

DOUBLE BEAM OPTICAL DILATOMETRY: A NOVEL RESEARCH TOOL FOR CERAMIC RESEARCH

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ABSTRACT:

Thanks to the new double beam optical dilatometer, the ceramic scientist has the possibility of following the behaviour of the sample during heat treatment without interfering with the process. The application has broken the limits of traditional dilatometry in many fields of research:

- *Incoherent materials, like the expansion and contraction of the raw glaze applied on the surface of a ceramic ware, or the behaviour of an incoherent granular frit.*
- *Plastic materials, like the behaviour of a glass above the transition temperature, where the surface tension starts to pull the edges and to make the sample shorter.*
- *Sintering kinetics: studying the relationship between time and temperature during a sintering process.*
- *Extremely thin samples, like tape cast substrates can be analysed with regard to thermal expansion and sintering behaviour.*

1. INTRODUCTION

Thermomechanical analysis plays a very important role in the ceramic field, and is used to check the thermal expansion coefficient of bodies and glazes to ensure an optimal match of thermomechanical behaviour.

There are several types of Thermomechanical Analyser for the measurement of different mechanical properties as a function of temperature. The simplest ones, commonly called dilatometers, measure the dimensional changes as a function of temperature. The instruments of this family may differ in the way they measure dimensional changes of the sample. One very relevant difference is if there is contact with the sample or not.

All the mechanical or electronic dilatometers use a push rod in contact with the sample to transfer the dimensional change of the sample inside the furnace to the transducer (dial gauge, differential transformer, capacitive).

The use of a push rod in mechanical contact with the sample requires correcting the measured data to take into account the expansion of the push rod, but nowadays, with computerised systems, this operation is carried out automatically. As long as the system is kept calibrated, the measurements are very reliable, even if sometimes the correction amounts to twice as much as the measured value.

The push rod dilatometer can follow the sample only as long as it is rigid enough not to be deformed by the pressure of the rod. When a sample is too thin to be pushed or too fragile to be pulled, or it is almost incoherent or plastic, it cannot be measured using this kind of dilatometer. It is necessary to use a non-contact measuring system.

Optical dilatometers use a beam of light to measure the dimensional changes and so the sample is not in contact with the measuring system.

2. OPTICAL DILATOMETERS

There are several methods for measuring the dimensional changes of the sample with a beam of light and they can be summarised in two categories: reflected beam and direct beam.

The first optical dilatometer was invented by Abbe and Fizeau in the second half of the XVIIIth century. This design uses a reflected beam of monochromatic light and the measurement of the displacement is carried out by counting the interference fringes between the forward going beam and the reflected beam. After the Abbe invention, many improvements were achieved on the original design and nowadays there are many models on the market, which use new optics and design. But in order to measure thermal expansion up to high temperatures the sample has to be set on a sample holder inside the furnace and the sample holder also has its own thermal expansion. In order to achieve good accuracy it is necessary to measure the expansion of the sample holder and to subtract it from the actual expansion of the specimen. The best way to do this is to split the laser beam into two beams of light, which are reflected by the top of the sample and by the sample holder or by both ends of the specimen. Measuring the sample from both ends the measure is absolute and there is no need for any

correction. This is the most accurate way of measuring thermal expansion and it may reach a nanometric resolution. This is the type of instrument used by the suppliers of standard materials for the thermal expansion. For example, the National Institute for Standards and Technology (NIST) uses a Fizeau double beam interferometer to certify the thermal expansion of their Standard Reference Materials for thermal expansion.

This method proved to be very accurate, with a resolution of a fraction of the wavelength of the incident light, but it is limited by the reflectance of the surface of the specimen. If the specimen is non-reflective, or becomes non-reflective during the test, it is then necessary to use a mirror, which is placed in contact with the specimen using a refractory push rod. Working in this way, this method loses the advantage of being non-contact and becomes substantially similar to the electronic dilatometer.

