Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Hakemi, H. and Varanasi, P. P.(1986) 'The determination of cholesteric pitch from the diffusion profile A new experimental approach', Liquid Crystals, 1: 1, 63 — 71

To link to this Article: DOI: 10.1080/02678298608086490

URL: http://dx.doi.org/10.1080/02678298608086490

LIQUID CRYSTALS, 1986, VOL. 1, NO. 1, 63–71

The determination of cholesteric pitch from the diffusion profile

A new experimental approach

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(*Received 26 September 1985; accepted 23 October 1985*)

The optical microscopic mass transport (OMMT) method was utilized to determine the cholesteric pitch values of the mixtures of mesogenic and non-mesogenic chiral species in nematic materials. The cholesteric pitch was determined by transient analysis of the diffusion profile established by allowing an initial cholestric composition (solute) to diffuse under semi-infinite linear boundary conditions into an oriented thin film of its corresponding nematic solvent. During the steady-state diffusion, where the initial concentration (pitch) remains constant, the transient analysis of the profile with a polarization microscope exhibits a maximum number of pitch discontinuity domains. The evaluation of the unknown pitch was carried out by extrapolation of the diffusion pitch gradient to the original diffusion source by using the exact relation between the pitch and the film thickness. The method is experimentally simple; at constant temperature and pressure, determination of the pitch depends only on the film thickness. There is a good agreement between the pitch values obtained with this method and those from conventional techniques.

1. Introduction

The unique optical properties of cholesteric liquid crystals are derived from molecular asymmetry and optical activity. The self-organized, twisted, cholesteric structure is characterized by a helical ‘pitch’ and ‘handedness’ (sense).

The cholesteric (or chiral nematic) structure is formed by a single-phase chiral mesogen, by mixtures of chiral materials [1] (at least one component should be mesogenic) or by mixtures of chiral species (mesogenic or non-mesogenic) with a nematic solvent [2, 3]. The magnitude and the handedness of the pitch depends on temperature, composition, molecular structure, surface effects and external fields. The relationship between the pitch and these parameters is integral to certain applications [4], as optical characteristics depend upon the pitch and its exact relationship with temperature, molecular chirality and composition.

In the literature there are a number of experimental techniques for determining the cholesteric pitch. The reported methods include: (*a*) the Grandjean–Cano wedge [5, 6], (*b*) the angular dependence of Bragg scattering [7, 9], (*c*) the wavelength of maximum reflection [8, 9], (*d*) optical rotation [10], (*e*) I.R. transmission [11], (*f*) direct microscopic determination of and the diffraction pattern from large finger-print pitch [12–14], and (*g*) small angle light scattering [15, 16]. Considering the advantages and limitations of each technique, the most suitable methods are claimed to be those of (*b*) and (*g*) [17], because they require simple instrumentation (polarization microscope and He–Ne laser) and the pitch is estimated in a relatively short time.

The purpose of the present study is to introduce a simple and accurate experimental approach for determination of the pitch via a direct microscopic analysis of a diffusion profile, from a well established concentration gradient texture established by an optically active impurity diffusing into a nematic liquid crystal. The diffusion profile is established by allowing a cholesteric mixture, with unknown pitch, to diffuse into an oriented nematic thin film [18]. The experimental details of this technique, which is referred to here as the optical microscopic mass transport (OMMT) method, have been described elsewhere [18, 19].

According to the OMMT method, the mass transport of a cholesteric or, in general, a chiral species into a homogeneously (parallel) oriented nematic thin film would provide a typical diffusion profile whose texture under a polarization microscope resembles that of a Grandjean–Cano wedge-type sample. An example of such a diffusion pattern is presented in figure 1. This texture, in analogy with the periodic disclination patterns in a Grandjean–Cano wedge sample, at constant concentration or pitch [20], consists of a series of domains having variable pitch values. At a uniform sample thickness d, the 'undisturbed pitch' p_k values are established only at locations where d is equal to an integer multiple of half-pitch according to [18, 21],

