilbig [149]	The same as in equation (14), see table 1 in part 1, but now in each layer the N rows of spheres which constitute the dispersed phase are divided in groups of N_i rows of spheres with refractive index n_{1i}.	The same as in equation (14), see table 1 in part 1 $\left(\mid (n_1/n_2)^{-1} \mid \leqq 0.005\right.$, detector at a great distance of the filter, reflection was neglected$\left.\right)$ and it is also supposed that σ_{n}^2 is the same for all layers (equation (39) in [149]).	$\tau_0 = \left\{1 - \frac{4}{9} \pi^5 \cdot C \cdot \lambda^{-2} \cdot d^2 \cdot [(\Delta\bar{n})^2 + \sigma_{\mathrm{n}}^2]\right\}^{z/d}$ (the second term of this equation is by a factor 2 smaller than equation (37) in [149], because an error of this magnitude was corrected in equation (29) in [149]). The constant C is the same as in equation (14), see table 1 in part 1.

equation (6), Hilbig [106]	The same as in equation (13), see table 1 in part 1, but the different layers which constitute the filter have different n_1 values.	The same as in equation (13b), see table 1 in part 1 ($\xi \leqq 0.5$; $a_1 \cdot d$ and $a_2 \cdot d \leqq 0.1$ and z/d great, reflection was not considered).	$\tau_0 = \exp\{-\bar{a} \cdot z - 4\pi^2 \cdot q_1 \cdot q_2 \cdot \lambda^{-2} \cdot z \cdot d \cdot [(\Delta\bar{n})^2 + \sigma_n^2] \cdot [1 - (a_1 + a_2) \cdot d/2]\}$, $\bar{a} = q_1 \cdot a_1 + q_2 \cdot a_2$

List of symbols:

τ_0 = transmittance for the directly transmitted radiation
λ = vacuum wavelength of that radiation
d = particle size of the dispersed phase
z = length of the filter
n_1, n_2 = refractive indices of the dispersed (1) and dispersing (2) phases, respectively
q_1, q_2 = volume fractions of the dispersed (1) and dispersing (2) phases, respectively
a_1, a_2 = Neperian spectral absorption coefficients of the dispersed (1) and dispersing (2) phases, respectively
σ_n^2 = variance of the refractive index of the dispersed phase
$\Delta n = \mid n_1 - n_2 \mid$
$\xi = 2\pi \cdot d \cdot \lambda^{-1} \cdot \Delta n$

The bars over the magnitudes denote mean values.

Table 2. Values of σ_n^2 for different optical glasses after equation (2) of table 1 with $\beta = 4$

author(s) and reference	optical glass	sample preparation and cut-off angle of the detector	method/evaluation of σ_n^2	$\sigma_n^2 \cdot 10^8$
Schilling and Weiss [160]	Zn crown (n_G = 1.51276 ± 0.00002)	Glass crushed in an agate mortar. Washed with ethanol. d = 0.3 to 0.4 mm. z = 10 mm. θ_c = 0.017.	$\Delta T/\sigma_n^2$ evaluated with equation (7).	1.32
Hilbig, Eifert and Ulrich [147]	n.d.	n.d.	$\Delta T/\sigma_n^2$ evaluated with equation (9).	68
Sakaino et al. [152]	BK-7 (1) BK-7 (2)	Glass grains washed with acetone. d = 0.105 to 0.125 mm. z = 10 mm. θ_c = 0.004.	$\Delta P/\sigma_n^2$ evaluated with equation (8) ($\beta = 5$).	8.32 6.90
Cable and Walters [157]	BSC 510644 BSC 517642 HC 524592	Glass crushed in a percussion mortar. Washed with 3N HCl, water and acetone. $\bar{d}$ = 0.222 mm. z = 10 mm. θ_c = 0.031.	$\Delta\lambda/\sigma_n^2$ evaluated with equation (2) neglecting the effect of the variation of λ and supposing $\beta = 3$.	2.84 2.62 1.53
Imagawa [135]	KF (n_e = 1.527)	Glass grains washed with acetone. d = 0.074 to 0.105 mm. z = 4 or 10 mm. θ_c = 0.001.	$\Delta T/\sigma_n^2$ evaluated with a method similar to equation (9) ($\beta = 4$).	0.51
Inoue et al. [202]	BK-7	Glass grains etched with 1 % HF – 5 % H_2SO_4 solution. d = 0.125 to 0.177 mm. z = 50 mm.	$\Delta P/\sigma_n^2$ evaluated with equation (8) ($\beta = 4$).	0.081

presented in [169] for longer etching times or higher acid concentrations.

3.5. Cell length

It was worked with cell lengths between 2 and 50 mm, but the most usual length was 10 mm. The optimum length depends on particle size since, as commented in the sections 2.3., 2.4. and 3.3., the quotient z/d should be fairly larger than 13. In experiments where that requirement was fulfilled, Schilling and Weiss [160] did not notice any difference between the values of σ_n^2 obtained for an optical glass using cell lengths of 5 mm ($z/d = 14$) to 20 mm ($z/d = 57$). It must be noted that a cell with a large z allows a more accurate distinction between values of σ_n^2 which differ by less than an order of magnitude, as can be seen from the equations (1 to 3) in table 1 and as was recently pointed out by Inoue et al. [202]. Experimental aspects must also be considered when the cell length is selected, since although it might be concluded from the preceding comments that a cell length as large as possible would be best, it must not be forgotten that with a larger cell length absorption would increase, complicating the evaluation of the results. Also, if the technique of temperature variation is used, temperature gradients would arise more probably in this case, which would introduce an error in the determination of σ_n^2. However, with an appropriate selection of the particle size, it is always possible to find a value of z that meets all the stated requirements.

3.6. Grain distribution in the cell

The filter is usually prepared by slowly dropping the glass grains in the cell filled about half-full with the chosen liquid. Sometimes it was proceeded otherwise, but there is evidence that with the first method the possibility of trapping air bubbles between the grains is very small, or the air bubbles are so small that they dissolve during the time required for the cell to reach constant temperature [93 and 160]. The cell filled with liquid and grains must be tapped in a standardized way in order to obtain an uniform packing of the grains. In a case where the grains were not uniformly packed by tapping the cell, a decrease of τ_M of 15 % was noticed [163]. Thus, it is desirable to attain an uniform and stable distribution of the grains in the cell in order to obtain reproducible values of σ_n^2. It was suggested that such a distribution could be reached by tapping 40 times [93].

3.7. Cut-off angle of the detector and aperture of the beam of radiation

The first determinations of the transmittance of Christiansen filters for the evaluation of σ_n^2 of the dispersed phase were performed in reformed [137 and 146] or automatized [170] photocolorimeters with cut-off angles in the order of the deciradians. Later, special equipments were constructed, whose detectors had cut-off angles in the order of the centiradians [160 and 171], or spectrophotometers with a similar acceptance angle were used [93, 125, 157 and 172]. Only in recent years, specially constructed equipments with acceptance angles of a few milliradians were often used [135, 151, 155, 158, 169 and 173]. Only with such cut-off angles the requirement $\theta_c < \lambda/d$ (see section 2.) is fulfilled in usual conditions and they were used before the just cited authors only by Vidro et al. [156] as they applied their method and by some investigators who used the Christiansen filter as monochromator (see section 3.2. in part 1).