The direct beam measuring system overcomes this problem because the specimen is measured by the image that it projects on a CCD when it is lighted by a direct beam of light. Using a beam of light with a short wavelength and a very high resolution CCD it is possible to achieve good resolution. For example, using a blue light with a wavelength below 0.5 micron, it is possible to have an image with an actual resolution of 0.5 micron per pixel of the camera (not an interpolated resolution, but an actual resolution). With a sample 50 mm long, the resolution becomes one part over 100,000.

Using two beams of light, which illuminate both the ends of the specimen, it is then possible to achieve an absolute measurement of the dimensional changes of the sample during heat treatment. The specimen is completely free to expand or contract; there is no measuring system in contact with it, but only a sample holder, to keep it in place inside the furnace. The displacement of the sample holder is not relevant for the result of the measurement because the optical system watches both ends of the sample.

3. THE DOUBLE DIRECT BEAM OPTICAL DILATOMETER

The idea of a double beam optical dilatometer is not new, but many attempts made in the past failed because of the limitation imposed by the image acquisition and image processing technology. Nowadays, the performance of digital cameras and personal computers enable designing a double beam optical dilatometer at a competitive cost.

As a first approach it may seem reasonable to use only one camera with a large CCD to collect the image of the sample as a whole. This kind of design looks cheaper at first sight, but becomes immediately unfeasible on thinking of the resolution required for a thermal expansion measurement on small size samples. In fact, to achieve a resolution of 0.5 micron on a sample 50 mm long, ensuring a resolution of the measurement of one part over 100,000 it would be necessary to use a CCD with 100,000 pixels per line, which is not yet available on the market and it may well not be available for a while.

The use of two beams of light implies the use of two microscopes and two digital cameras. Focusing the image of the tip of the sample on the CCD of the camera, with the maximum magnification achievable using visible light, means being able to see

only few hundred microns of the sample. A sample 50 mm or 50,000 microns long which reaches an expansion of 1% will expand 500 micron. Using blue light with a wavelength of 478 nanometres and magnifying up to 0.5 micron per pixel, the image will shift 1000 pixel. Since the sample is free on the sample holder, it may move in one direction only, going out of the field of view of a video camera with 1 mega pixel (1000x1000). The use of line cameras is unfeasible because the measurement will be strongly affected by edge imperfection. The use of larger area CCD implies being able to obtain a perfectly flat field over a large area CCD, and working with this magnification is close to impossible.

The solution to this problem is to move the optical path in order to follow the expansion or contraction of the sample. In order to do this it is necessary to use two linear translation stages equipped with a step motor controlled by the computer and able to make the shift in a very short time with very high accuracy.

This new design allows building optical dilatometers with unprecedented features: using a sample 50 mm long placed horizontally in the furnace it can measure expansion with a resolution of one part over 100,000, or using a sample 15 mm long placed vertically inside the furnace it can measure a sintering or bloating process with no limitation in dimensional changes. Figure 1 shows the scheme of a horizontal double beam optical dilatometer.

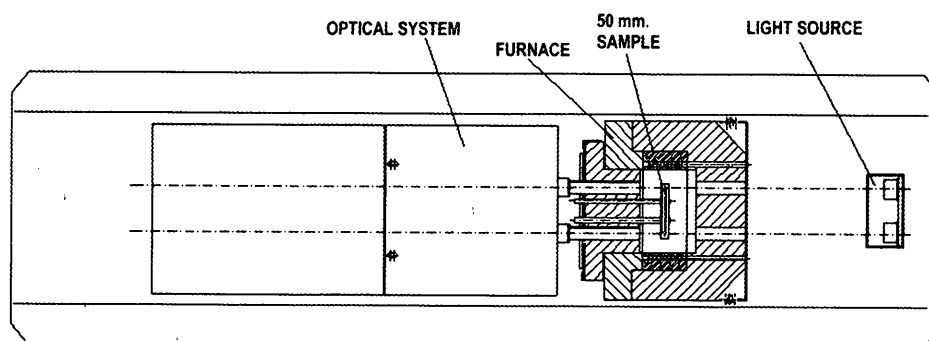


Figure 1. Scheme of a horizontal double beam optical dilatometer

One relevant feature of this kind of dilatometers is the fact that the calibration curve is unnecessary. Once the magnification of the two optical paths is carefully established, there is no need for further calibration, unless the instrument is mechanically taken apart. In fact, the magnification of the optical system does not change with time or with the number of tests performed. To verify this, it is possible to check the calibration using a Standard Reference Material supplied by NIST. Figure 2 shows the perfect match between the curve measured on a certified sample and the curve obtained plotting the certified data from NIST.

