From Containment to Immersion

A history of sample handling in optical analysis

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Whether your application is for simple photometry or UV/Vis spectroscopy; for fluorescence measurement or light scattering; for polarimetry, circular dichroism, cytometry, imaging, or any of the many other forms of optical analysis, your sample must always be presented to the instrument in a container that is as transparent to the light source as possible and one that has a minimal impact on the measurement process.

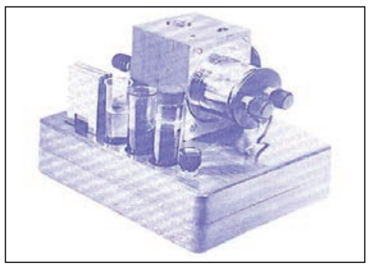

Figure 1: An early photometer from Evans Electroselenium Ltd

In the earliest photometers, like the EEL (Evans Electroselenium Ltd) model shown in *Figure 1*, ordinary test-tubes were used, because that was the only transparent sample holder available at the time; and the resolution of the instrument was too low to detect the problems and errors they introduced anyway.

As instrument performance improved specially selected and matched test-tubes, with index marked orientation had to be used. But eventually the benefits of flat optical-grade windows in square-section cuvettes were the only way to keep up with the ever improving specifications. To make the most of the more sensitive detectors being developed cuvettes manufactured with special optical glass and high-quality quartz were introduced to expand the measurable range further into the UV and infra-red regions.

The earliest cuvettes were nearly all manufactured from windows glued to a frame, but many soon came un-stuck, especially when used for applications with acids, organic solvents and other aggressive samples! With the development of novel manufacturing techniques, introduced by Hellma GmbH, modern cuvettes no longer needed to be manufactured with the use of glue or adhesive. The special wringing and fusion processes that were developed resulted in cuvettes being produced using just one material and in what is effectively a one-piece construction.

From large blocks of glass or quartz, a section is first cut down to a workable size using various techniques (*Figure 2*). Special cutting and lapping procedures are then used to get the parts to the exact size. After this the optical surfaces, and the edges to be joined, are polished to a very fine finish ensuring they are completely free from defects and have a level of flatness that is better than 1µm. To ensure these demanding requirements can be met specially designed machinery, operated by experienced and highly qualified operators has to be used.

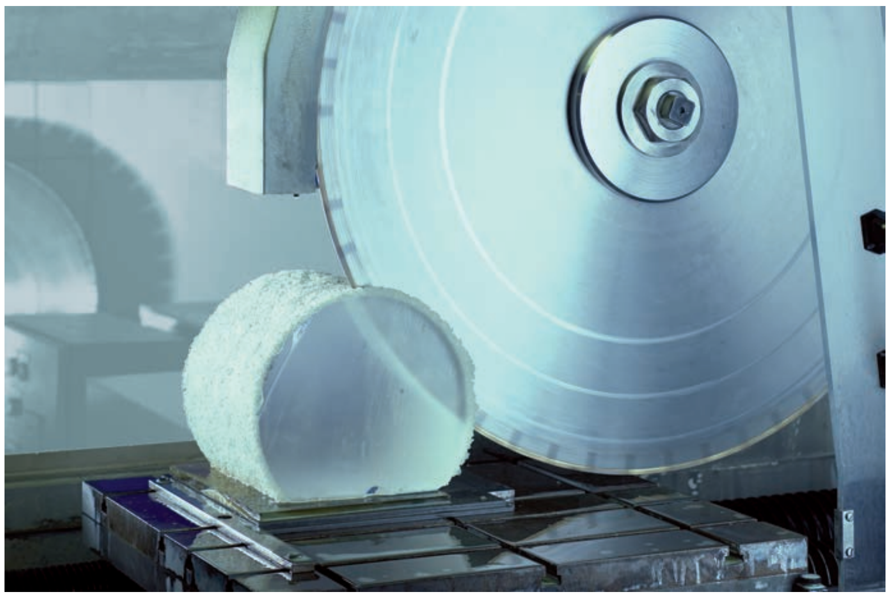

Figure 2: Cutting a block of Quartz to a workable size

Finally, before assembly all the parts are cleaned in an automated, multi-stage, precision-cleaning process that is computer controlled and under clean-room conditions. Because of the flatness and cleanness of the surface finish the edges can then be joined by wringing; a process that uses the forces of molecular attraction to hold together and seal the joints.