As indicated in section 2.4., a detector with a too large cut-off angle can impair the determination of σ_n^2 because of a decrease in the parameter α, which would be more evident as θ_c increases. This would also explain why values of $\sigma_n^2 < 10^{-8}$ could be reached only as the cut-off angle of the detector, decreased down to a few milliradians (see table 2). A more direct evidence can be found in Shelyubskii and Megerdicheva's paper [172], where transmission data are obtained using a detector with $\theta_c = 0.21$ and adding an accessory which reduces θ_c to 0.035. In the case of an optical glass, this decrease of θ_c caused an increase of 3 % in τ_M and a decrease of 73 % in the half-bandwidth, which implied in turn a decrease of 95 % in σ_n^2; a similar effect was noted in flat glass.

Recently, determinations were performed positioning the detector at different distances of the cell and obtaining by extrapolation the values of τ_M and $\Delta P_{1/2}$ corresponding to infinite distance (that is, $\theta_c = 0$) [173 and 202]. The extrapolation is easy because τ_M and ΔP depend linearly on θ_c if $\theta_c \leqq 7.5 \cdot 10^{-3}$ [202]. Proceeding in such a way and using a He-Ne laser as source and glass grains washed with 1 % HF and acetone, surprisingly small values of σ_n^2 were obtained for glasses of normal homogeneity. It is not possible to say on the basis of the available data which of the cited factors were mainly responsible for these results, but in view of the above discussion it is probable that they were the equipment improvements. The given values for flat, hollow and pressed glassware ranged from $1 \cdot 10^{-9}$ to $2 \cdot 10^{-8}$, that is, values which in earlier works were obtained only for optical glasses. These values are however not so surprising considering that from macroscopical determinations of the refractive index at 24 points across a flat glass ribbon [174] a value of $\sigma_n^2 = 5 \cdot 10^{-10}$ can be calculated, which can be considered as an inferior limit for those measured using Shelyubskii's method (see section 2.3.).

Inoue et al. [202] verified that the dependence of τ_0 on θ_c can be expressed, if ΔP, σ_n^2, d, q_1, z and λ are constant, by:

$$\tau_c = \tau_0 + A \cdot R(\theta_c) \qquad (13)$$

where $R(\theta_c)$ is the fraction of radiation diffracted within the angle 0 to θ_c by a circular aperture [203] and A is a constant. The values of τ_0 obtained by extrapolating the straight lines of the τ_c vs. $R(\theta_c)$ plots at different values of ΔP, can be used to obtain the $\tau_0(\Delta P)$ curves, whose τ_{0M} and $\Delta P_{1/2}$ values differ on average with the ones obtained by extrapolation of the experimental values of τ_M and $\Delta P_{1/2}$ to $\theta_c = 0$, by 1.5 and 3 %, respectively, if $d < 0.25$ mm. Equation (13) can be justified theoretically starting from the most rigorous equation (9b), see table 1 in part 1, which tends to equation (13) if z/d is large or θ_c small (see equations IV (10, 11 and 14) in [110]). For low values of z/d or high θ_c values, the coincidence is not so good, which would explain why the difference between the values of τ_M and $\Delta P_{1/2}$ obtained by extrapolation and by equation (13), increases to 11 and 29 %, respectively, if d is larger than 0.25 %.

Although the most studied parameter of the optical system has been the cut-off or acceptance angle of the detector, there are other parameters which may alter the result of the determinations of σ_n^2. Schilling and Weiss [160] studied the influence of the aperture of the diaphragm that acted as secondary source in their equipment on the obtained transmission curves. If that aperture was high, similar values of σ_n^2 were obtained for every tested glass. These authors also studied the influence of the bandwidth of the monochromator (source) on σ_n^2 verifying increments between 9 and 16 % when it was increased from 1 to 10 nm. Remarkable improvements in these aspects and simplifications in the optical system may be expected from the use of lasers as sources, as has been done recently [173 and 175]. With them it is possible to obtain more parallel beams of small aperture without using optical systems. It would be interesting to repeat some calibration experiments, such as those cited in section 2.3., with this type of source since the transmission curves obtained in [175] using it show some differences with respect to those obtained using conventional sources as in [172].

3.8. Characteristic experimental aspects of the different versions of the method

In the original version of Shelyubskii's method, the temperature is varied at constant pressure and wavelength. In this case the heating rate is important because with a too high rate, temperature gradients would arise easier, which would in turn produce inhomogeneities in the refractive index of the liquid and since such inhomogeneities are not considered in the deduction of the equations of table 1, they would erroneously increase the value of σ_n^2. On the other hand, if the selected rate is too low, the measurements would be very time-consuming. The heating rates (in one case [166], the filter was cooled during the measurements) used in practice were between 0.1 and 4 K/min. Studies on the influence of this factor were performed by Cable and Bower [171], who measured temperature gradients of 0.7 K in a cell of 2.5 mm length heated at 1 K/min, by Schilling and Weiss [160], who obtained the same values of σ_n^2 using heating rates ranging from 0.1 to 1 K/min in a 10 mm length cell and by Škultéty [164], who verified a negligible increase of σ_n^2 (in the order of the reproducibility of its measurements) as he increased the heating rate from 0.1 to 1 K/min in a 10 mm length cell. Škultéty reported also an increase of σ_n^2 of 17 % with respect to the value corresponding to a heating rate of 0.1 K/min if the same cell was heated at 4 K/min. As discussed above, this increase of σ_n^2 is probably due to the formation of temperature gradients inside the cell, which cause inhomogeneities in the refractive index of the liquid.

It may be also inquired on the influence of the two parameters which are kept constant during the measurements in the original version of the method. In fact, only the wavelength could be of importance, since the small differences of the atmospheric pressure which could arise between different experiments have no influence on the refractive index of the phases of the Christiansen filter, as can be seen from the data published in [152 and 153]. With respect to the wavelength, La Due [166], who used wavelengths between 500 and 650 nm, noted variations of σ_n^2 which are within the reproducibility range of its measurements, while Paoletti [161] verified that σ_n^2 at 476 nm was larger than the corresponding value at 625 nm (10 % in the case of an optical glass and 22 % in an industrial glass). Although Paoletti, like Budd and Blanchard [150], connected that increase with the absorption by the glass, which would explain why it was smaller in the less absorbing optical glass, it must also be considered that the temperatures corresponding to τ_M were not the same at both wavelengths in the two glasses, but higher at the wavelength for the glass that showed the largest values of σ_n^2, so that it is probable that the cited increase was due to temperature gradients rather than to absorption effects, which are generally small in colourless glasses at those wavelengths.

