Bellingham + Stanley Technical Bulletin

Bulletin No: **R006**
Title: ***Measurement of the Refractive Index (RI) of solid materials***

Generally speaking, B+S refractometers are designed to measure the RI of liquids. However, they can be used to measure the RI of solid samples. Examples are solid test (calibration) plates, optical glasses and plastics used to manufacture contact lenses.

However, the use of critical angle refractometers for measuring solids is limited by a number of factors. The following notes serve as background information for distributors and customer enquiries.

Types of solid

Solids can be in various physical forms: powders, granules, crystals, plates/castings, thin films etc. Also, they can be further classified into *amorphous* or *crystalline*. Amorphous materials have no crystalline structure; molecules are randomly dispersed with no 'ordering'. This means the solid is isotropic (properties equal or uniform in all directions).

For isotropic solids, physical properties such as RI are not direction-dependant and therefore have a single value at a given temperature. In contrast, a crystalline solid may have different properties according to the direction with respect to crystal planes (anisotropic). For such materials it would be necessary to define a physical property such as RI as a composite of three-dimensional components, RI_x, RI_y and RI_z, corresponding to the x,y and z co-ordinates respectively.

Some powdered materials are semi-crystalline with physical properties often quoted as a spacially-averaged value. Some materials (e.g. sulphur) exist in different crystalline forms and each type may have a different RI.

Therefore, depending on the degree and type of crystallinity, a solid may not have a unique RI.

Use of a spectrometer

It may be possible to make a prism from the test material. Using a spectrometer, it may then be possible to measure the angles of a monochromatic light beam as it enters and emerges from the prism. These angles, together with the prism angle can be used to calculate the RI of the prism (test) material. The method is sometimes referred to as the Minimum Deviation Method and is described in the literature.

Methods for measuring RI of solids using a Refractometer

It's often not easy and sometimes impossible! Some methods might work and experimentation is usually needed to find out.

1. Solid available in sheet/plate form

If the solid is available in a sheet/film/plate form, then attempts should be made to apply it to a prism directly using a contact liquid.

It is necessary to make a coherent contact between the refractometer prism and the solid sample. To do this, there are two requirements. Firstly, the sample should be as flat as possible. Secondly, a contact fluid must be used to form a coherent film between sample and prism. The RI of this contact fluid must be higher than that of the sample to ensure light refracts through into the sample interface.

Notes:

- Sample flatness will vary according to the nature of the material and its preparation.
- The surface of some materials will be affected by mechanical (machining/polishing) treatment such that the RI will be affected.
- The flatness of the refractometer prism is also a factor. Sapphire prisms used in automatic refractometers are less flat than the glass prisms used in Abbe refractometers because the latter can be machined to higher precision.
- The choice of contact fluid could be critical. It needs to be a non-solvent for the sample material. It could be absorbed/imbibed by the sample material to cause swelling or even true solution of the material (polymer films?) and this would of course result in a meaningless RI.
- Typically, a contact surface of between 0.5 and 1 cm^2 is needed.

2. Powders/dispersed form

It is not possible to measure the RI of a powder directly using a critical angle refractometer and it is not easy to relate the RI of solutions of the material in a given solvent to the RI of the solid itself. The phase change on going from solution (liquid) to solid usually involves some unpredictable change in a physical property such as density or RI and, although there have been attempts at a theory, there is no reliable method to predict such fundamental properties.

For powdered or finely divided materials, the following methods can be considered.

a) Casting method

For some materials, typically amorphous polymeric materials, it may be possible to dissolve the polymer in a suitable solvent and cast a film directly onto the refractometer prism by allowing the solvent to evaporate. This relies on the film acquiring the exact micro-relief of the prism surface without the need for a contact fluid. Mixed success can be expected!

A crystalline or semi-crystalline material when precipitated in this way may acquire a different crystal morphology. There may be no crystallinity , partial crystallinity, mixed crystal forms etc. Variable RI will then be observed and experimental procedure critical to ensure repeatable sample ‘history’.

Alternatively, it may be possible to make a film of the solid and then place it on a prism using a suitable contact fluid.

a) Immersion Method

One method that is sometimes used for particulate solids (powders) is to suspend the solid in a series of non-solvents with variable RI that spans the range in which the RI of the solid occurs. When the RI of the suspending liquid equals that of the suspended solid, the mixture should become transparent – the solid particles become invisible. This is often referred to as the immersion method.

A practical approach to this method is to choose two liquids (non-solvents) that are completely miscible; one with a low RI and one with a high RI. The solid is then dispersed in one liquid and the second liquid is slowly added (titrated). The opacity of the mixture can be monitored using a simple spectrophotometer and the ''end-point'' determined as the RI of the liquid blend at the point of minimum opacity or optical density (= maximum transmittance).

Conclusions

Solids, by their nature, are often complex materials and the RI is not always a unique number as with liquids. RI can depend on morphology, sample history, crystal orientation and so on.

Direct methods require a substantial uniform amount of material to be available, either to make a prism (spectrometer method) or to make a test plate for placing on a refractometer.

If the above methods are not possible, it may be necessary to cast a film of material onto a prism, hoping that a coherent contact is achieved or it may be necessary to consider an 'indirect' method such as the Immersion Method.

There is not a lot of relevant literature because it is not a subject which has warranted wide practical investigation. The main area where solids have been studied is for the manufacture of optical components: traditional applications such as lenses, prisms etc and more recently in the area of contact lens manufacture.

For research materials, it may be necessary to try one or more of the methods briefly outlined above.