

## New optical instruments for laboratory and process testing

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Expert System Solutions has recently developed new no-contact and high temperature measurement techniques for the laboratory and for testing processes. The first results in this field were the automatic heating microscope, essential for studying the fusion process of the frits, glazes and ceramic or metallurgical powders. The double beam optical dilatometer was developed for studying the sintering process, and is capable of carrying out absolute no-contact measurements on a sample subjected to a sintering heat treatment. The latest developments in this technology have produced the horizontal optical dilatometer and the optical fleximeter, two highly innovative instruments which complete the options for analysis of the behaviour of ceramic materials subjected to heat treatments. The four instruments provide a complete view of thermo-mechanical phenomena which occur during the heating and cooling cycles, providing an unequalled depth of analysis and synthesis, and enabling the operator to tackle and resolve even the trickiest problems. The horizontal optical dilatometer uses a sample 50mm long and carries out measurements to the resolution of one in 100,000. The sample is measured by two beams of light, which illuminate both ends, in this way providing an absolute measurement, without the need for an correction curve to eliminate interference due to thermal expansion in the measuring system.



**The new MISURA LT horizontal optical dilatometer**

The optical flexion meter measures the flexion of a ceramic sample suspended between two supports with an inter-axis of 70mm. The measure is taken thanks to a beam of light that illuminates the central area of the sample and determines any upward or downward shift. Measuring the flexion makes possible different types of assessment, which until now had been impossible or very difficult:

- for example, it is possible to ascertain the pyroplastic behaviour during the sintering phase of the body mixtures, or to check the type of deformation caused by the presence of an engobe or of a glaze during the heating cycle.
- A measurement that is very useful but currently quite difficult is the temperature at which the enamel joins the support, to calculate the compression level of the glaze on the support, which used to be measured using the old Steger tensiometer.



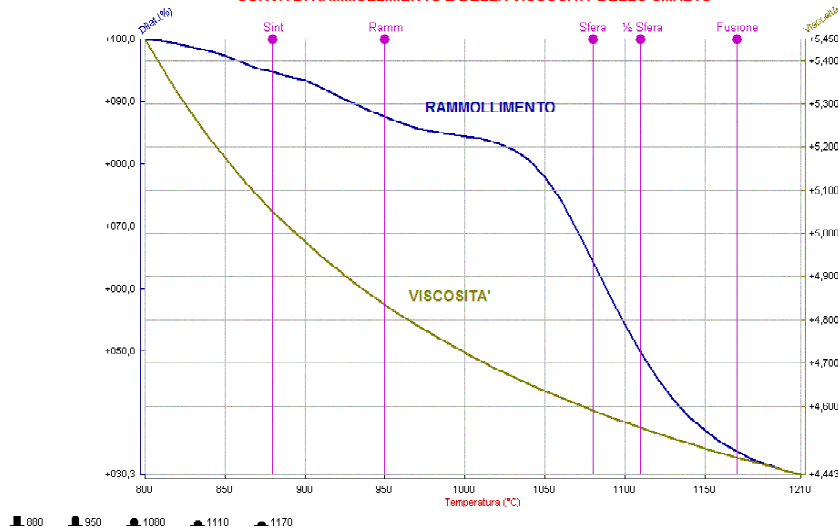
**Detail of the no-contact measuring system of the optical flexion meter MISURA FLEX, with sample suspended between two supports 70mm apart.**

We see three ways in which these instruments can be used.

Study of the dilatometric coupling between glaze and support for a porous covering product. This study requires a complete review of all the components of the system. We start therefore by looking at the thermomechanical behaviour of the raw glaze, using the heating microscope MISURA HSM. This instrument enables the accurate measurement of the temperature at the beginning of the sintering phase of the glaze, the temperature of the softening, the sphere, the fusion and the trend of the viscosity as a function of the temperature.