The other versions of the method don't have the drawback of the formation of gradients, so that pressure or wavelength (according to the selected version) may be varied at rates so high as the response time of the detector allows. There are no studies on the influence of the parameters which are kept constant in these versions of the method on the values of σ_n^2 obtained by using them.

The additional experimental work of determining the refractive index of the solid as a function of λ arises if the wavelength is varied. In the case of optical glasses, these values can be supplied by the manufacturer, but they must be determined for other glasses. This can be done refractometrically, which implies the additional work, with respect to liquids, of grinding and polishing the samples and, if the glass is very inhomogeneous, of measuring many samples in order to obtain the mean value of n_1. Another way, proposed by Cable [125], is to use the Christiansen filter itself and determine the $n_2(\lambda)$ curves for a series of liquids using a set of optical glasses of known refractive indices (see section 4.5.) and subsequently determine those of the sample to be tested using those liquids.

In fact, many investigators varying the wavelength avoided these experimental difficulties by adopting Vidro and Khorol'skii's criterion and judging the homogeneity of the glass on the basis of $\tau(\lambda_{\text{Chr}})$ and/or $\Delta\lambda$ (see section 2.2.). Another way would be Hilbig and Groll's method [154], which was described in section 2.2., but some problems of it should be cleared before applying it. For example, values of σ_n^2 in the order of 10^{-8} were obtained for E-glass [154 and 176] although a detector with large cut-off angle was used (as may be deduced from the large reported values for $\Delta\lambda_{1/2}$ which were of 60 to 100 nm against usual values of 10 nm at the same wavelengths [26]) and no special washing was performed (excepting an annealing that would not affect the results, as discussed in section 3.4.). On the other hand, the reproducibility of their results is very poor (see section 3.9.) and the values of σ_n^2 obtained for mixtures of glasses are smaller than those corresponding to the pure glasses, which is contradictory. A reason for these abnormal results could be the expression used for $n(\lambda)$, which was not tested experimentally and which differs from the expressions due to Cauchy, Ketteler-Helmholtz, Sellmeier or Hartmann (which were applied with success to glasses in the visible spectrum) mainly because it does not include negative powers of λ. It was also suggested [176] that another reason could be that only a few experimental points (usually three) are used to determine c_0 (see equation (10)), but if more points were necessary, it would be simpler to use Shelyubskii's original method directly or perhaps that of Vidro and Khorol'skii, since the obtained values of $\tau(\lambda_{\text{Chr}})$ showed a good reproducibility.

3.9. Reproducibility and accuracy

The reproducibility of the method will be discussed here since it depends on all the other factors discussed previously in this section. The reproducibility measures the degree of constancy of that factors, attained by an author in a set of determinations on the same glass. The values of σ_n^2 obtained by different authors for the same glass in the same nominal conditions differed by: ± 4 % [150], ± 1 to ± 2 % [160], ± 4 to ± 18 % [147], ± 5 % [166], ± 2 to ± 4 % [161] and ± 2 % [164] (if a range of values is given, it corresponds to different glasses). These reproducibilities were all attained with the original version of Shelyubskii's method, where the temperature is varied and the results are evaluated by means of equation (7). As can be seen, they are similar in all the cases with exception to the value corresponding to [147], that belongs to the optical glass with an abnormally high value of σ_n^2 in table 2 and which is probably due to avoidable experimental failures (such as temperature gradients and too large cut-off angle).

As showed in [160], the reproducibility values of ± 1 to ± 2 % are due to the accuracy in the determination of τ_M and $\Delta T_{1/2}$. The errors corresponding to that parameters are related to that corresponding to σ_n^2 by:

$$\varepsilon(\sigma_n^2) = 2 \cdot \varepsilon(\Delta T_{1/2}) + \frac{\varepsilon(\tau_m)}{|\ln \tau_M|}, \qquad (14)$$

which may be deduced from the equations (7 and 8) and where ε is the relative error of the implied parameter. The largest source of error is probably the determination of the bandwidth, at least if the technique of variation of λ is used, as showed by statistical analysis by Cable and Walters [157], and thus it would be erroneous to neglect the corresponding term in equation (14) when $\varepsilon(\sigma_n^2)$ is calculated, as done by Shelyubskii [146] and many authors after him. Vidro et al. [156] reported that the values of $\Delta\lambda_{1/2}$ that they used in order to characterize the homogeneity of glasses were reproducible within ± 2 %, the same value as that determined by the above cited Cable and Walters, who also worked varying the wavelength. These are the only available data on reproducibility for the versions of Shelyubskii's method where other variables than temperature are employed. Data on the reproducibility of the measurements performed according to Hilbig and Groll's method were also published, but the reproducibility is very low as discussed in section 3.8.: the values of σ_n^2 obtained for the same glass can differ by ± 94 %.

3.10. Final remarks on the influence of the different characteristic experimental parameters

It can be seen from what discussed in this section that the values of σ_n^2 obtained by Shelyubskii's method depend strongly on the experimental conditions under which they were determined. Although the used conditions coincided in almost all the works with those under which a correlation between measured and calculated values of σ_n^2 was verified (see sections 2.3. and 2.4.), which is also corroborated by the results that will be presented in the next section, it would be desirable to find the optimum values of the experimental parameters so that in the future comparable results could be obtained by different authors, all using that conditions.

Some of those optimum experimental conditions must still be determined. One factor that deserves attention is the optical system, where the introduction of lasers as radiation sources and the attainment of very small cut-off angles has led to values of σ_n^2 two orders lower than those previously obtained and brought new possibilities which must be worked out (specially the aspects of divergence and aperture of the beam).

Another aspect which should be cleared is the influence of the grain size on the experimental values of σ_n^2, since the published results are contradictory in this respect. Finally, it would be desirable to corroborate the effectiveness of the washing of the grains by etching, keeping all the other parameters constant and testing also less homogeneous glasses than the optical ones and glasses of poor durability.

4. Applications of the Christiansen filter in glass technology

The different applications of Shelyubskii's method and its variations to problems related with the production and structure of glasses will be discussed here. The numerical values of σ_n^2 will not be given since, as discussed in section 3., they would be valid only in the particular conditions under which they were determined and very difficult to reproduce since generally those conditions were not sufficiently detailed.

The correlation between the homogeneity degree predicted by Shelyubskii's method and that predicted by other techniques on the same glass will also be discussed here. Finally, reference will be made to the application for which the filter was originally developed: the determination of the refractive indices of finely dispersed systems.

4.1. Production control

Shelyubskii was the first in using his method to control the production of complicated components made from an electrovacuum glass with barium and lithium [145 and 146], verifying that an increase in the value of σ_n^2 was related to an increase in loss. Shelyubskii further worked on this subject and in [137 and 177] he published data on the variation of the thermal shock resistance with σ_n^2 for electrotechnical glasses, which show that that resistance decreases as σ_n^2 increases. In [172] it is reported that the loss of glass articles during tempering can also be correlated with σ_n^2, the lots of articles of larger values of σ_n^2 being those which fractured easier during tempering.