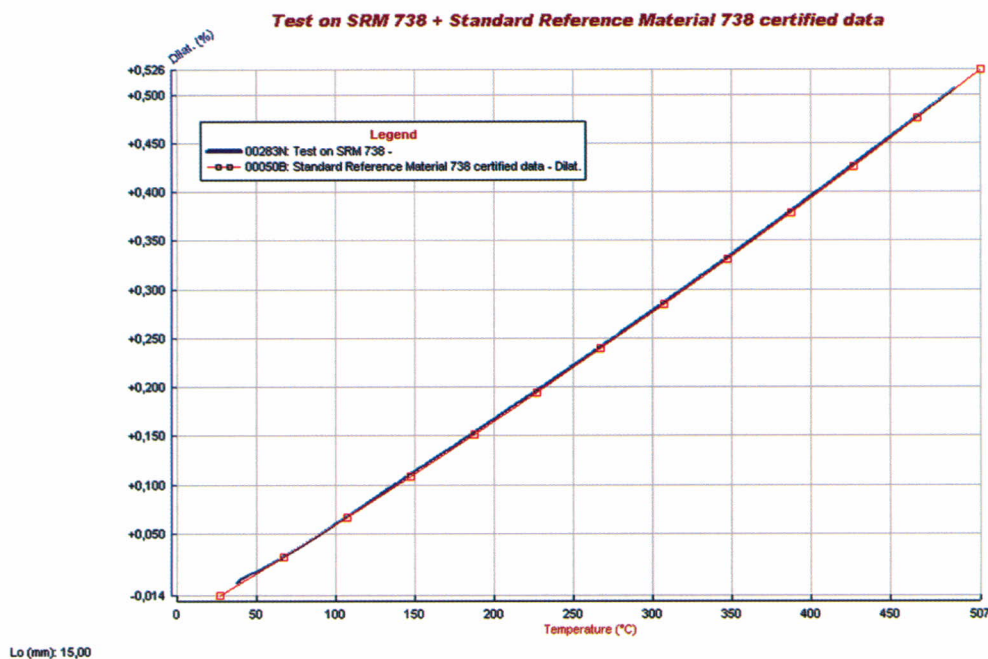


Figure 2. Thermal expansion of the Standard Reference Material SRM 738 from NIST as measured with a double beam optical dilatometer (Blue line) in comparison with certified data (Red dotted line).

4. NEW FIELDS OF RESEARCH

Now the ceramic scientist has the possibility of following the behaviour of the sample during heat treatment without interfering with the process. The application has broken the limits of traditional dilatometry in many fields of research:

- Incoherent materials, like the expansion and contraction of an incoherent granular frit, as applied on a raw tile.
- Plastic materials, like the behaviour of a glass above the transition temperature, where the surface tension starts to pull the edges and to make the sample shorter
- Sintering kinetics: studying the relationship between time and temperature during a sintering process
- Extremely thin samples, like the thermal expansion and sintering behaviour of the extremely thin layer of glaze as applied on a ceramic tile.

5. THERMAL EXPANSION ON INCOHERENT MATERIALS.

Ceramics is the science of sintering powders and powders can be incoherent. Optical dilatometry can be used to check the behaviour of uncompacted powders which have no mechanical strength, like a layer of granular frit.

Thermal expansion of a granular frit can only be measured with no contact because, with no addition of a binder, the material is completely incoherent. The thermal expansion test with traditional dilatometers on these raw materials is normally carried out adding clay as a binder, but by doing so, behaviour changes

completely. Using an optical dilatometer it is possible to achieve accurate measurement of the thermal expansion even on a granular frit which was held together simply by wetting with a drop of water.

Figure 3 shows the sample before (in the foreground) and after the thermal expansion test.



Figure 3. Sample of incoherent granular frit before (in the foreground) and after the thermal expansion and sintering test.

