Then There Was Light…

The development of fibre-optical systems has caused a small revolution in chemical analysis. The technology makes it possible to carry out photometric measurements not only under laboratory conditions with cells, but through the development of fibre-optical probes, analysis has moved directly to the process measurements. Continuous measurements can be made in situ without sampling. This allows for better control of ongoing processes with much less effort.

A New Core Competence for Hellma

Hellma quickly recognised the potential of this new method of analysis. After all, the work with optical glass has always been one of the core competences of the company. As a result the development of fibre-optical probes at Hellma was in the best of hands, right from the start.

Custom-made Solutions for You

You can trust the proven quality from the house of Hellma with fibre-optical systems too. Whether you want a probe from the existing catalogue range, need a custom-made product, or have a completely new application for which there has as yet been no satisfactory technical solution, the Hellma specialists from the fibre-optical team will gladly take up the challenge and develop a product designed to meet your needs.

Hellma®
Precision in Spectro-Optics. Worldwide.

3.1.1 Applications and Advantages

Through the development of fibre-optical systems, spectrophotometric analysis has been expanded into a wide variety of new applications. With the help of immersion probes liquids can also be analysed remote from the spectrophotometer. During immersion of the probe, sample solution fills the measuring slit of the probe. The light beam can be passed through the sample in the measuring slit with the help of the optical fibres. This measurement principle makes the immersion probes independent of the instrument, therefore they can be used for various applications in both the laboratory and process area.

For example the following spectrophotometric measurements can be carried out with fibre-optic probes:

- Determination of concentration (quantitative analysis)
- Determination of colour
- Measurement of turbidity
- Identification (qualitative analysis)

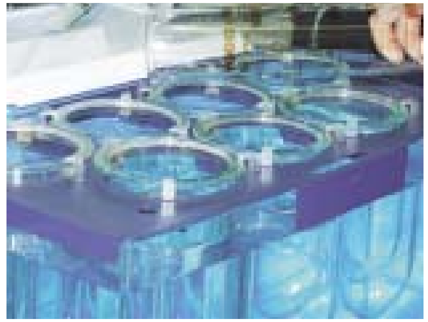
Advantages of Fibre-optical Probes

Unlike cells there is no need to take a sample. The sample is measured in situ. This has several advantages:

- Safe:
  Safe measurement of poisonous and dangerous substances as there is no need to handle the sample.
- Non-destructive:
  The product can be measured safely without destruction or danger of modification. The effort involved in reaching just the right temperature beforehand for example thus becomes superfluous.
- Economical:
  Saves valuable product, as laboratory samples usually have to be thrown away.
- Fast:
  Measurement of samples without delay as transportation is not necessary. Measurement results for purposes of regulation can be made available in real time (online process control).
- Reduced costs:
  Reduction of costs involved in sampling and analysis.

Special Solutions for Special Situations

Since the introduction onto the market of the first Hellma probes in 1995, this area of production has grown steadily at Hellma and offers optimal solutions for a wide variety of measurement tasks. A small selection of fibre-optical immersion probes can be found in chapter 3.2. Because we are developing and producing the probes ourselves we are established as a probe specialist and competent consultant in industry and research. Together with our clients we have developed several individual solutions. Hellma can develop an ideal probe for your needs too. Just ask us.



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3.1.2 Measurement Principles

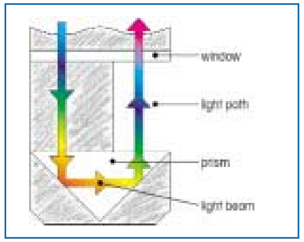
In addition to the external characteristics of our range of models, such as dimensions, flange types and materials, the probes differ in terms of the way in which the light beams are transmitted in the measuring slit. Depending on the application, various forms of optical geometry have proved optimal. You can find out which measuring principle is right for your application by talking freely to our experts.

Irrespective of these various optical geometries, the measurement principle of a fibre-optic immersion probe is in most respects similar to that of a cell.

Measurement principle 1: Light passes through horizontal measuring slit only once

The collimated light beam passes through the solution to be measured only once, as with a cell measurement. The use of a deflecting prism with two total reflection surfaces leads to very low stray light values.

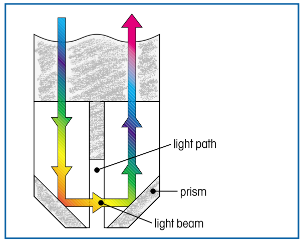
Probe types: 661.000/661.302/661.500/661.760-661.763



Measurement principle 2: Light passes through vertical measuring slit only once

The collimated light beam passes through the solution to be measured only once. The use of two total reflections prisms leads to very low stray light values. When the measuring head is immersed, the liquid sample pushes bubbles out of the vertically placed measuring slit.