Almost simultaneously with the first results of Shelyubskii, those obtained by Vidro and Khorol'skii (section 2.2.) were also published. They also studied the loss in electrovacuum glasses and found a very good correlation between $\Delta\lambda_{1/2}$ and the percentage of rejects of such glasses. This correlation was corroborated by Oshchipov and Yurkova [178] in vacuum tubes of glass with a high PbO content, also for electrotechnical uses. Schilling and Weiss [160] also applied the method to this sort of glasses, specially for incandescent lamp bulbs and tubing. They verified that the difference between the values of σ_n^2 of an optical glass and a soda-lime-silicate glass with many streaks was 26 %, which is small relatively to the reproducibility of the method. In the case of potash-lead glass that difference rose to 400 %, notwithstanding that the tubes were at least as good in appearance as the others; the borosilicate glass articles showed an intermediate difference of σ_n^2. Although this range of values of σ_n^2 only holds under the experimental conditions used by Schilling and Weiss, and could vary with the new measuring equipments described in section 3.7., it is interesting to discuss the difference observed between glasses with and without lead. As pointed out by the just cited authors, when judging the quality of hollow glassware, the variations in the wall thickness (due to variations in the viscosity of the glass) are critical while the optical homogeneity is of little importance. Thus, a volatilization of PbO during the manufacture of the glass articles can produce large variations of the refractive index (and consequently a large value of σ_n^2) without affecting appreciably the viscosity, a magnitude which is markedly affected by variations in the content of SiO_2 or Al_2O_3, which would in turn affect σ_n^2 to a minor degree only. These facts must be considered whenever the homogeneity of different glasses is judged on the basis of their values of σ_n^2.

In respect of flat glass, this method was first applied in 1963 by Sankova et al. [179], who used the $\Delta\lambda_{1/2}$ criterion suggested by Vidro and Khorol'skii in order to compare the homogeneity of a series of flat glasses. Shortly afterwards, Makhnavetskii and Gorina [175] proposed the application of the same method to sheet glass, but using the value of $\tau(\lambda_{Chr})$ as criterion for judging the homogeneity. Later, Paoletti determined the values of σ_n^2 for flat glasses of ten different European manufacturers using Shelyubskii's method [162], verifying that it varied ± 27 % with respect to the mean value. This author also followed the values of σ_n^2 during periods from up to 16 months in two factories which had no production problems. Finally, the method was applied to flat glasses by Blokhina et al. [137], who determined limit values of σ_n^2 under which a satisfactory quality was obtained in the case of float glass, and by Rykiert [163] who, after applying the method for many years to sheet glass, concluded that the values of σ_n^2 obtained by Shelyubskii's method can be used in order to control systematically the homogeneity and the perturbations arising in the manufacturing process, providing that the conditions of sample collection and preparation were constant.

The application of Shelyubskii's method to glass fibres (generally made from E-glass) dates from 1966, when it was used by Tichý [180] who concluded that the values of σ_n^2 obtained by that method allow an objective control of the production of fibres and the comparison of different lots. He reported that although this method does not allow the identification of the inhomogeneities, this is not a decisive fact for a fibre manufacturer. Ehrhardt and Händel [176] also proposed this method as routine control in the production of E-glass fibres.

Concerning glass containers, although some isolated values of σ_n^2 or $\Delta\lambda_{1/2}$ were given in [160 and 179], the first who applied Shelyubskii's method for the container production was La Due [166]. He compared the cases of two companies, one of which reported forming problems such as excessive checks, that were revealed by abnormally high values of σ_n^2 at the start of the operations which fell down to normal values a few hours later, but not by chemical analysis or the usual physical tests. When the problems were under control the values of σ_n^2 varied in the same range in both companies. From this evidence, La Due concluded that σ_n^2 can be correlated with the "glass workability" better than the other measured magnitudes of the glass. Paoletti [162] stated that the Stazione Sperimentale del Vetro followed the value of σ_n^2 during many production campaigns in hollow glass factories, verifying an inversely proportional relation between σ_n^2 and the daily output of the furnace.

4.2. Melting process

Many authors studied the influence of different parameters on the melting process of the glass batch by means of the values of σ_n^2 obtained on the glass produced by cooling the studied melt. Melts at laboratory scale [93, 162, 171, 181 and 182], in pot furnaces [137, 147, 164, 177 and 183] and in tank furnaces [162, 173 and 185] were studied. The studied parameters were melting time [93, 137, 147, 162, 164, 171, 177, 182 and 183], melting temperature [162 and 182], stirring speed [171 and 183], the grain size of the batch [162, 171 and 182] and its composition [93, 162, 164 and 171]. The obtained results can be summarized as follows: σ_n^2 decreased down to a minimum value at which it remains constant as melting time increases in laboratory melts. This is not the case for industrial melts where, once reaching its minimum value, σ_n^2 increases if the melting time is extended [177]; this fact was verified in pot furnaces and is also supported by measurements carried out on glasses produced in tank furnaces, where the values of σ_n^2 were larger for decreasing pull rates [162] or increasing loads [173]. With respect to the influence of the other cited factors, it was verified that σ_n^2 decreased as the melting temperature increased, that τ_M tended to a maximum value at which it remained constant as the stirring speed or time were increased, and that the smallest values of σ_n^2 were obtained with batches of low grain size or, if the grain sizes were the same, with batches that were more intimately and uniformly mixed, such as those obtained by the solution mixing-gellation technique [182]. It was also verified that batches of certain compositions yielded glasses with smaller values of σ_n^2 if all the other melting parameters were kept constant.

There are also experiments on the influence of the addition of glass cullet to the batch on the values of σ_n^2 of the resulting glass. Yamane et al. [173] varied the percentage of cullet added to the batch, the load and the temperature of two tank furnaces (one oil-fired and the other electric-heated). Although those parameters were varied almost always simultaneously, in one experiment they varied the cullet percentage from 41 to 50 % without varying the other parameters, and no change of σ_n^2 could be observed. From the results obtained varying temperature and load at constant cullet ratio or the three parameters simultaneously, it can be deduced that the values of σ_n^2 depend mainly on the load, and thus on the residence time of the batch in the furnace. Schumacher [185] stated that a filter prepared with a glass melted with 60 % cullet had a 3 % larger value of $\Delta\lambda_{1/2}$ and a 3 % smaller value of $\tau(\lambda_{Chr})$ than another one prepared with a glass melted with 52 % cullet. As the other melting parameters were not specified, it is not possible to verify if that variation was due to the cullet ratio difference or to differences in the other parameters.