The measurement is carried out through direct observation of the glaze sample placed inside the tubular kiln. The sample, which measures 2mm by 3mm, can be heated to high temperatures rates, simulating the heating cycle of industrial ovens. The images are captured and analysed automatically so as to provide all the information on the behaviour during fusion of the glaze sample. The information is transformed into numeric data and imported into a temperature graph.

**Graph 1: Softening curve and viscosity trend on basis of temperature.**  
**CURVA DI RAMMOLLIMENTO E DELLA VISCOSITA' DELLO SMALTO**



Using this data and data supplied by the dilatometer it is possible to calculate the viscosity curve of the glaze. Thanks to the VFT equation, and using three pairs of temperature-viscosity values, the viscosity trend can be completely reconstructed, right across the temperature range. In this case the values employed corresponded to the temperature of glass transition, to the temperature of dilatometric softening and to the temperature of half sphere, for which it has been established that the viscosity values are always fairly constant.

The next step is to establish the thermo-mechanical behaviour of the glaze after firing. These analyses are carried out by the optical dilatometer with double horizontal beam, which provides an accurate reading of the

linear thermal expansion coefficient, the temperature at the start of the glass transition and the temperature of the dilatometric softening.

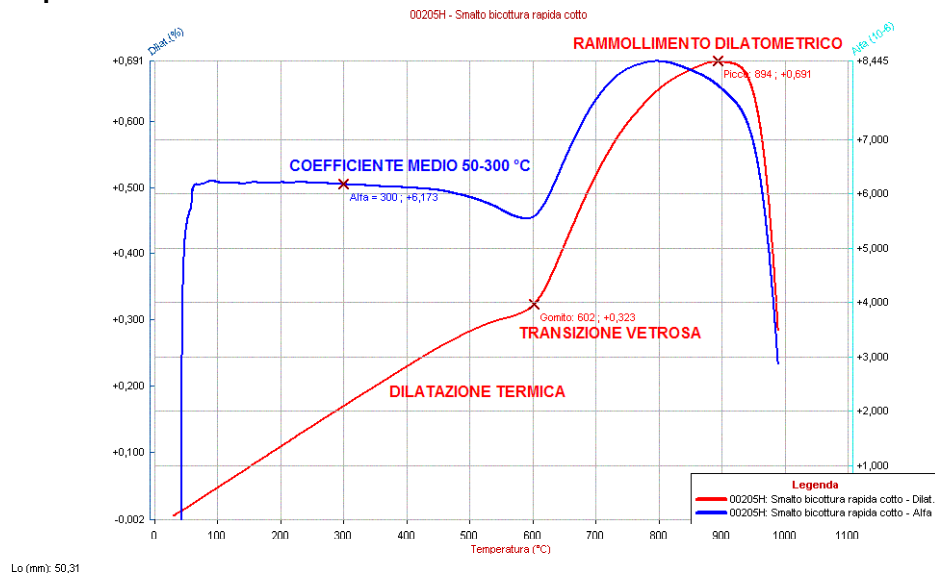
The main characteristic of the new horizontal optical dilatometer MISURA LT is that the measurement is taken by two beams of light. Therefore, the behaviour of the sample is not affected by the presence of a mechanical measuring system and by the presence of a probe which applies pressure on the sample. The material can expand or contract freely, so the dilatation curves, as well as the sample's softening temperature, can be recorded.

Most mechanical dilatometers have to apply pressure on the sample to take a measurement, so the sample starts to deform at a temperature slightly higher than that of the glass transition. With the optical dilatometer, the expansion curve has a much wider rising section after the glass transition point because the sample is not subject to any pressure. The dilatometric softening measured with an optical dilatometer is similar to the softening measured with a heating microscope.

Another difference is that the rising section of the thermal expansion and therefore the average coefficient demonstrate a constant slope because the material is capable of showing its thermo-mechanical properties from the beginning, and the measurement is not influenced by the thermal expansion of the measurement system inside which the sample is placed.