$$d = k(1/2p_k), \quad (k = 1, 2, 3, \ldots), \tag{1}$$

where the integer k increases with decreasing p_k. With reference to figure 1, k increases from right to left (i.e. from the diffusion front towards the source). Between the undisturbed pitch locations, the variable helical structure is subjected alternately to succesive compression and dilation on either side of p_k. When the pitch increases (i.e. from left to right in figure 1), on passing through a particular p_k value, it is subjected to increasing compression. Depending upon the degree of the twist elastic modulus and the overall gradient of the concentration, the number of turns (or k value) remains constant until a break point at which the helix structure cannot sustain further distortion and, consequently, experiences a discontinuous relaxation jump. These jumps are manifested by a series of periodic singularity lines in the texture (see figure 1) at locations where the pitch relaxes and its number of turns decrease by one-half. Assuming that a non-linear pitch gradient gives symmetric contributions to the helix compression and dilation on both sides of an undisturbed pitch location, then, the mid-distance between successive disclination lines should represent the locations of the undisturbed pitch p_k (equation (1)). The validity of this assumption is supported by the maximum reflection wavelength measurement in a Grandjean–Cano wedge sample, which has shown that the pitch value at the mid-point of domains is equal to the undisturbed pitch of the same concentration in a uniform film thickness [23]. The disclination lines shown in figure 1, therefore, represent the locations of the 'disturbed' pitch discontinuities by one-half value from $k = i$ to $k = i + 1$, and the diffusion texture consists of an alternating series of half-strength ($s = \frac{1}{2}$) $\tau^- \lambda^+$ and $\lambda^- \tau^+$ pair singularities [19, 22]. Their occurrence in cholesteric structures, due to either a thickness or a concentration gradient, is a manifestation of the minimization of distortion free energy of the system by the viscoelastic relaxation mechanism.

The implication of the textural characteristics in a typical cholesteric/nematic diffusion profile is that under optimum experimental conditions of constant pressure, temperature and sample thickness, the unknown helical pitch value of a cholesteric diffusant, p_k^0, can be determined via a dynamic (transient) analysis of the diffusion texture. In an optimum steady-state time range, where the concentration of the