Other papers on the melting process were published by Paoletti [162], who determined the values of σ_n^2 on samples taken at different places of a tank furnace, verifying that σ_n^2 was larger in samples from the fining zone than in those from the finished article; by Hilbig and Schwarz [184], who verified that the values of σ_n^2 of glasses produced in furnaces with electric boosting were smaller than those of glasses melted in normal tank furnaces, and by Bonetti [181], who intended to clear the mechanism of interaction between $SiO_2-Al_2O_3-ZrO_2$ refractories and soda-lime-silicate glasses studying the values of σ_n^2 of glasses obtained from melts of the glassy phase of those refractories with the addition of sheet glass. Finally, the papers by Yamane et al. [186 and 187] shall be cited, although they are not so strictly related to this subject. These authors obtained glasses by melting gels of the same composition in the system SiO_2-TiO_2. These gels were obtained by four different ways and it was verified that the glasses with the smallest value of σ_n^2 were obtained from gels prepared using alkoxides of similar hydrolysis rates.

4.3. Studies on structural modifications

It was observed that the curves of σ_n^2 as a function of the temperature of heat treatment at constant time for glasses which can devitrify show a maximum. In the case of Vycor type or fluorine opal glasses, it was verified that these maxima appear at the same temperatures as those obtained when plotting birefringency or nucleation as a function of temperature [162].

Besides this qualitative characterization of the phase separation and devitrification processes, Hilbig and Schwarz calculated quantitatively the degrees of crystallinity and of phase separation as a function of the treatment temperature or time for a silica glass obtained by leaching a heat-treated Vycor type glass and for that Vycor glass, respectively. The calculation was performed on the basis of the values of $\bar{n}_1$ as a function of the treatment temperature (at constant treatment time) or of the treatment time (at constant temperature). The values of $\bar{n}_1$ were obtained by application of the parabola method (see equation (9) and section 4.5.) to the transmission curves of Christiansen filters prepared with the corresponding glasses, and the volume fractions of the crystalline phase or of the separated glassy phase were calculated thereof supposing that only two phases were always present and that the refractive index of the segregated phase was always the same.

4.4. Comparison with other methods for the characterization of the homogeneity of glass

It is interesting to compare the results obtained by Shelyubskii's method or its variations with those obtained by other methods deviced for the characterization of the homogeneity of glass in order to verify possible correlations. This would help to determine the efficiency of Shelyubskii's method for solving particular problems and to find complementary methods that could be applied together with it allowing a better insight in the homogeneity problem.

Apparently, only in two cases Shelyubskii's method was used parallel to another one. Cable and Bower [171] used in their previously commented work Löffler's method [140] jointly with that of Shelyubskii (but determining only τ_M). As could be expected from what was discussed in section 1., they verified that once a high value of τ_M was reached, no inhomogeneities were detected by the other method, and that holds for medium or low values of τ_M, Shelyubskii's method gives information on the "mean homogeneity" of the body, but not on the size, intensity and distribution of the inhomogeneities, which can in turn be obtained by Löffler's technique. Correlations between the width of cords and depth of etching (the characteristic parameters of Löffler's method) and τ_M were not found, and a particular value of τ_M could result from a wide range of combinations of the other two parameters.

The other study in which Shelyubskii's method was applied parallel to another one was that by Schwarz and Hilbig [183], where the melting process was studied by means of the values of σ_n^2 (determined by Shelyubskii's method) and σ_ϱ^2 (the variance of the density, determined with a density gradient column, such as that described in [191]). As could be expected of two integral methods, the results obtained using them were coincident and a linear correlation was verified between $\sigma_n^2/\bar{n}_1^2$ and $\sigma_\varrho^2/\bar{\varrho}_1^2$. The values of $\sigma_\varrho^2/\bar{\varrho}_1^2$ were approximately twenty times smaller than those of $\sigma_n^2/\bar{n}_1^2$, a fact which can be explained considering that the samples for density determination were ten times larger than the grains of the Christiansen filter, and this causes a better apparent homogeneity, as discussed in section 1. With respect to works where it was intended to find a correlation between σ_n^2 and the characteristic parameters of another method, the paper by La Due [166] can be cited again. He studied the correlation between σ_n^2 and the ring section grades of Swicker's method [192], where rings cut from glass containers are observed under polarized light and evaluated subjectively considering the position and intensity of the observed cords. As could be expected when comparing a differential method with an integral one, it was not possible to correlate them. Different values of σ_n^2 could correspond to an intermediate grade after Swicker's classification, which would indicate different "mean homogeneities" that did not imply the presence of very intense or unfavourably positioned cords; on the other hand, a ring section rated with the worst grade because of a small but undesirable surface cord showed a good "mean homogeneity" as measured by σ_n^2.

Sankova et al. [179] compared values of $\Delta\lambda_{1/2}$ according to Vidro and Khorol'skii's method with the range of densities (expressed as temperature range) determined by Turnbull and Ghering's technique [138 and 139], but they did not intend to find any correlation. This correlation was found later by Shelyubskii et al. [137], who verified a linear correlation between the just cited parameters, as could be expected when comparing two integral methods. Finally, Blokhina et al. [137] verified a correlation between $\Delta\lambda_{1/2}$ and σ_n^2 (determined by varying the temperature after Shelyubskii's method), which does not coincide with that derived theoretically by Vidro and Khorol'skii [148] (see section 2.2.). These authors also determined the values of σ_n^2 beginning with glasses which produce deformation in shadowgraphs or geometric patterns.

The parameters of all the correlations cited here are only valid for the experimental conditions under which they were determined.

4.5. Determination of the refractive index of finely divided systems

Finally, one application which is more related with the original application considered by Christiansen for his filter than with glass homogeneity will be commented. As it requires the use of Christiansen filters where the temperature is varied at constant pressure and wavelength as in Shelyubskii's method, it was carried out many times simultaneously with the determination of σ_n^2 in glasses. This application is the determination of refractive indices in finely divided systems, which is very simple using Christiansen filters since at the temperature corresponding to τ_M, the refractive index of the grains is equal to that of the liquid, which can be determined easier.

This method is specially useful when a substance is available only as a powder whose particles are so small that the immersion methods which are usual in mineralogy can not be applied, although it may also be used if it is not desired to perform the laborious and tedious sample preparation required in order to measure refractive indices on solid bulk samples. This may be the case, for instance, when the dependence of the refractive index of a series of glasses on their composition is studied, as in [193] where Christiansen filters were used with that purpose.

Apparently, the first who applied a Christiansen filter varying its temperature in order to measure refractive indices was Turunen [194]. Later, Landgraf [195], Hilbig and Schwarz [196 and 197] and Hübner [198] developed instrumental modifications that should allow to perform measurements on submicroscopical particles, where the fact must be considered that if the beam traverses too many particles, the direct transmittance may be too small to be detected. This can be avoided using suspensions, in which case they must be homogenized by stirring [195]; another way is to use short cells with $z < 1$ mm [196 to 198]. A good concordance (in the order of 10^{-3}) with tabulated values obtained on bulk samples or by other methods was reached with both solutions.