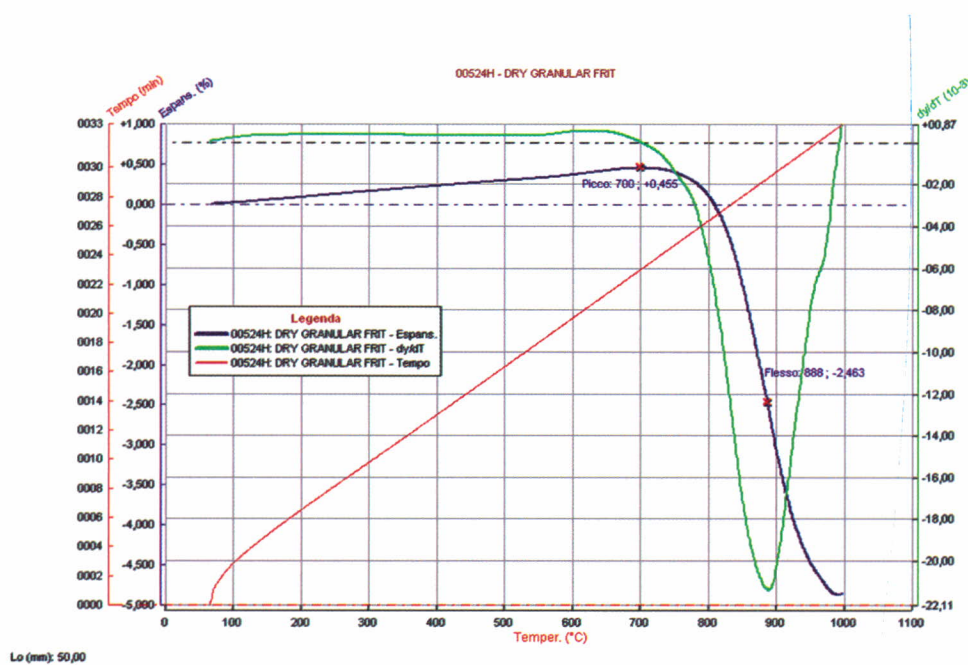


Figure 4. Thermal expansion and sintering of an incoherent granular frit (blue curve), derivative curve (green), Time (red curve)

The result of the measurement clearly shows the sintering and melting behaviour of the material.

6. MEASUREMENT OF THERMAL EXPANSION ABOVE THE GLASS TRANSITION TEMPERATURE UP TO MELTING.

Most of the sintering mechanisms which evolve during heat treatment in traditional ceramics involve the development of a liquid phase. The presence of the liquid phase during sintering makes the material substantially plastic. The dimensional changes during the sintering process can be studied only if the measuring system does not interfere with the sintering mechanism itself. Non-contact measurement is ideal for the study of the transition from solid to liquid even in the glassy state. The measurement of thermal expansion is substantially identical to the measurement obtained with a push rod dilatometer as long as the sample is still rigid. When the temperature exceeds the glass transition, viscosity drops exponentially and the sample becomes soft. With a non-contact system it is possible to continue the measurement up to complete melting of the glass.