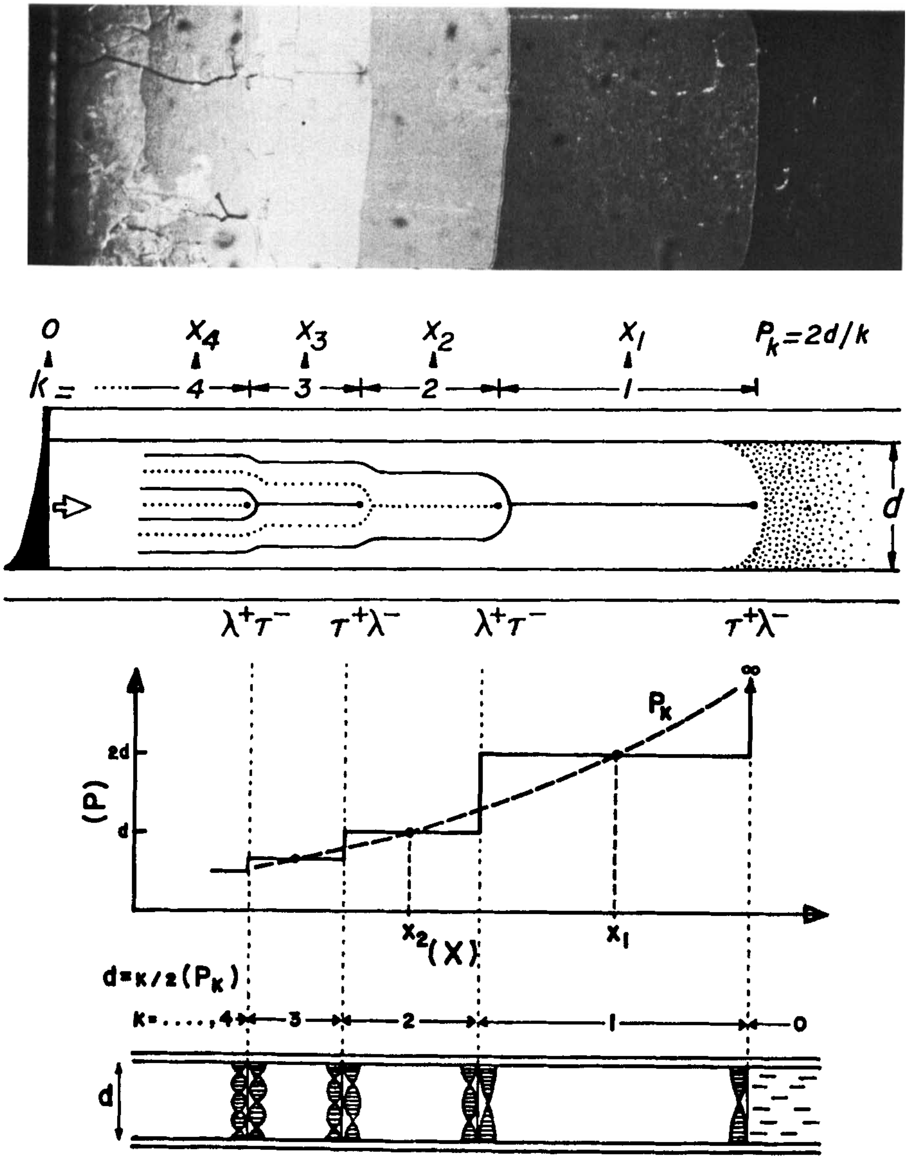

Figure 1. Photomicrograph and cross section of the cholesteric pitch discontinuities of the diffusion profile of a chiral–nematic/nematic mixture with parallel orientation (top) and cross section of the diffusion profile (bottom). The dashed curve represents the continuous behaviour of undisturbed pitch p_k occurring at mid-distance between disclination lines; the solid line is the observed pitch gradient. (See also [18, 19].)

cholesteric material at the source remains constant, the linear $x = 0$ extrapolation of a p_k versus x^2 plot (where x is the distance of the p_k from the diffusion source) would give the exact pitch value of the initial cholesteric material. Notice that the use of the steady-state terminology is to refer to the constancy of concentration at the source and not, necessarily, to the steady-state diffusion boundary conditions. In addition to the experimental simplicity (the sample thickness is the only adjustable experimental parameter), the present method is capable of measuring a wide range of pitch values.

In §2, the experimental set-up is described. In §3, we describe the method for evaluation of the pitch; the results of the pitch measurements on some selected cholesteric/nematic mixtures are given in §4.

2. Experimental

The nematic and the cholesteric materials for the present study were supplied by EM Chemicals and the samples were used without further purification. The nematic materials were: 4-cyano-4′-n-pentylbiphenyl (5CB) and the eutectic mixtures; E3 and E7. The cholesteric and chiral species were: 4-cyano-4′-(2-methyl) butylbiphenyl (CB15) and 4-cyano-4′-(2-methyl) butoxybiphenyl (C15). The thermal properties of these materials have been reported in the literature [8–10]. The mixtures with various pitch values were prepared by weighing the chiral solute and nematic solvent in a micro-vial on a Mettler model AE163 microbalance. The solutions were then allowed to mix thoroughly above their cholesteric–isotropic transition temperatures in an oven for about $\frac{1}{2}$ hour. Determination of the pitch for each cholesteric solution was carried out by establishing a diffusion concentration gradient, i.e. by allowing the cholesteric solution to diffuse linearly into an oriented thin film of the corresponding nematic solvent. In all pitch measurements, the diffusion cell consisted of a thin film of the homogeneous (parallel) nematic matrix sandwiched between a pair of surface treated microscope slides. The uniform thickness of the film was adjusted by the use of Mylar spacer sheets with thicknesses of 3·5, 6, 12 and 23 μm. The unidirectional parallel alignment of the nematic director was achieved by coating the glass surfaces with polyvinyl alchohol (PVA) and rubbing unidirectionally with a cheese cloth. The direction of the nematic alignment was always perpendicular to that of the diffusion concentration gradient.

The diffusion pathway in a typical mass transport cell was established by a rectangular cut into the Mylar spacer, with approximate dimensions of 0·1 × 2·5 cm. All studies were carried out at ambient temperature (20 ± 1°C). The analysis of the diffusion concentration gradient was accomplished via direct measurements of the corresponding observable pitch disclination lines under a Universal Zeiss polarization microscope. The details of the diffusion experiments have been described elsewhere [18, 19].

3. Method

In figure 1, we present a photomicrograph of a typical concentration gradient profile and the corresponding pitch variations in a cholesteric/nematic mixture. The boundary condition is semi-infinite linear diffusion, where the diffusion source (i.e. $x = 0$) is on the left-hand side of the photograph. The block diagram at the bottom of figure 1 shows a cross-section of the diffusion profile and represents the locations of pitch discontinuities and the undisturbed pitch p_k values at a given diffusion time.