In all their works Hilbig and Schwarz applied the parabola method (see equation (9)) in order to evaluate $\bar{n}_1$ from the transmission curves. They also showed that it is possible to obtain information on the values of q_{1i} if the solid is a mixture. This can be seen by inserting equation (12) in equation (1) of table 1, and the resulting expression (deduced in another way) was applied by the cited authors in order to determine the refractive indices and volume fractions in a mixture of two glasses [199] and in the already mentioned studies on crystallization and phase separation (see section 4.3.).

4.6. Final remarks on the applications of the Christiansen filter in glass technology

The works commented in this section support the considerations made in the introduction in the sense that the values of σ_n^2 obtained using Christiansen filters give a good insight into the variations of the "mean homogeneity" of glass and can be useful in the diagnosis of progressive impairments of glass homogeneity, but without ascertaining if that impairment is due to the apparition of many inhomogeneities of low intensity or to few of high intensity, and how they are distributed, composed or where they come from. In other words, with this method, as with the other integral methods, it is possible to foresee general trends of the homogeneity and in many cases it was possible to determine ranges of values of σ_n^2 within which it was possible to work without homogeneity problems. But beyond these ranges and when an undesirable level of inhomogeneities is reached, the method is of limited utility in order to determine if those inhomogeneities can be harmful to the finished product because of their intensity or distribution, which may be determined more exactly by a differential or an intermediate method, such as Löffler's, which can also give information about the composition and thus on the origin of the inhomogeneity.

Thus, the evaluation of the homogeneity of glass by means of σ_n^2 will be more complete in glass products where the inhomogeneities are always uniformly distributed as in optical glasses or, to a smaller extent, in flat glass. In both these glass types, the most important inhomogeneities are the optical ones, which are also those sensed by the method. The evaluation will be also complete in sorts of glass products where the distribution and nature of the inhomogeneities are not decisive factors, such as in glass fibres. In glass containers or tubing glass where the glass thickness distribution (determined by the viscosity) is more critical than optical inhomogeneities and where more intense inhomogeneities may be accepted if they are properly situated, the method must be applied with care and possibly together with other ones, but it can be helpful.

5. Conclusions

The Christiansen filter is a unique apparatus that has fascinated many scientists during a whole century. At first, its beautiful chromatic effects stimulated the search for new systems whereby they could be observed better and for longer times. Later, they were applied as monochromators in a range of the visible spectrum where no other filters were then available and, although they were later displaced by interference filters, they still play a role in the infrared spectrum. These filters can also be used as polarizers and thermometers as foreseen by its inventor and, when all possible applications appeared to be exploited, a new one was found as a means of characterizing the homogeneity of glass, which renewed the interest in them.

Together with these experimental works, the Christiansen filter promoted a great number of theoretical speculations, stimulated by many aspects: for some scientists (like Rayleigh, Raman et al.) it was an example of a system where despite of the large particle size when compared with the wavelength, wave optics was still useful due to the low values of Δn; others (like Schrader and Prishivalko) were interested in the possibility of applying the diffraction theory to different phase changing screens; and Clarke saw it as a simple means to verify theories originally developed for the propagation of microwaves in the ionosphere. The possibility of applying schemes to the Christiansen filter derived from the treatment of the scattering of small particles by thin foils was studied by Gosar and finally, it was intended to clear theoretically some aspects of the application of the filter as monochromator in the visible (Geffcken) or IR (Vereshchagin et al.) or for the evaluation of glass homogeneity (Hilbig, Cable et al.). In spite of the accumulated theoretical work, some aspects (specially those related with the influence of the shape and distribution of the grains of the dispersed phase) still remain unsolved and some approaches (such as focusing the problem as random walk applying Markov's method [200]) also remain without solution. All these facts show the great complexity of this apparently simple apparatus. Thus, it is hoped that this review will call attention to the points that need to be cleared for a deeper understanding of the Christiansen filter in the future.

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The author sincerely thanks Dr. E. A. Mari for suggesting this subject, Prof. Dr. H. A. Schaeffer for his encouraging interest in this work and Dr. W. Geffcken for providing unpublished theoretical work.

6. References

[136] Cable, M.; Hakim, J.: A quantitative study of the homogenising of laboratory melts using simple stirrers. Glass Technol. **14** (1973) No. 4, p. 90–100. [Rev. Glastech. Ber. **47** (1974) No. 9, 74R1232.]

[137] Shelyubskii, V. I.: (Orig. russ.) Fiz. Metody Issled. Neorg. Mater. **19** (1976) p. 286–299.

[138] Turnbull, J. C.: Separation of inhomogeneities in bottle glass by density differences. J. Am. Ceram. Soc. **24** (1941) No. 2, p. 37–43. [Rev. Glastech. Ber. **20** (1942) No. 5, p. 152.]

[139] Turnbull, J. C.; Ghering, L. G.: Cord analysis. J. Am. Ceram. Soc. **24** (1941) No. 8, p. 264–270. [Rev. Glastech. Ber. **22** (1948/49) No. 5/6, p. 109.]

[140] Löffler, J.: Die Analyse von Schlieren und Schichten durch Ätzung und Interferenzmessung. Glastech. Ber. **27** (1954) No. 10, p. 381–392.

[141] Löffler, J.: Die Analyse von Schlieren und Schichten durch Ätzung und Interferenzmessung//Pt. 2. Glastech. Ber. **30** (1957) No. 11, p. 457–463.

[142] Löffler, J.: Die Analyse von Schlieren und Schichten durch Ätzung und Interferenzmessung//Pt. 3. Glastech. Ber. **37** (1964) No. 12, p. 548–553.

[143] Goerk, H.; Waldecker, G. G.; Scholze, H.: Einfluß von Scherbenzusätzen auf die Homogenität und Läuterung von Glasschmelzen. Glastech. Ber. **54** (1981) No. 5, p. 109–119.

[144] Shelyubskii, V. I.: (Orig. russ.) USSR pat. No. 106702, Cl. 42 h. 1956.

[145] Shelyubskii, V. I.: Eine neue Methode zur Bestimmung der Gleichmäßigkeit von Glas. (Orig. russ.) Dokl. Akad. Nauk. SSSR **133** (1960) No. 3, p. 572–574.

[146] Shelyubskii, V. I.: A new method for determining and controlling the homogeneity of glass. (Orig. russ.) Steklo Keram. **17** (1960) No. 8, p. 17–22.

[147] Hilbig, G.; Eifert, U.; Ulrich, P.: Inhomogenitätsbestimmungen von Gläsern mittels Christiansenfilter. Silikattechnik **19** (1968) No. 2, p. 48–50. [Rev. Glastech. Ber. **41** (1968) No. 11, S. 460.]