In the horizontal optical dilatometer, the sharp fall that manifests itself beyond the softening temperature demonstrates that the ends of the sample are rounding off, even though the volume of the material continues to increase as a consequence of thermal expansion, but its length reduces as a result of surface tension. In fact, it will be found that the sample, once the measuring is completed, has rounded ends.

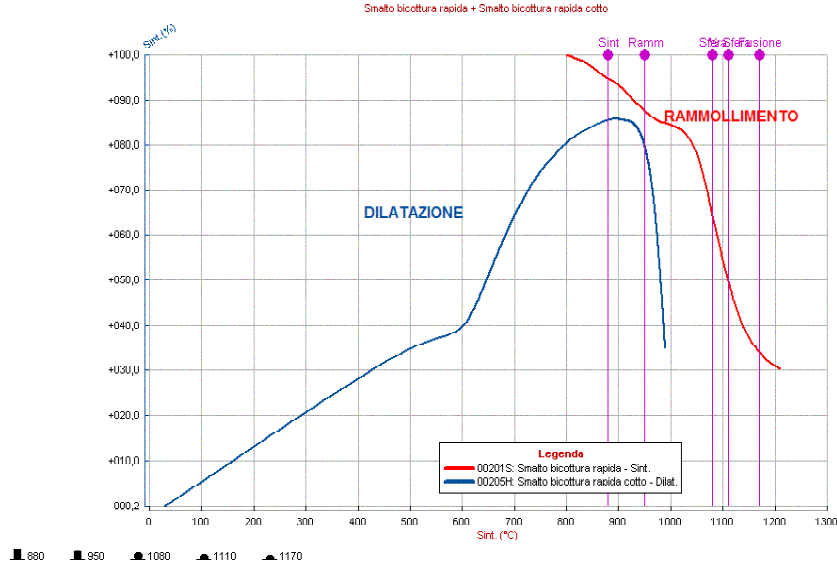
**Graph 2: thermal dilatation and median coefficient of linear thermal dilatation of the enamel**



The tests carried out with the optical dilatometer and the heating microscope have been overlaid onto the same temperature scale as in Graph 3, where the softening curve is coloured red and the thermal expansion curve is coloured blue.

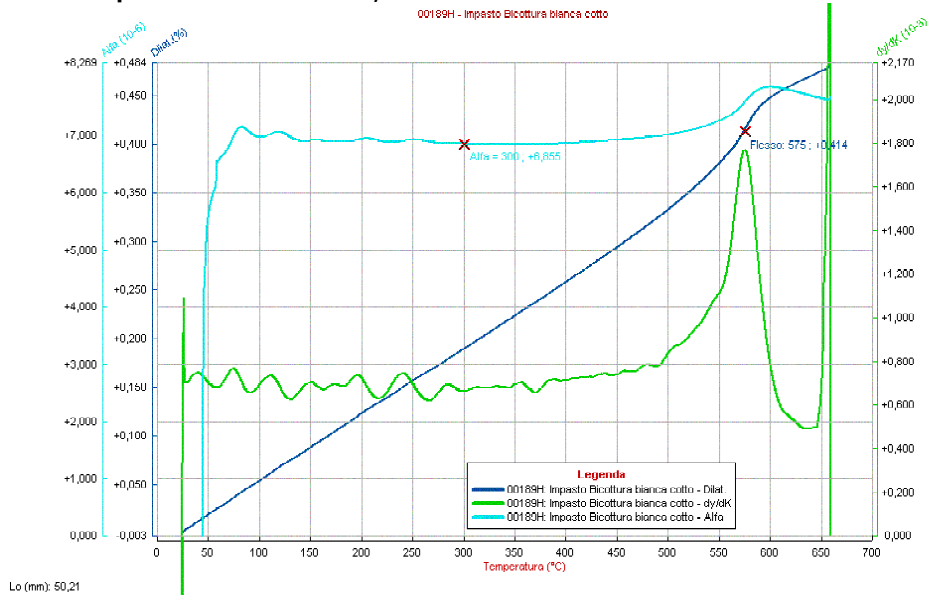
The thermal expansion curve has been amplified to make possible a comparison with the softening curve. The sintering and softening temperatures measured with the heating microscope straddle the temperature of maximum expansion measured with the optical dilatometer.