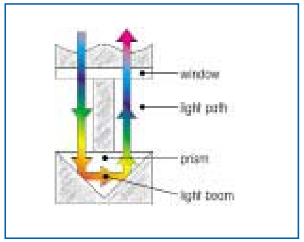
Probe type: 661.082



Measurement principle 3: Light passes through horizontal measuring slit twice

The collimated light beam passes through the solution to be measured twice. The separate beam path and use of a deflecting prism with two total reflection surfaces leads to very low values for stray light.

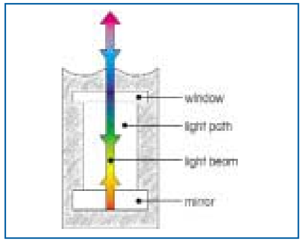
Probe types: 660.602/661.112



Measurement principle 4: Light passes through horizontal measuring slit twice by means of reflected light beam

After passing through the solution to be measured, the light beam is reflected by a rear-coated mirror and passes through the solution a second time.

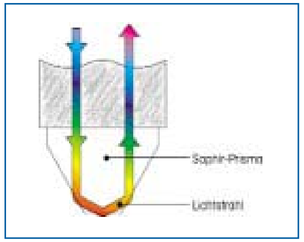
Probe types: 661.610/661.611/661.622



Measurement principle 5: Measurement of attenuated total reflection (ATR)

The measuring head made from sapphire functions according to the principle of attenuated total reflection (ATR) and is equipped with three reflecting surfaces.

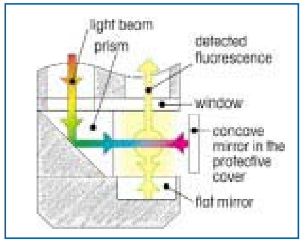
Probe types: 661.812/661.820



Measurement principle 6: Fluorescence measurement

By means of 90 degree deflection of the incident light, the excitation and fluorescence beams are well separated. Integrated mirrors increase the light yield.

Probe types: 661.052



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3.1.3 Connection to Spectrophotometer

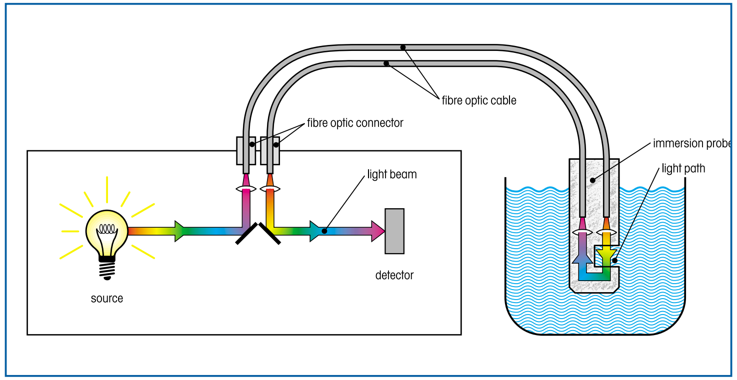
Each immersion probe has two fibre-optic cables: One fibre-optic cable is used for the transmission of the light from the light source of the spectrophotometer to the measuring head in the immersion probe. The second fibre-optic cable conducts the signal, i.e. the light that has passed through the sample, back to the spectrophotometer.

Glass Fibres in Protective Cover

The light is transmitted by means of glass fibres inside the fibre-optic cables. In order to protect the delicate fibres, fibre-optic cables usually have an additional plastic jacket, which normally is sheathed by a flattened wire spiral of stainless steel in a plastic cover. Optionally, there are fibre-optic cables equipped with a mechanically robust jacket sheathed by a stainless steel double spiral.

Easy Handling with SMA Couplers

The ends of the fibre-optic cables are usually equipped with SMA connectors, which connect to the corresponding sockets on your spectrophotometer. Fibre-optic cables can also be extended easily by means of the SMA couplers. Couplers for other standard optical connectors are also available on request.