[148] Vidro, L. I.; Khorol'skii, Yu. M.: (Orig. russ.) Inzh.-fiz. Zh., Akad. Nauk. Belorus. S.S.R. **3** (1960) No. 7, p. 112–116.

[149] Hilbig, G.: Eine neue Theorie des Christiansenfilters. Silikattechnik **22** (1971) No. 4, p. 128–132. [Rev. Glastech. Ber. **45** (1972) No. 10, R72–1570.]

[150] Budd, S. M.; Blanchard, M.: Micro-inhomogeneity of glass as determined from measurement of refractive index distribution. Glass Technol. **7** (1966) No. 1, p. 12–14. [Rev. Glastech. Ber. **42** (1969) No. 3, S. 101.]

[151] Sakaino, T.; Yamane, M.; Inoue, S.: A method for rapid determination of glass heterogeneity under pressure. In: Proc. XIth Int. Congr. Glass. Vol. III. Praha: CTVS Dum techn. 1977. p. 407.

[152] Sakaino, T.; Yamane, M.; Makishima, A. et al.: An improved method for measuring the homogeneity of glass by Shelyubskii's method. Glass Technol. **19** (1978) No. 4, p. 69–74. [Rev. Glastech. Ber. **52** (1979) No. 3, 79R0540.]

[153] Hilbig, G.: Spektrale Transmission eines Christiansenfilters. Silikattechnik **23** (1972) No. 6, p. 208–210. [Rev. Glastech. Ber. **47** (1974) No. 9, 74R1166.]

[154] Hilbig, G.; Groll, U.: Homogenitätsbestimmung von Gläsern über die spektrale Transmission von Christiansen-Filtern. Glastech. Ber. **55** (1982) No. 9, p. 194–197.

[155] Inoue, S.; Serizawa, T.; Yamane, M.: Measurement of the homogeneity of coloured glass by Shelyubskii's method. Glass Technol. **22** (1981) No. 2, p. 95–98. [Rev. Glastech. Ber. **55** (1982) No. 1, 82R0019.]

[156] Vidro, L. I.; Khorol'skii, Yu. M.; Mironenko, L. A.: Apparatus for controlling the degree of homogeneity of glass. (Orig. russ.) Steklo Keram. **17** (1960) No. 8, p. 22–25.

[157] Cable, M.; Walters, S. D.: A test of Shelyubskii's method for determining the homogeneity of glass. Glass Technol. **21** (1980) No. 6, p. 279–283. [Rev. Glastech. Ber. **54** (1981) No. 7, 81R1032.]

[158] Inoue, S.; Omi, S.; Yamane, M.: A calibration curve for the quantitative measurement of glass homogeneity by Shelyubskii's method. J. Ceram. Soc. Jpn. **89** (1981) No. 5, p. 260–265.

[159] Lenhart, A., Erlangen: Pers. Commun.

[160] Schilling, G.; Weiss, W.: Experiments to determine the homogeneity of glasses by the Shelyubskii method. Glass Technol. **7** (1966) No. 2, p. 66–71. [Rev. Glastech. Ber. **40** (1967) No. 6, S. 233.]

[161] Paoletti, G.: Possibilità di applicazione del metodo di Sheljubskii per la determinazione dell'omogeneità dei vetri.//Parte prima. Riv. Stn. Sper. Vetro **2** (1972) No. 4, p. 157–163. [Rev. Glastech. Ber. **46** (1973) No. 5, 73R0637.]

[162] Paoletti, G.: Possibilità di applicazione del metodo di Sheljubskii per la determinazione dell'omogeneità dei vetri.//Parte seconda. Riv. Stn. Sper. Vetro **2** (1972) No. 5, p. 201–207. [Rev. Glastech. Ber. **46** (1973) No. 10, 73R1287.]

[163] Rykiert, E.: Homogenitätskontrolle von Glas nach der Shelyubskii-Methode. (Orig. pol.) Szklo Ceram. **29** (1978) No. 4, p. 89–94. [Rev. Glastech. Ber. **52** (1979) No. 8, 79R1748.]

[164] Škultéty, Š.: Einige Erkenntnisse aus der praktischen Anwendung der Sheljubskij-Methode zur Messung der Homogenität eines Glases. (Orig. czech.) Sklar Keram. **30** (1980) No. 8, p. 230–235. [Rev. Glastech. Ber. **54** (1981) No. 7, 81R1033.]

[165] Sykes, R. F.: The preparation of glass grain samples for durability tests. Glass Technol. **6** (1965) No. 6, p. 178–183. [Rev. Glastech. Ber. **39** (1966) No. 10, S. 468.]

[166] La Due, A. W.: Relation between glass problems and homogeneity of commercial glasses by the Shelyubskii technique. Am. Ceram. Soc. Bull. **49** (1970) No. 6, p. 568–571. [Rev. Glastech. Ber. **45** (1972) No. 4, 72R0588.]

[167] Moore, D. J.: The homogenization of glass. Sheffield Univ., Ph. D. Thesis. 1972.

[168] Debye, P.; Beek, L. K. H. van: Effect of adsorbed water on the optical transmission properties of isotropic powders. J. Chem. Phys. **31** (1959) No. 6, p. 1595–1597.

[169] Inoue, S.; Serizawa, T.; Takizawa, K. et al.: Sample preparation for precise measurement of glass homogeneity by Shelyubskii's method. J. Ceram. Soc. Jpn. **90** (1982) No. 7, p. 343–348.

[170] Shelyubskii, V. I.; Gefen, A. G.: Automatic apparatus for determining the heterogeneity of glass. Glass Ceram **19** (1962) No. 11, p. 596–599.

[171] Cable, M.; Bower, C.: The homogeneity of small-scale laboratory glass melts. Glass Technol. **6** (1965) No. 6, p. 197–205.

[172] Shelyubskii, V. I.; Megerdicheva, I. A.: Installation to determine the index of the heterogeneity of glass. Glass Ceram. **39** (1982) No. 6, p. 271–274.

[173] Yamane, M.; Inoue, S.; Tabata, S. et al.: Homogeneity of table glassware manufactured by an electric melting furnace and an oil fired furnace. Glastech. Ber. **56K** (1983) Vol. 1, p. 331–336.

[174] Makhnavetskii, A. S.; Gorina, I. N.: (Orig. russ.) Steklo Inform. Byull. Vses. Nauchn.-Issled Inst. Stekla (1964) No. 2, p. 91–96.

[175] Shelyubskii, V. I.; Zadorozhnaya, T. D.: Laser equipment for determining the nonuniformity of glass. Glass Ceram. **41** (1984) No. 5/6, p. 215–218.

[176] Ehrhardt, E.; Händel, B.: Die Christiansen-Filter-Methode//Ein Verfahren zur Bestimmung der Glashomogenität. Silikattechnik **33** (1982) No. 10, p. 305–307. [Rev. Glastech. Ber. **56** (1983) No. 10, 83R1342.]