**Graph 3: thermal dilatation and softening curve on the same temperature scale.**



As well as the characteristics of the glaze, the thermo-mechanical behaviour of the fired support must be established, by measuring the linear thermal coefficient and the transition temperature of the quartz, which are the two main features. The blue curve represents the expansion of the support, the sky blue is the average coefficient of the linear thermal expansion, while the green curve is a first derivation of the thermal expansion, which peaks when the quartz transition reaches 575°C.

**Graph 4: Thermal dilatation, median coefficient and first derivation of the biscuit.**

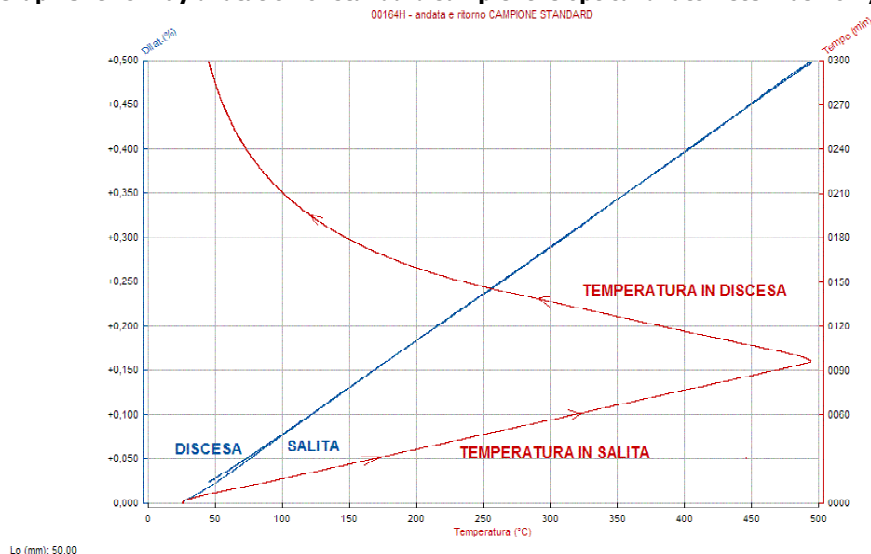


The biggest problem with porous ceramic material is the expansion because of humidity caused by ageing. To measure the expansion in humidity of a porous support, a test has to be carried out in an autoclave and the increase in size of the sample must be measured physically. There remains the problem, however, of establishing how much the material has expanded after years of use under real conditions. An optical dilatometer measures how far an aged sample has expanded over time. This measurement can be taken if the dilatometer being used has had no mechanical hysteresis.

The curve in Graph 5 was obtained with a standard sample, by which is calibrated the dilatometer, based on a heat cycle featuring an upward temperature slope and a downward temperature slope. The two curves are

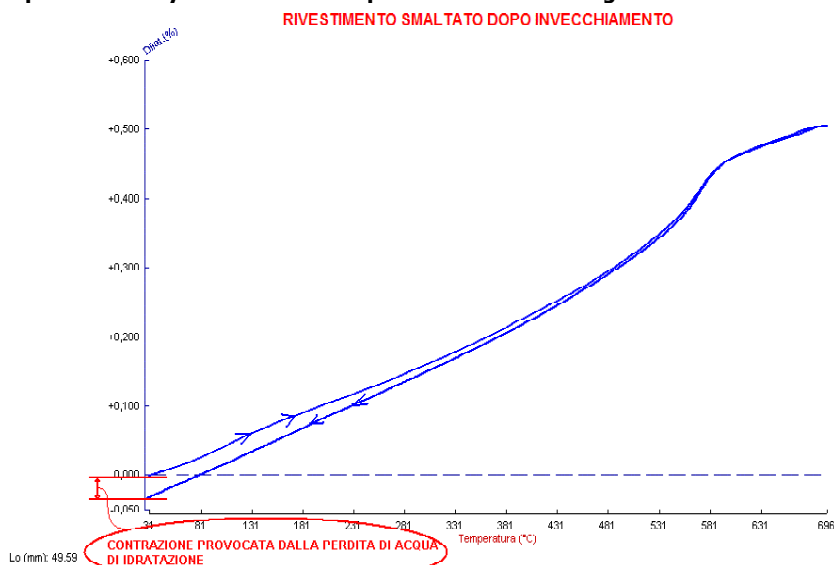
almost perfectly superimposed because the optical dilatometer is almost wholly without mechanical hysteresis. The measurements made with the heating and cooling cycles on real samples therefore become very important.