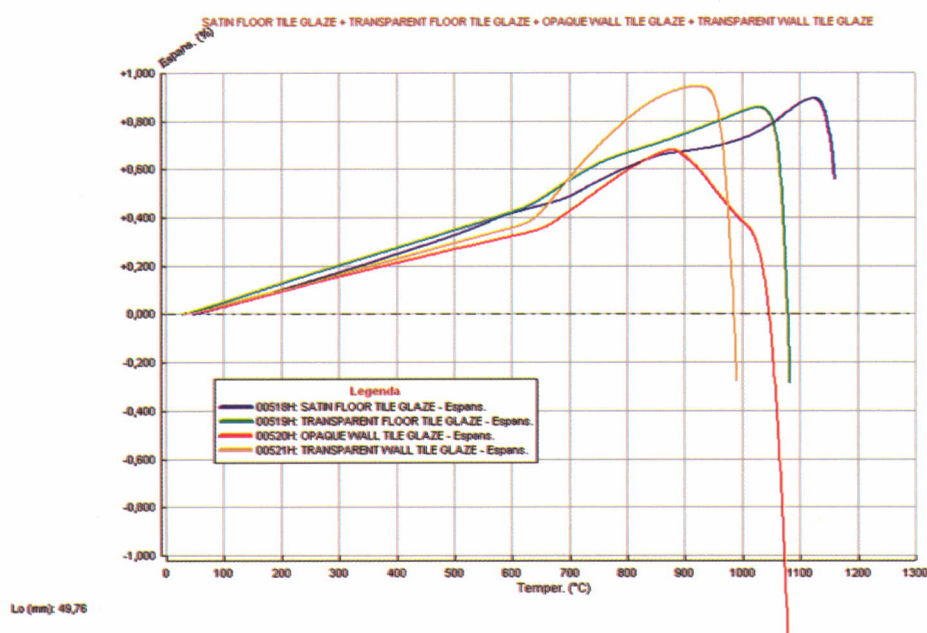


Figure 5: Thermal expansion up to melting of several glazes. The part of the curve above the glass transition temperature keeps going up to melting of the sample.

Figure 5 shows the measurement on different glass and glazes samples while Figure 6 shows the samples after the measurement.

The graph reaches a maximum point and then starts falling. The reduction in size of the sample is given by the surface tension of the glass, which makes the tip rounded and the sample shorter.

The part of the curve above the transition point is hundreds of degrees long and this allows the extrapolation of the thermal expansion of the molten glass. Knowing the thermal expansion of the molten glass, it becomes possible to calculate the density of the molten glass at any temperature and this is crucial information for the calculation of the surface tension of the molten glass using the sessile drop analysis method.

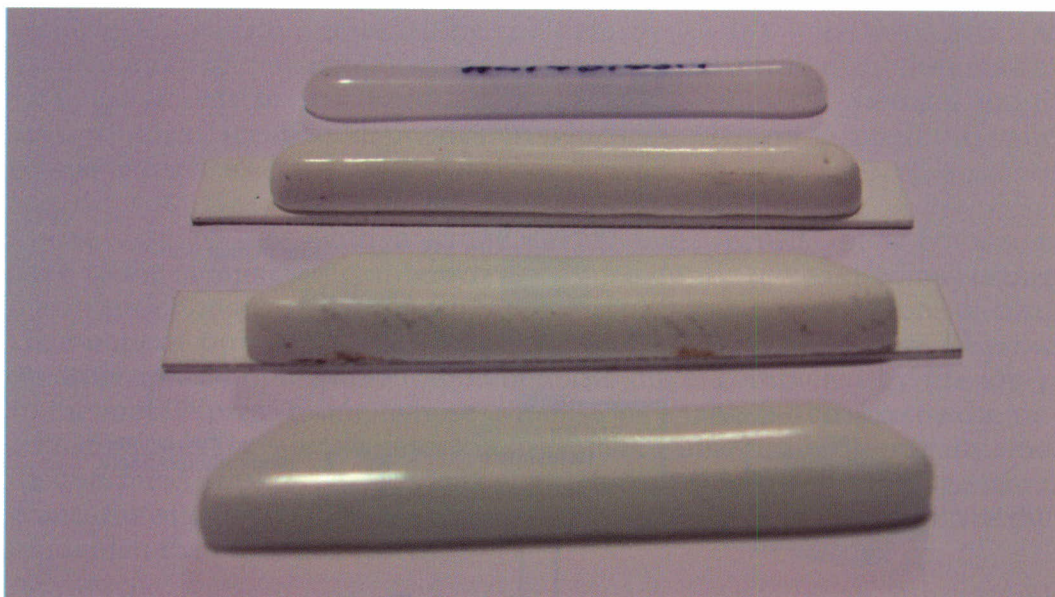


Figure 6: Samples of glazes after the thermal expansion test: the edges of the samples become round because the glaze is melting.