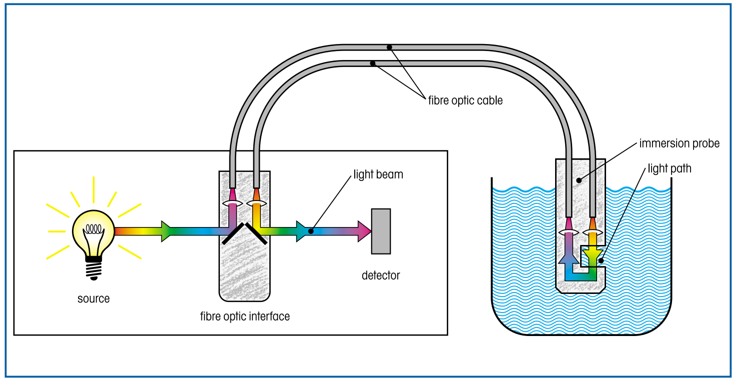


Fibre-optic Cable Interface Instead of Cells

With spectrophotometers without SMA connectors the use of a fibre-optical probe is made possible by using fibre-optic cables with collimating lenses, together with the Hellma interface.

The fibre-optic cable interface is equivalent in its external dimensions to a standard cell with 10mm light path (12,5mm x 12,,5 mm x 60 mm) and is placed like a cell in the cell holder of the photometer. The deflection of the light beam inside the interface occurs by means of two total reflections in a double prism. For measurements in the UV/Vis or NIR spectral ranges two versions of the interface (662.000-UV/ 662.000-NIR) are available. In order to obtain the appropriate fibre-optic cable interface the centre height of the photometer must be supplied.

To guarantee optimum linking of the light beam to the fibre-optic cable interface and back to the spectrophotometer, the interface in the cell holder of the photometer must be carefully adjusted. For devices with light beam cross sections much bigger than 4 mm x 4mm the light yield may be lower.



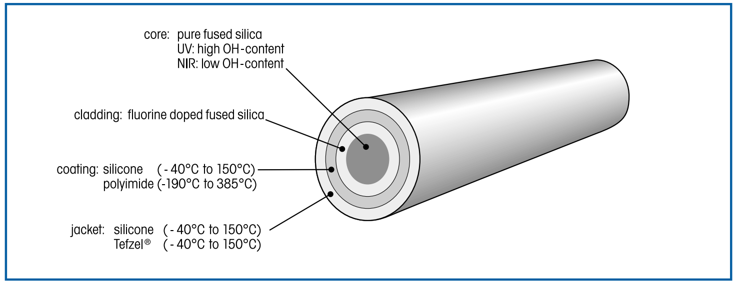
Additional information on the connection of fibre-optic immersion probes to spectrophotometers can be found in 3.3. Fibre-optics.

3.1.4 Fibre-optic Cables

Construction of the Quartz Fibres

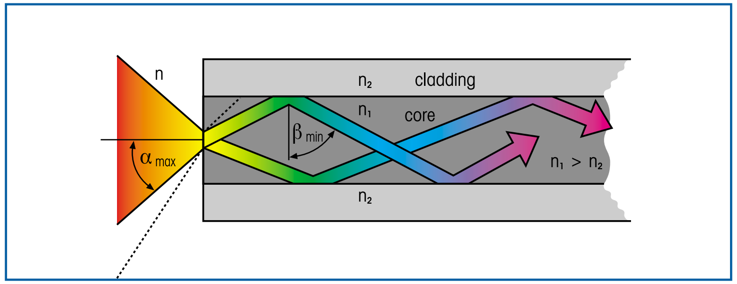
Quartz fibres for fibre-optic cables are drawn from short, very pure fused silica rods (preforms). They consist of a fused silica core and a fluorine-doped fused silica jacket (cladding) with a lower refractive index than the core material.

The additional layer which surrounds the core and cladding (also called coating) determine the thermal and mechanical characteristics of a fibre. The diagram below illustrates the typical structure of the fibre used in fibre-optic cables.



Transmission of Light by Means of Total Reflection

The transmission of the light in the fibres occurs by many total reflections on the interface between core and cladding, but only when the light strikes the end face of the fibre within a specific acceptance angle. The size of the numerical aperture (NA) is linked to this angle which is determined by the refractive indices of core and cladding. For Hellma fibre-optic cables single fibres made of quartz are used. They have a core diameter of 600 µm and a numerical aperture of ~0.22.



There is a limit to the extent that a fibre-optic core can be bent. As a rule of thumb the minimum curvature radius should not be less than 100 times the radius of the cladding for short periods. The minimum curvature radius over extended periods may not be less than 600 times the radius of the cladding

With fused silica fibres one mainly distinguishes between fibres for the UV-Vis and the NIR spectral range. UV fibre-optic cables can be used for the wavelength range of 240 nm to 1100 nm, (see below) NIR fibre-optic cables from 400 nm to 2300 nm. With UV fibres in particular the existing residual content of OH-groups in the core material shows undesirable absorption bands. This is why only fibres with very low OH-content are used in NIR fibre-optic cables.