The temporal appearance and the number of Grandjean–Cano domains, represented by integer k in equation (1), depend upon the initial amount and the concentration of the deposited cholesteric dopant, respectively. Within a relatively short diffusion time after the deposition of cholesteric material with unknown pitch value, the number of disclination lines (and, consequently, the k values) would increase rapidly.

This rapid increase is a consequence of convective flow created by a large concentration gradient near the diffusion source; which has been observed in all diffusion experiments. After a certain characteristic time (about 1 hour for the present system), the k values would reach a maximum level and, depending on the initial amount of cholesteric dopant, remain at this level for some time. This time-independent behaviour of k is a reflection of the steady-state diffusion during which the concentration (or pitch) of the diffusant at the source ($x = 0$) remains constant.

At relatively longer diffusion times, a free-diffusion condition is usually achieved which is accompanied by a monotonic depletion of the concentration (or increase of the pitch) at the diffusion source. The establishment and prolongation of each of the above mentioned diffusion states mainly depends on the initial amount and concentration of the chiral material at the source, as well as the temperature of the cell.

The appropriate solution of Fick's second law for the semi-infinite one-dimensional diffusion is given by [18]

$$C = [M/(\pi Dt)^{1/2}]\exp(-x^2/4Dt), \tag{2}$$

where C is the concentration of the diffusing material at the penetration distance x and the diffusion time t, M is the initial amount of diffusant and D is the diffusion coefficient. Assuming that the usual first-order linear relation between concentration and pitch is given by [18 (a)]

$$C = \gamma p^{-1}, \tag{3}$$

then by successive substitution of equations (3) and (1) into equation (2), a simple relation between the integer k and the corresponding penetration distance x is established [19 (c)]

$$k = [2dM/\gamma(\pi Dt)^{1/2}]\exp(-x^2/4Dt). \tag{4}$$

According to equation (4), a typical $\ln k$ versus x^2 plot would predict a linear relationship. Linear extrapolation of such a plot to $x = 0$ is, therefore, an estimate of k^0 and its corresponding p_k^0 (from equation (1)) at the diffusion source. The transient behaviour of the extrapolated k^0 (or p_k^0) is, then, a direct measure of the concentration of the initial cholesteric (or chiral) material at the source. Obviously, during the steady-state diffusion, where the concentration of the dopant remains constant, the extrapolated k^0 would exhibit a maximum value k_m^0 at a plateau level and the corresponding $p_{k_m}^0$ value from equation (1) would represent the unknown pitch value of the deposited chiral solution.

Consequently, the general procedure for the measurement of the 'actual' or 'virtual' pitch of any chiral material would require: (*a*) the establishment of a one-dimensional diffusion profile of the chiral dopant diffusing into a parallel aligned nematic thin film of uniform thickness and, (*b*) the identification of the maximum number k_m^0 from Grandjean–Cano domains at the steady-state time interval. By a simple argument from the diffusion texture (see figure 1), it can be shown that within the steady-state time, the best estimated pitch of the chiral dopant should lie within a Grandjean–Cano domain between the observed k_m^0 and the virtual $k_m^0 + 1$. The latter is the upper bound of the pitch which, hypothetically, should exist at $x < 0$. With a first-order approximation, the best evaluated unknown pitch p^* value, would be an arithmetic mean-value of $p_{k_m}^0$ and $p_{k_m+1}^0$ obtained by successive substitution of k_m^0 and $k_m^0 + 1$ in equation (1) which is represented by

$$p^* = \tfrac{1}{2}(p_{k_m}^0 + p_{k_m+1}^0) = d[(2k_m^0 + 1)/k_m^0(k_m^0 + 1)]. \tag{5}$$

In short, the measurement procedure of the pitch of any chiral species is reduced to a simple evaluation of k_m^0 from its corresponding diffusion profile and calculation of p^* from equation (5). Independent of the experimental variables k and t, the present method is based on only one geometrical 'constant', d—the same thickness.