7. SINTERING OF A GLASS POWDER

The study of sintering kinetics is an ideal application for the optical dilatometer. The relationship between sintering speed at constant heating rate versus temperature, or shrinkage versus time at constant temperature can be exactly determined. Only with a non-contact dilatometer does it become possible to follow the sintering behaviour of a ceramic material when the driving force of the sintering process is the surface tension of a liquid phase. This study yields extremely valuable information, which can be used to define the best heat treatment for each specific material.

Figure 7 shows the sintering curve of a glass powder.

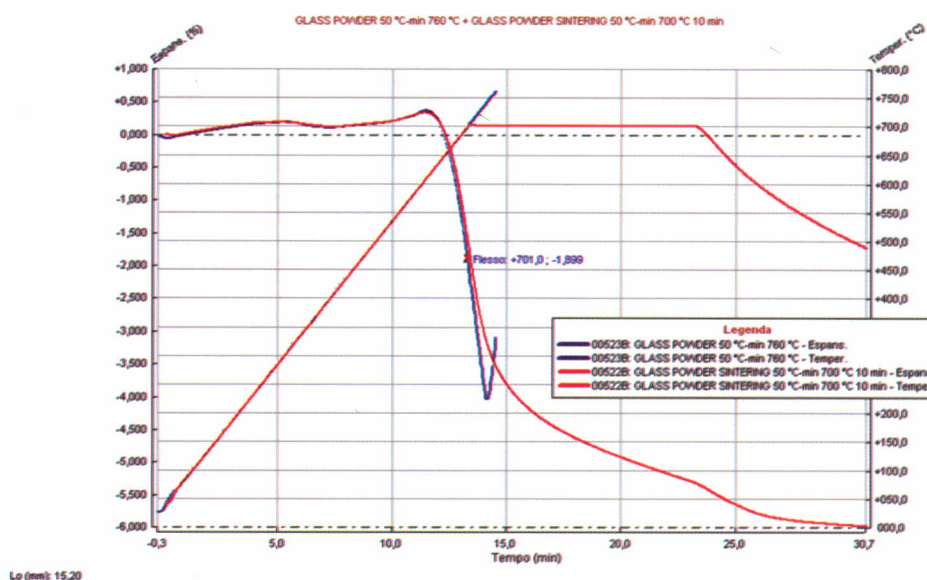


Figure 7: Sintering of a glass powder. The blue curve is the first test, carried out at a constant heating rate up to bloating. The maximum sintering rate is identified at 701 °C. The red curve is a second test carried out with the same heating rate up to 700 °C, then holding this temperature for 10 minutes. The sintering proceeds with no sign of bloating.

The sample of compacted glass powder was first heated with a constant heating rate up to complete melting. This test allows defining the temperature of maximum sintering speed. Designing a second heat treatment with a dwell at that temperature, we can identify the time necessary to achieve a stable sintering condition, preventing melting or bloating of the material.

As expected, sintering speed decreases exponentially against time at constant temperature, while it increases exponentially versus temperature at a constant heating rate.

8. EXTREMELY THIN SAMPLE: LAYER OF GLAZE AS APPLIED ON A CERAMIC TILE

The behaviour of the raw glaze can be followed up to complete melting, up to the point it becomes shorter because the surface tension rounds the edges of the sample.

Figure 8 shows the result of a test made on a transparent wall tile glaze (red curve).