Reduction of Photodegradation

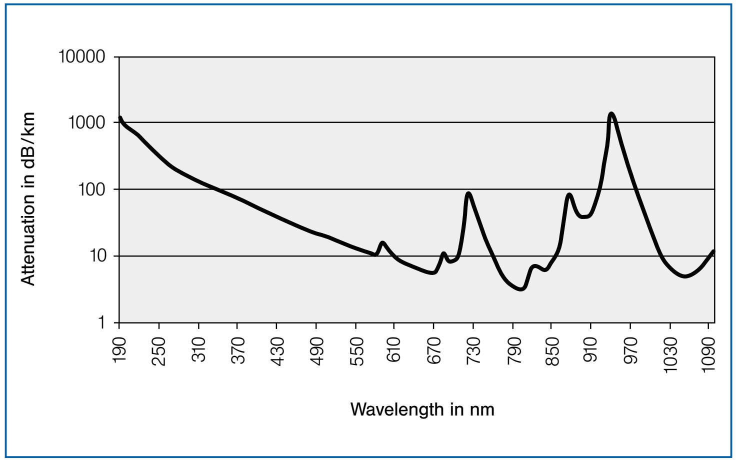
Photometric applications with UV fibre-optic cables, which use standard fibres made from fused silica are limited to wavelengths above 240 nm. When radiated with UV wavelengths less than 240 nm, colour centres develop with a very strong absorbing band at 214 nm. Trace impurities in the core material of the fibres are, among other things, responsible for these colour centres.

The photodegradation of the fibres described is also referred to as solarisation. Through the development of highly purified preforms it has now been possible to produce low-solarisation fibres with much lower degradation. The use of these fibres enables photometric measurements with fibre-optic cables below 240nm.

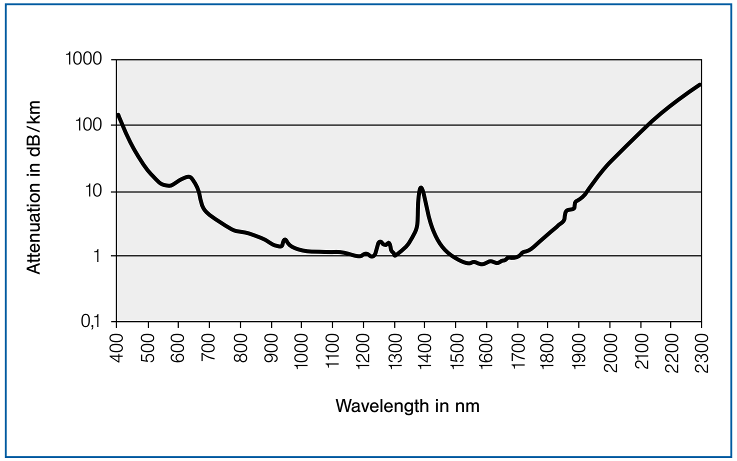
Another way to produce fibres with low solarisation is the subsequent diffusion of hydrogen in the fibre core (loading). As fibres processed in this way slowly release the hydrogen back to the environment, this loading produces a reduction in solarisation only transiently and is therefore not widely used.

The diagrams below illustrate typical attenuation values of the quartz fibres for the UV-Vis or NIR range.

Attenuation of UV fused silica fibres



Attenuation of NIR fused silica fibres



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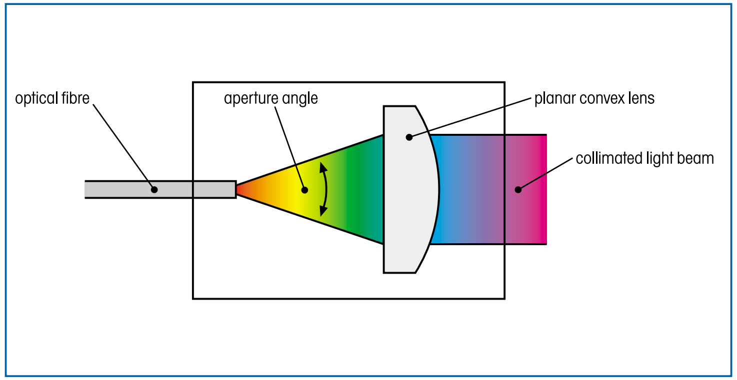
3.1.5 Fibre-optic Collimators

Fibre-optic collimators typically have a cylindrical metal casing with a built-in plano-convex lens as well as a retainer for a fibre-optic cable. The position of the lens in the collimator is such that its focus is on the end face of the fibre of the attached fibre-optic cable.