4. Results and discussions

In figure 2 we give an example of typical $\ln k$ versus x^2 plots as a function of diffusion time for a 19·9 per cent (w/w) CB15/E7 mixture at $d = 6\,\mu$m. The plots, as expected from equation (4), are effectively linear and show the time evolution of the concentration (or pitch) distribution function. The linear extrapolation of these plots to $x = 0$ shows that the resultant k^0 (i.e. k at $x = 0$) values are changing with time. In the cases where the $\ln k$ versus x^2 plots do show curvature (convergence or divergence), the data points near the diffusion source were used for linear extrapolation.

The transient behaviour of k^0 is represented by semi-logarithmic plots of k^0 versus time in figure 3 for CB15/E7 at two different thicknesses of $d = 3{\cdot}5$ and $6\,\mu$m. The error bars are the uncertainty limits of those k^0 values in which the extrapolation does not correspond to integer values. The data in figure 3 clearly show the corresponding convection, steady-state and free diffusion regions. The linear increasing trend of k^0 with time, which represents the region of the convective flux in the diffusion profile, has been observed in all diffusion experiments. The data also clearly illustrate the existence of the steady-state time range, at which k^0 reaches a maximum plateau value of k_m^0.

The table shows the experimental data of the cholesteric mixtures whose pitch values are determined by the present method. In column 4 we tabulate the integer

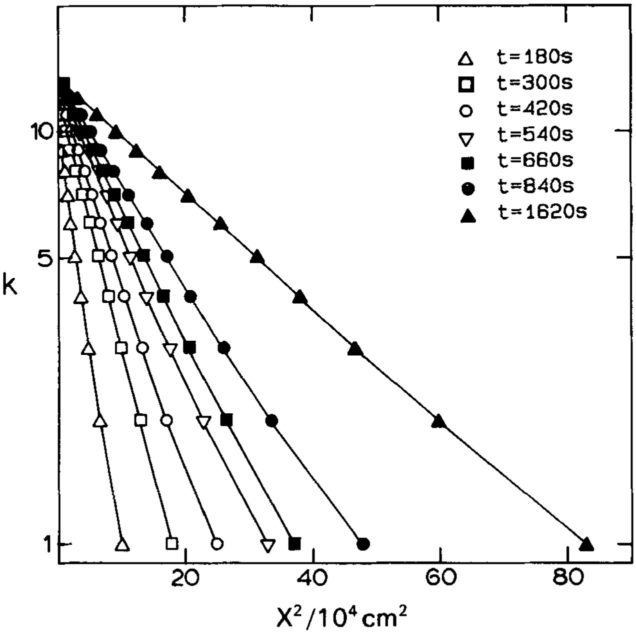

Figure 2. Time evolution of the linear plots of $\ln k$ versus x^2 from the diffusion profile of a 19·9 per cent (w/w) CB15/E7 solution diffusing into a parallel oriented nematic E7 thin film at $d = 6\,\mu$m.

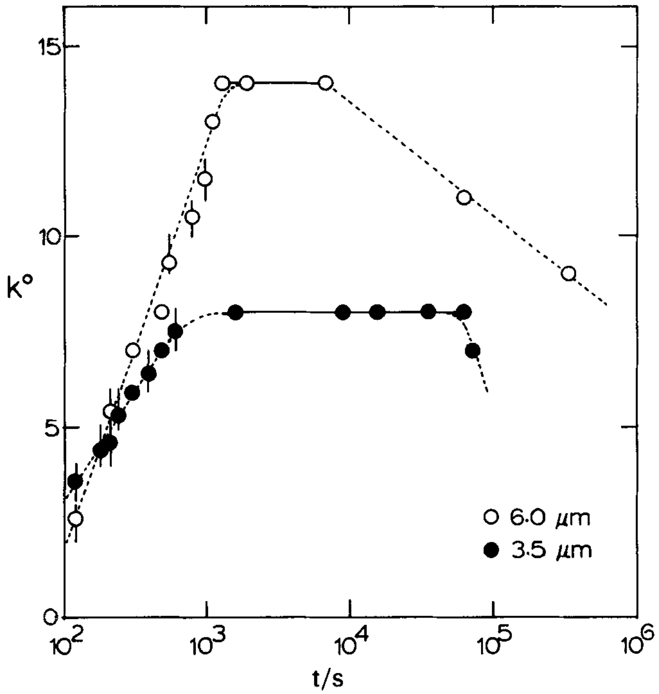

Figure 3. Time dependent behaviour of the extrapolated domain number k^0 in CB15/E7 mixture at; ●, 3·5 μm; and ○, 6 μm film thicknesses. The plateau levels of the curves represent k_m^0 values.