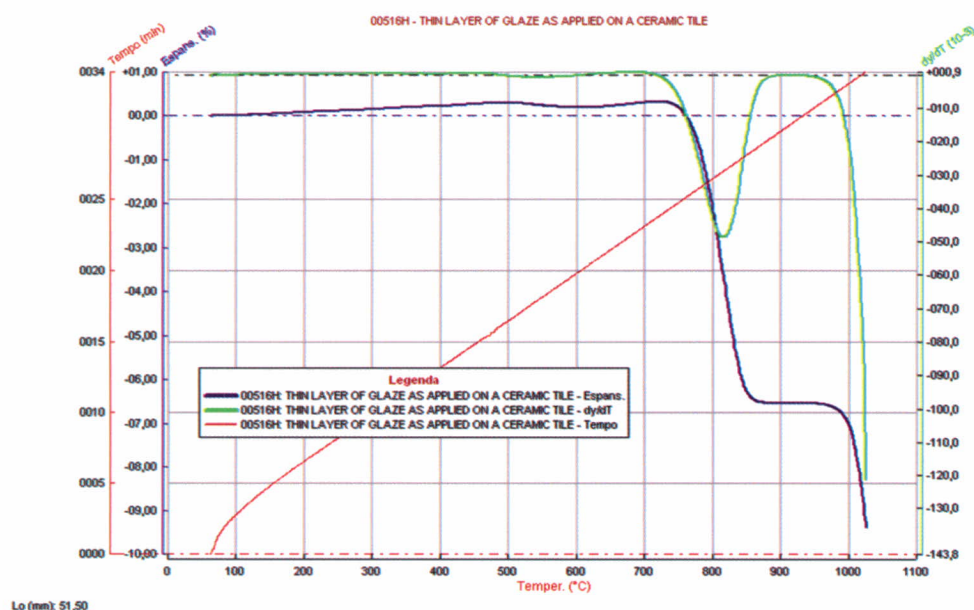


Figure 8. Thermal expansion and sintering of a glaze layer as applied on a ceramic tile (red curve), Derivative curve (green), Time (red)

The samples were obtained laying an ashless filter for chemical analysis on the ceramic tile before the glaze application, directly on the glazing line, as shown in Figure 9.

The amount of glaze and the nature of the deposit of glaze particles is exactly the same as in the industrial application. The filter is then removed from the surface of the tile and it is cut in a suitable size for the measurement inside the optical dilatometer (typically 50 mm long, 5 mm wide). The sample is then set on the special sample holder for thin samples (Figure 10) and the measurement is started.

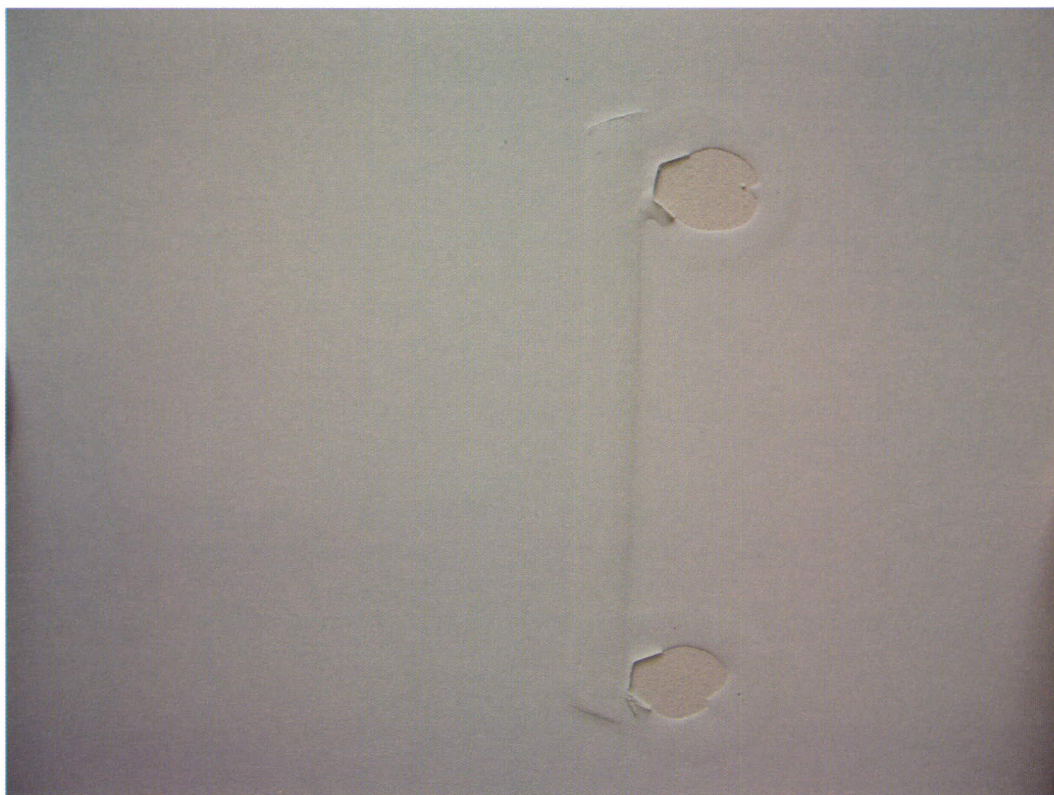


Figure 9. Experimental method for collecting the glaze layer as applied in the glaze line. A small tape of ashless laboratory filter is set on the tile before the application. After the application, the relief caused by the paper is visible under the glaze.