**Graph 5: two-way dilatation of standard sample: the optical dilatometer has no hysteresis.**



Measurements of a sample taken from an aged biscuit show a curve similar to the one in Graph 6: the higher curve is the result of heating up, which drops when there is a loss of water. The ageing of the material is mainly due to the absorption of water, which enters the clay, breaking up its structure and causing an increase in volume. On reaching 200 °C, the water is released, causing a contraction. The return curve superimposes itself on the outward curve up to 500 °C, then deviates and follows a straight line all the way to room temperature. The deviation of the two curves at room temperature represents a contraction caused by the loss of water. In this case we have a value of around 0.03%, or 0.3 per thousand.

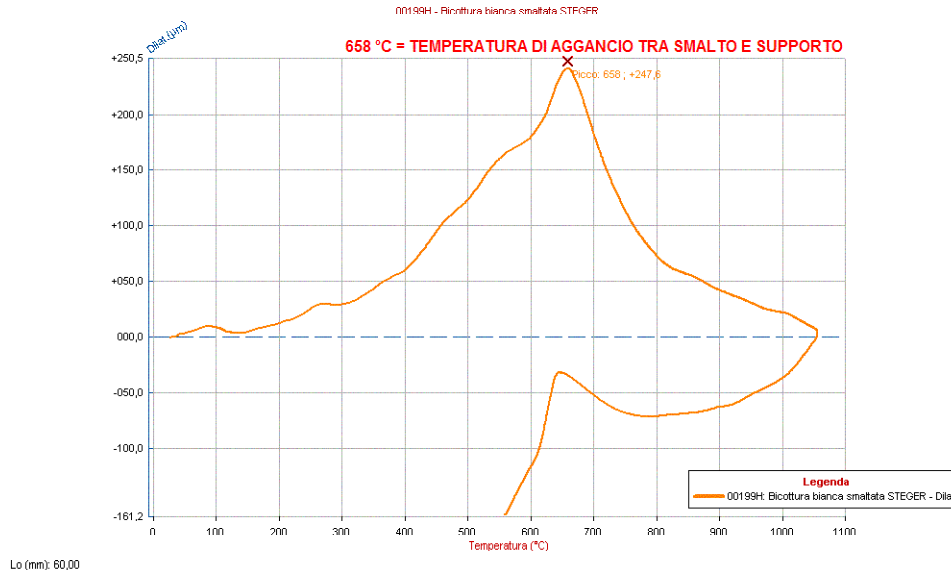
**Graph 6: two-way dilatation of sample taken from a tile aged under conditions of normal use.**



When the glaze and the support are once again subjected to heating, thermo-mechanical deformations follow. Measuring the thermo-mechanical deformations with the non-contact optical fleximeter means the compression level of the glaze can be established, as well as a simple and accurate temperature reading of when the glaze takes to the base material. This test used to be carried out with the Steger tensiometer, which is not so successful from a practical point of view because so complicated to use. The optical fleximeter works with a