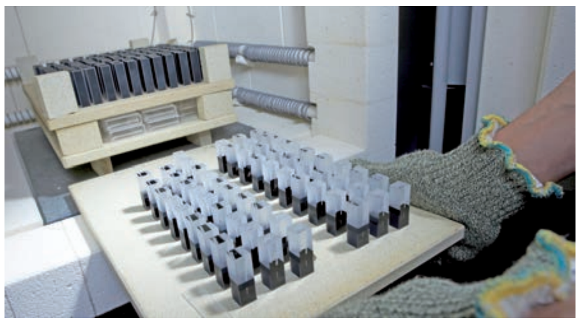

Figure 3: Cuvettes being stacked in an oven for the fusion process

To ensure these wrung joints can withstand the physical, mechanical and chemical demands, that they may be subject to in use, the joints are then thermally bonded. This is a fusion process that is carried out by heating the parts to a level well below the material's melting point to ensure no changes occur to the quality of the prepared optical surfaces (*Figure 3*). Complex items often go through this cycle many times, while special temperature controlled annealing processes are required for stress-relief in those items destined for use in applications such as polarimetry and circular dichroism. Even for a standard cuvette around 100 work steps may be needed from raw material to the finished item.

Throughout the production process Quality Control must ensure that the dimensions and tolerances of the original design are met. An obvious candidate is the optical path-length that will have a direct bearing on the accuracy of your readings, for short path-length quartz cuvettes tolerances as low as +/-0.003mm can be achieved and even up to path-lengths of 100mm they can be as small as +/- 0.02mm. But a spot measurement of the path-length is pointless if the windows are not parallel and their surfaces are not flat. The interferometry scans of window flatness in *Figure 4* compare a top quality quartz cuvette (a) with a similar one of lower quality (b).

The transmission of quartz cuvettes is around 87%, even down into the UV region, this ensures a good level of light passes through your sample and on to the instrument's detector (most of these losses are due to reflection off the external and internal surfaces). Compared to this, modern UV plastic cuvettes have transmission levels as low as 50% in the UV, significantly reducing the dynamic range of your instrument at these wavelengths. A limited choice of path-lengths is available in plastic versions, while the path-length tolerances, inherent in the moulding process for them, are also much greater. Some manufacturers of plastic cuvettes ensure every cuvette in each pack comes from the same mould cavity to help reduce this variation, while regular re-blanking is advised, especially when changing from one batch to another.

Reducing the width of the central chamber of a cuvette is one way to reduce the overall sample volume required to make a measurement. However where the light beam is wider than this aperture light can pass through the walls of the cuvette without going through the sample, leading to significant measurement error. Although many plastic cuvettes have frosted areas around the central sample chamber light can still pass through this to reach the detector. For this type of low-volume cuvette a separate masking aperture should always be fitted to the cuvette holder; however many low volume glass and quartz cuvettes are supplied with black material