The purpose of collimators of this type is to convert the divergent light beam, which leaves a fibre into a parallel beam. In this way, as with a cell measurement, the solution to be measured can be radiated by a parallel beam. Conversely the identically built collimator forms a convergent beam which can be coupled back into the fibre of a fibre-optic cable.



This type of collimator is used in almost all Hellma probes. Likewise collimators are necessary for the connection of fibre-optic cables to the cable interface. They are also available in various models (spectral range, diameter etc) as accessories for transmission measuring cells.

3.1.6 Selection of Materials

Optimal Combination of Various Materials

Hellma probes are constructed in such a way that they are optimally adapted to the relevant environmental conditions. A precise knowledge of the chemical and physical parameters in normal measuring conditions and during cleaning is essential for the selection of the right model. A combination of materials will be selected for the immersion probe for each individual case.

- Probe body
  Metallic materials, synthetics and quartz are used for probe bodies
- Optics
  The optical components are made of quartz or sapphire
- Seals
  For gasket materials elastomers and adhesives are used.

Hellma has vast material data bases at its disposal from which the ideal material combination can be chosen for your needs. Further indications can be provided by the materials used at the point of use. When in doubt, the resistance of the materials can be tested by means of a material sample.

For the Toughest Problems: the Materials of Hellma Probes

Metallic materials such as.

- Stainless steel 1.4571 (316 Ti)
- Stainless steel 1.4404 (316 L)
- Stainless steel 1.4435 (316 L)
- Material 2.4602 (Hastelloy® C-22)
- Titanium
- Tantalum

Elastomers used such as

- FFPM (Kalrez®, Chemraz®)
- FPM (Viton®)

Optical materials

- Quartz glass SUPRASIL® 300
- Quartz glass SUPRASIL®
- UV Sapphire
- NIR Sapphire

3.1.7 Installation Instructions

In principle fibre-optic immersion probes are appropriate for manual measurements in the laboratory as well as for on-line measurements in vessels and piping, for example in industrial use.

The Conditions Under Which The Measurements Take Place Must Be Taken Into Consideration!

When choosing an immersion probe, be careful never to go over the allowed pressure and temperature limits. The chemical resistance of the materials to be used can be checked on the basis of the detailed information in the documentation which comes with the probe. This is particularly important when the place of installation of the immersion probe is not the location originally planned for.

Avoid Mechanical Damage!

In order to avoid damage to optical components in the case of a fixed installation using a clamping ring (e.g. Swagelok®), the immersion probe should never be clamped close to the measuring slit.

The Ideal Alignment Is Crucial!

You are advised to insert the probe horizontally or slightly sloping downwards and to position the measuring slit pointing upwards. Thereby a good flow through the measuring slit will be ensured and bubbles can escape upwards easily without disrupting the measurement. A slight downwards incline will ensure that the product does not accumulate near the entry point of the probe into the sample container or into the pipeline.

Sample Replacement and Mechanical Stress

In the case of samples with higher viscosity and a narrow measuring slit it is particularly important to ensure the free flow of sample. To achieve this the probe can be placed in an area with stronger sample flow. It is possible that the immersion probe will be exposed to considerable strain depending on its installation length, which must be considered when deciding on the diameter and material.

3.1.8 Maintenance and Service

Regular Cleaning

Hellma immersion probes are optical precision instruments made for long-term use. To avoid premature deterioration in its performance check the probe regularly for impurities, especially around the measuring slit. The probe must be cleaned regularly as a matter of routine: in the laboratory after each sample measurement, in the process area as soon as the probe head is no longer in contact with the sample.

Clean the immersion probe as follows:

1. Immerse the probe in a cleaning solution and move the immersion probe carefully back and forth. The solvent used in the previous measurements can be used (undiluted) as a cleaning agent, as can Hellmanex® II, the cleaning concentrate from Hellma (see chapter 2.5.1).
2. Repeat the cleaning procedure several times, changing the cleaning solution often.
3. Rinse the immersion probe head several times after cleaning with distilled water and then dry it in clean, oil-free air.

No Ultrasonic Baths!

Do not clean the immersion probe in an ultrasonic bath nor in an autoclave. With some special models, however, sterilisation of the parts which have touched the solution using steam under express pressure (autoclaving) is possible directly at the place where the measurements took place. Hellma's technical advisers will gladly give you more information.

Hellma Service: Service of Industrial Probes

During applications in industrial processing plants it may be desirable, depending on the applications, to have the probe serviced, particularly when the probe has been exposed to corrosive solutions or extreme temperatures and/or pressure. You can send the immersion probe to Hellma on arrangement and we will service it at short notice.