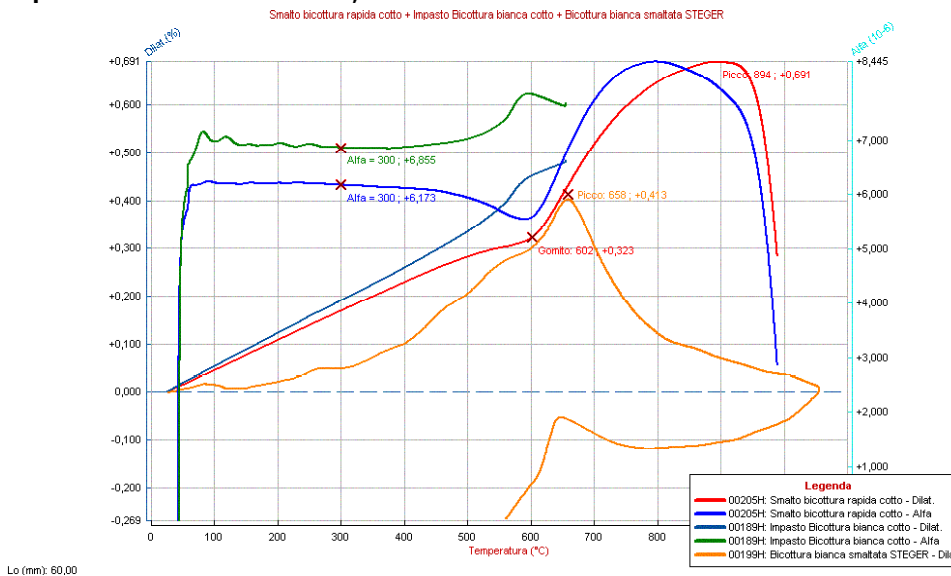
piece of actual tile 8.5cm long, suspended on two supports with an inter-axis of 70mm inside the kiln. The flexion measured represents the bending that has actually affected the sample inside the kiln. The Graph 7 shows, in this case, where the sample under examination flexed by 250 micron. The flexion increases progressively until it reaches a peak and, once the tension is released, returns to being flat. The peak temperature represents the temperature at which the glaze releases all its tensions, or when the glaze takes to the support. Increasing the temperature returns the material to flatness and, then lowering the temperature, the flexion reappears and increases once more.

**Graph 7: flexion curve of a sample of enamelled biscuit**



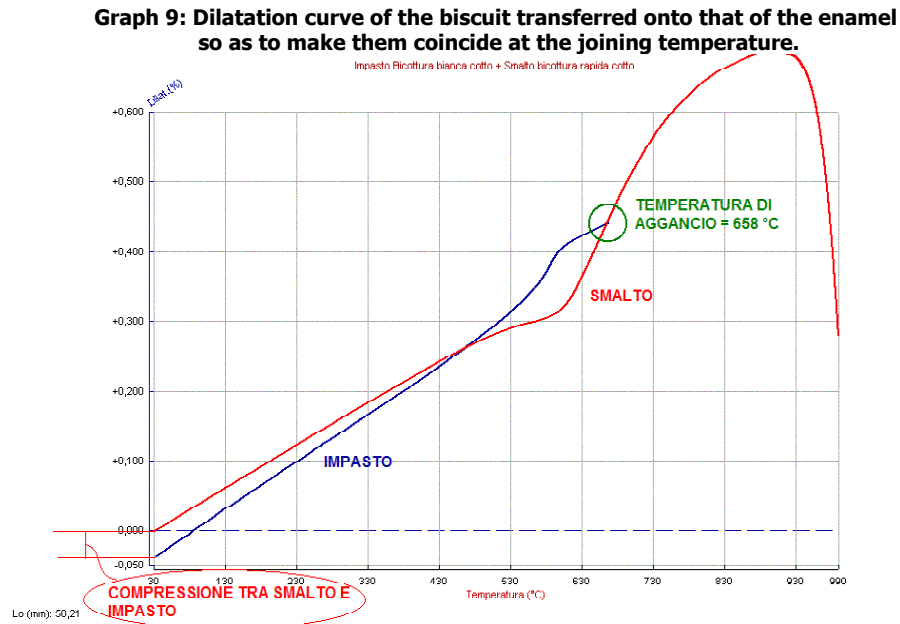
All results obtained with different measurements can be transferred onto the same graph, so as to obtain a direct comparison. Graph 8 shows us the dilatation curves of the glaze and the support superimposed onto the flexion curve.