Pitch data as a function of concentration and thickness (T = 20 ± 1·0°C).

Chol/nem mixture	[Chol] per cent (w/w)	Thickness $d/10^4$ cm	k_m^0	$p^*/10^4$ cm	
				This work	Literature
CB15/E7	5·1	3·5	2	2·9 ± 0·6	3·0†
		6·0	4	2·7 ± 0·3	
		12·0	8	2·85 ± 0·15	
CB15/E7	19·9	3·5	8	0·83 ± 0·05	0·75†
		6·0	14	0·83 ± 0·03	
		12·0	29	0·815 ± 0·015	
CB15/E3	10·0	3·5	4	1·6 ± 0·2	1·5‡
		12·0	16	1·45 ± 0·05	
C15/K15-21	40·0	23·0	12	3·70 ± 0·15	3·7§
CB15/5CB	4·95	23·0	7	6·15 ± 0·40	—
CB15/5CB	13·1	3·5	11	0·61 ± 0·03	—
COC/5CB	30·0	12·0	18	1·30 ± 0·05‖	—

†BDH Chemicals, Ltd, 1979, *Liquid Crystals*, 79, p. 7, [Chol] = 5 per cent and 20 per cent respectively.

‡Gray, G. W., and McDonnell, D. G., 1976, *Molec. Crystals liq. Crystals*, **37**, 189.

§Gray, G. W., Harrison, K. J., Nash, J. A., and Raynes, E. P., 1973, *Electron Lett.*, **9**, 616.

‖Calculated from data in [19 (a)].

k_m^0 values obtained from k^0 versus time plots (see figure 3); the reported pitch p^* values in column 5 are those calculated from equation (5). The data are in good agreement with the available literature values tabulated in column 6 of the table.

According to the table, for the same concentration of a cholesteric/nematic mixture, k_m^0 is directly proportional to the sample thickness d. Such a direct correlation can be deduced from equation (1). By increasing d, the number of disclination lines would increase and, consequently, according to equation (5), the uncertainty range of the p^* would diminish. Examples of this thickness effect is clearly evident in the table from the uncertainty limits on the calculated p^* values for CB15/E7 and CB15/E3 mixtures at different film thicknesses. It is seen, for example, in the 19·9 per cent (w/w) CB15/E7 mixture, that increase of sample thickness from 6 μm to 12 μm would decrease the uncertainty of p^* from $\sim$4 per cent to $\sim$2 per cent. The conclusive interpretation of this observation is that assuming all other physical parameters remain unchanged, the diffusion profiles with larger thicknesses would provide more precise pitch values. A restriction may, however, arise from the loss of surface induced orientational order in very thick samples ($>$ 100 μm), which results in diminishing the consistency of the pitch discontinuities. Generalization of this argument, in fact, requires further experimental verification.

The accuracy in the pitch results depends, mainly, on the accuracy of the sample thickness, which is the only experimental parameter in the OMMT method. Errors in the thickness may be minimized by increasing its value and/or by decreasing the dimensions of the diffusion pathway.

In this study, the order of magnitude of the cholesteric pitch measured was in the range 0·6 to 6·0 μm. However, it is possible to extend this range up to about three orders of magnitude in pitch variation. For example, a simple calculation from equation (1) shows that measuring a cholesteric pitch $p^* = 0{\cdot}2\,\mu$m at $d = 5\,\mu$m, would give a diffusion profile consisting of $k = 50$ domains, whereas for $p^* = 20\,\mu$m at $d = 50\,\mu$m, the number of observed domains are $k = 5$. This range is well beyond the experimental limits of any of the existing pitch measurement techniques.

In conclusion, we have utilized the OMMT method and introduced a new approach to determine a wide range of values of pitch in cholesteric or chiral solutions with unknown pitch values. The method is both conceptually and experimentally simple. It is based on counting the maximum number of pitch discontinuity domains in a well established diffusion profile within an optimum time scale. Depending upon the order of magnitude of the pitch and the sample thickness, the experimental error can be reduced to $<$ 1 per cent.

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