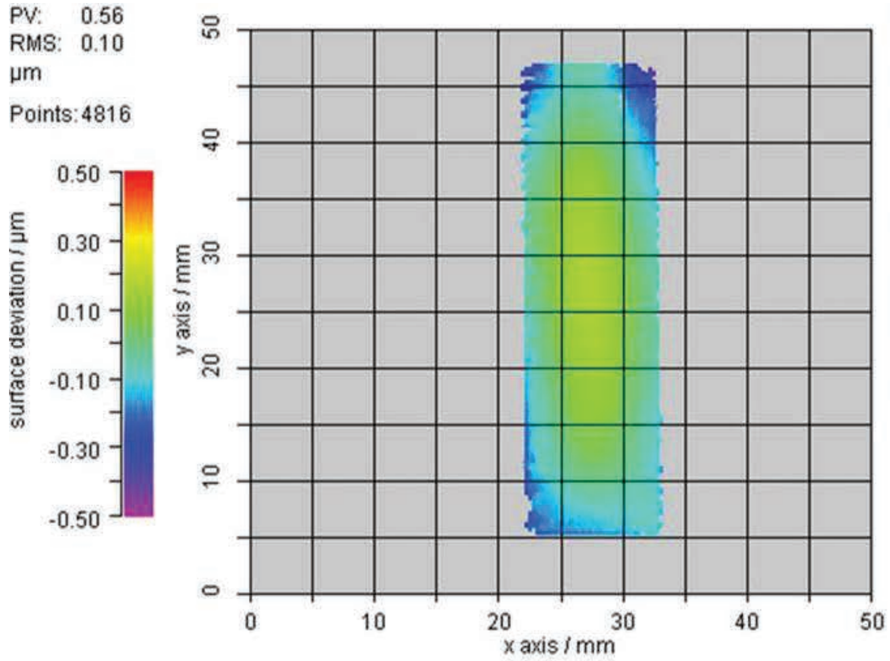

Figure 4 (a) surface scan of a quality cuvette

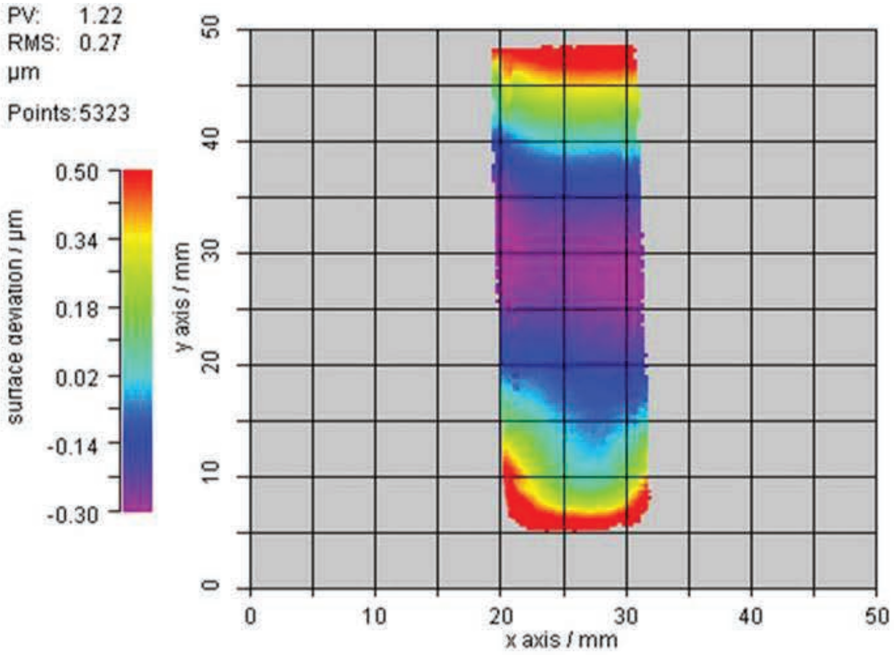

Figure 4 (b) surface scan of a lower quality cuvette

Figure 5: From left to right unmasked and partially masked plastic cuvettes along with a fully self- masking quartz cuvette

surrounding the central chamber (see *Figure 5*), making them self-masking and suitable for the beam geometry of almost any instrument.

Quartz cuvettes are most often chosen for their superior performance in the UV wavelength range but in many other instances their impressive chemical resistance and physical durability, along with excellent temperature, mechanical and dimensional stability, make them ideal for other applications in both the visible and NIR wavelength ranges too. With adherence to a few simple care and handling guidelines they will give a lifetime of dependable and repeatable measurements.

When it comes to automation and more complex designs, glass and quartz cuvettes come into their own, with many different flow-through configurations and temperature controlled versions, with others for high pressure or vacuum operation, some fully sealed or with a septum for sample injection, as well as demountable cells for path-lengths as small as 0.01mm!

Figure 6: Glass and Quartz cuvettes offer solutions to many applications

It's inevitable that established analytical procedures carried out in a laboratory will migrate over time to become on-line or remote measurements made as close to the sample source or process as possible. For many types of optical analysis this has been a relatively slow process, but driven by recent developments in optical-fibre technology, alternative light sources and CCD array detectors these traditional laboratory techniques are venturing out into the wider-world at an ever increasing rate.

In most cases the transfer from laboratory to on-line analysis requires the change from putting a sample in a container to the immersion of an optical probe into a vessel or flowing stream of sample. The importance of the path-length range and accuracy, as well as total transmission values, remain as important for probes as they are for cuvettes, while a number of other characteristics become key considerations for probe-based measurements as well.

For use in these generally more rugged and demanding situations optical elements of Quartz, Sapphire or even Diamond become the materials of choice, while the body or stems of the probe can be constructed from Quartz, PTFE, Stainless-Steel, Hasteloy, Titanium or even Tantalum for resistance to the widest range of aggressive samples and compatibility to specific conditions of temperature and pressure.

The huge benefit of the continuous monitoring of reactions or processes brings with it another variable, and that is how the probe is mounted into its vessel or pipe-line. There are many standard flanges and compression fittings that can be used in different situations, adding further options to the probe design. To enable the optimum selection to be made from all these choices a probe configurator is now available at www.mypatprobe.com which enables relevant decisions to be made for Transmission, Transflection, Reflection and ATR probes.

Often the advantages of continuous monitoring can be just as important in the laboratory environment as they are in the process environment, so in the opposite direction process hardware is being adapted for use in the laboratory. Optical immersion probes are being integrated into an ever increasing range of laboratory instruments dedicated to specific measurement techniques; from photometric end-point detection in titrations, to identifying the cloud and crystallisation points in lab-scale reactors, for solubility and dissolution experiments, for colour comparison in quality control, for the remote measurement of hazardous materials in glove boxes and many more.

Figure 7: Industrial probes for process monitoring/control

The rapid growth of MEMS (Micro Electro-Mechanical Systems) in spectrophotometer design has led to many new micro-modular systems being available from a broad range of manufacturers. These have all strongly supported the application-specific approach to satisfying the analytical and measurement requirements of individual customers; creating in effect a growing market for bespoke optical instrumentation. The adaptability and flexibility of optical immersion probes makes them an ideal sample interface for this type of approach to many applications.

For many years traditional laboratory spectrophotometers have, in the main, only supported the analysis of your samples when contained in cuvettes; perhaps the next generation will embrace both containment and immersion, and let the routine laboratory access the advantages of discrete measurement and continuous monitoring using optical immersion probe technology.

Figure 8: Experience the potential of using an immersion probe with a lab spectrophotometer