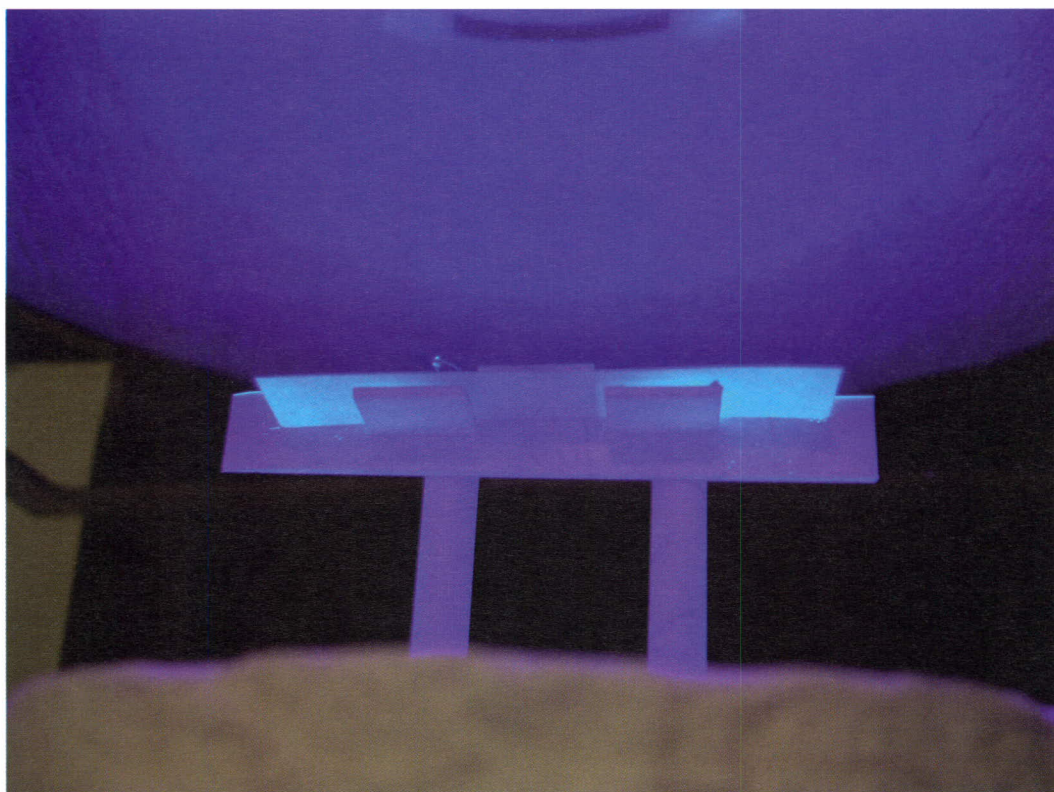


Figure 10. The layer of glaze is carefully removed from the surface of the tile, while still on the filter paper. The sheet is set on a sample holder inside the furnace of the double beam horizontal optical dilatometer.

The filter paper will burn out leaving no ash and with no interference on the measurement.

From the result of the test we can clearly see that the layer of glaze undergoes sudden shrinkage in the initial sintering phase. Since the material is incoherent and not plastic, this shrinkage may produce extensive microcracking on the surface of the glaze. The scars of these small cracks will make the surface of the glaze slightly hammered, even though the application is perfectly smooth.

9. CONCLUSIONS

This is only an overview of the new research possibility made available by the new technique of double direct beam optical dilatometry. Ceramic science is the ideal field of application of this testing method because of the specific characteristics of ceramic materials. It is now possible to follow all the stages of the ceramic process with no interference due to the presence of a measuring system in contact with the material.