[177] Shelyubskii, V. I.; Megerdicheva, I. A.: Monitoring the nonuniformity in batch production of industrial glasses. Glass Ceram. **39** (1982) No. 10, p. 481–484. [Rev. Glastech. Ber. **57** (1984) No. 8, 84R1209.]

[178] Oshchipkov, F. P.; Yurkova, T. A.: Influence of the heterogeneity of glass on the strength of articles made from it. Glass Ceram. **25** (1968) No. 9/10, p. 568–569. [Rev. Glastech. Ber. **43** (1970) No. 11, p. 462.]

[179] Sankova, L. I.; Kurguzova, F. I.; Gorobinskaya, V. D. et al.: Optical method of determining the chemical homogeneity of glass. Glass Ceram. **20** (1963) No. 5/6, p. 274–275. [Rev. Glastech. Ber. **39** (1966) No. 6, p. 305.]

[180] Tichý, P.: Beitrag zur Eigenschafts- und Qualitätsauswertung der Gläser für die Glasseidenerzeugung. Silikattechnik **19** (1968) No. 10, p. 314–318. [Rev. Glastech. Ber. **44** (1971) No. 1, 71R0011.]

[181] Bonetti, G.: Comportamento delle fasi vetrose degli elettrofusi A.Z.S. al contatto con un vetro di tipa sodico-calcico. Riv. Stn. Sper. Vetro **4** (1974) No. 3, p. 97–106. [Rev. Glastech. Ber. **48** (1975) No. 6, 75R1007.]

[182] Russak, M. A.: Homogenization of multicomponent glasses. J. Am. Ceram. Soc. **61** (1978) No. 3/4, p. 181–182.

[183] Schwarz, F.; Hilbig, G.: Christiansenfiltermethode und Dichtegradientensäule zur Bestimmung der Glashomogenität. Silikattechnik **23** (1972) No. 5, p. 160–162.

[184] Hilbig, G.; Schwarz, F.: Untersuchungen an mit elektrischer Zusatzbeheizung geschmolzenen Gläsern. Silikattechnik **19** (1968) No. 12, p. 380. [Rev. Glastech. Ber. **42** (1969) No. 12, p. 520.]

[185] Schumacher, L., Essen: Pers. Commun.

[186] Yamane, M.; Inoue, S.; Nakazawa, K.: Preparation of gels to obtain glasses of high homogeneity by low temperature synthesis. J. Non-Cryst. Solids **48** (1982) No. 1, p. 153–159. [Rev. Glastech. Ber. **56** (1983) No. 11, 83R1531.]

[187] Yamane, M.; Inoue, S.; Nakazawa, K.: Homogeneity of the glass of TiO_2-SiO_2 system prepared by low temperature process. J. Ceram. Soc. Jpn. **90** (1982) No. 10, p. 622–624.

[188] Schwarz, F.; Hilbig, G.: Die Christiansenfiltermethode zur Bestimmung des Kristallinitätsgrades in Gläsern. Silikattechnik **21** (1970) No. 9, p. 300–303. [Rev. Glastech. Ber. **45** (1972) No. 4, R72-0587.]

[189] Hilbig, G.; Schwarz, F.; Schulze, K.: Physikalische Untersuchungen an Gläsern vom Vycor-Typ//T. 2. Untersuchung von Entmischungsvorgängen in Vycorgläsern. Silikattechnik **21** (1970) No. 7, p. 239–242. [Rev. Glastech. Ber. **45** (1972) No. 5, R72-0748.]

[190] Schwarz, F.; Hilbig, G.: Der Christiansenfilter zur Untersuchung von Phasentrennungen im Glas. Silikattechnik **22** (1971) No. 12, p. 410–414. [Rev. Glastech. Ber. **46** (1973) No. 9, 73R1065.]

[191] Pelsmaekers, I.; Amelinckx, S.: Simple apparatus for comparative density measurements. Rev. Sci. Instrum. **32** (1961) No. 7, p. 828–830.

[192] Swicker, V. C.: Ring-section examination of glass containers. Am. Ceram. Soc. Bull. **18** (1939) No. 4, p. 143–147. [Rev. Glastech. Ber. **17** (1939) No. 11, p. 313.]

[193] Schnapp, J. D.; Petzold, A.; Busch, H.: Mathematische Beziehungen zwischen der Zusammensetzung und einigen Eigenschaften im Glassystem $SiO_2-B_2O_3-Al_2O_3-MgO-Na_2O-K_2O$. Glastech. Ber. **53** (1980) No. 1, p. 16–25.

[194] Turunen, L.: New method for determination of refractive indices and study of continuous reactions. Anal. Chem. **33** (1961) No. 11, p. 1617–1621.

[195] Landgraf, K. F.: Ein Apparat zur Bestimmung der Lichtbrechung submikroskopischer Teilchen. Silikattechnik **15** (1964) No. 9, p. 297–299. [Rev. Glastech. Ber. **38** (1965) No. 9, p. 370.]

[196] Hilbig, G.; Schwarz, F.: Turbidimetrische Korngrößenbestimmung von feindispersen technischen Systemen. Staub.-Reinhalt. Luft **27** (1967) No. 6, p. 278–281.

[197] Schwarz, F.; Hilbig, G.: Brechzahlbestimmung disperser Systeme. Silikattechnik **18** (1967) No. 12, p. 375–377. [Rev. Glastech. Ber. **41** (1968) No. 10, p. 415.]

[198] Hübner, M.: Registrierende Lichtbrechungsmessungen an submikroskopischen Teilchen. Silikattechnik **28** (1977) No. 11, p. 344–346.

[199] Hilbig, G.; Schwarz, F.: Der Christiansenfilter zur Untersuchung von Mehrkomponenten-Systemen. Optik **28** (1968/69) No. 1, p. 37–43. [Rev. Glastech. Ber. **43** (1970) No. 6, p. 253.]

[200] Chandrasekar, S.: Stochastic problems in physics and astronomy. Rev. Mod. Physics **15** (1943) No. 1, p. 1–88.

[201] Kuz'min, V. N.; Prishivalko, A. P.: Light transmission by a dispersive filter filled with anisotropic particles. J. Appl. Spectrosc. (USSR) **41** (1984) No. 2, p. 934–938.

[202] Inoue, S.; Yamane, M.; Serizawa, T.: An apparatus for precise measurement of glass homogeneity by Shelyubskii's method. Am. Ceram. Soc. Bull. **63** (1984) No. 11, p. 1412–1415.

[203] Nagaoka, H.: Diffraction phenomena in the focal plane of a telescope with circular aperture, due to a finite source of light. Phil. Mag. (ser. 5) **45** (1898) No. 1, p. 1–23.

[204] Varshneya, A. K.; Loo, M. C.; Soules, T. F.: Glass inhomogeneity measurement using the Shelyubskii method. J. Am. Ceram. Soc. **68** (1985) No. 7, p. 380–385.

87R0160