**Graph 8: Dilatation of the enamel, the biscuit and the curve of flexion of the enamelled biscuit**



The flexion curve shows a peak at 658 °C, effectively the temperature at which the glaze binds to the clay. To establish properly the compression level when the glaze and the clay bind, the curve of the clay must be transferred onto that of the glaze and made to coincide at 658 °C.

In this way, we obtain Graph 9.



It is clear that the clay, after cooling, is shorter than the enamel and therefore keeps it compressed. The compression level in this case is of about 0.04%, or 0.4 per thousand. In Graph 6 we saw that the expansion level of the material being measured was followed by a contraction of 0.03% caused by loss of water and we can conclude that the glaze is still in the compression phase and is not at risk of a crazing.

The same test can be carried out on the material after completing the autoclave test to check that the compression level of the glaze is truly greater than the level of contraction caused by the loss of water, or the expansion in the autoclave.

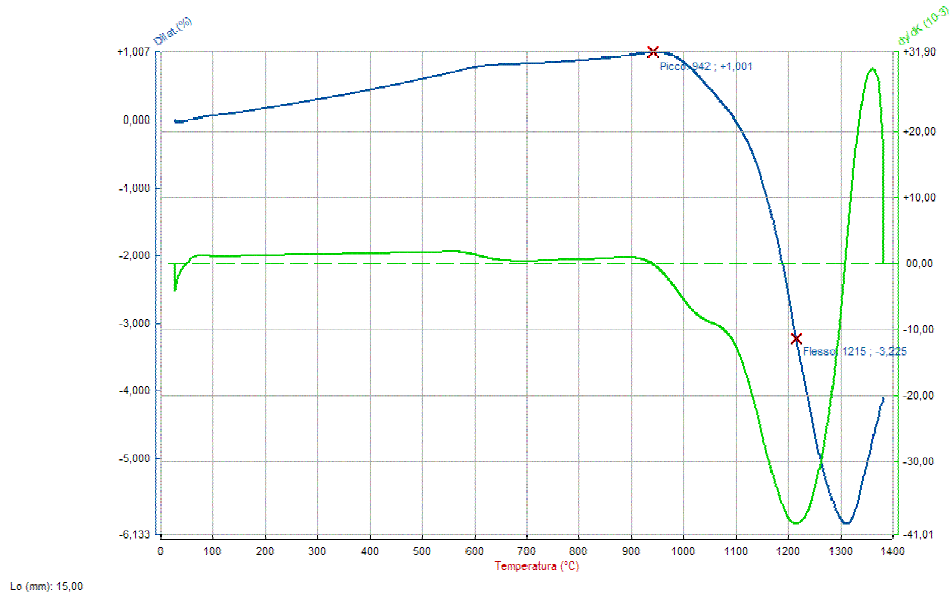
Study of the deformations that occur during the firing cycle in an glazed floor tile product that is completely sintered (glazed porcelain).

The second example concerns the study of the deformations that occur during the firing cycle in an glazed floor tile product that is completely sintered (glazed porcelain). The first feature concerns the sintering curve of the raw clay measured by the double beam, vertical optical dilatometer which establishes the initial sintering temperature, the temperature of the maximum sintering speed and the study of the kinetics of the sintering at constant temperature.

Graph 10 shows a sintering curve obtained with a heating rate of 50 °C/minute up to 1400 °C.

The sample initially achieved a thermal expansion until 942 °C and then began the sintering phase, which reached maximum speed at 1215 °C, followed by an expansion phase. The temperature of maximum sintering speed is identified by the variation in differential of the curve, or the negative peak on the first derivation.

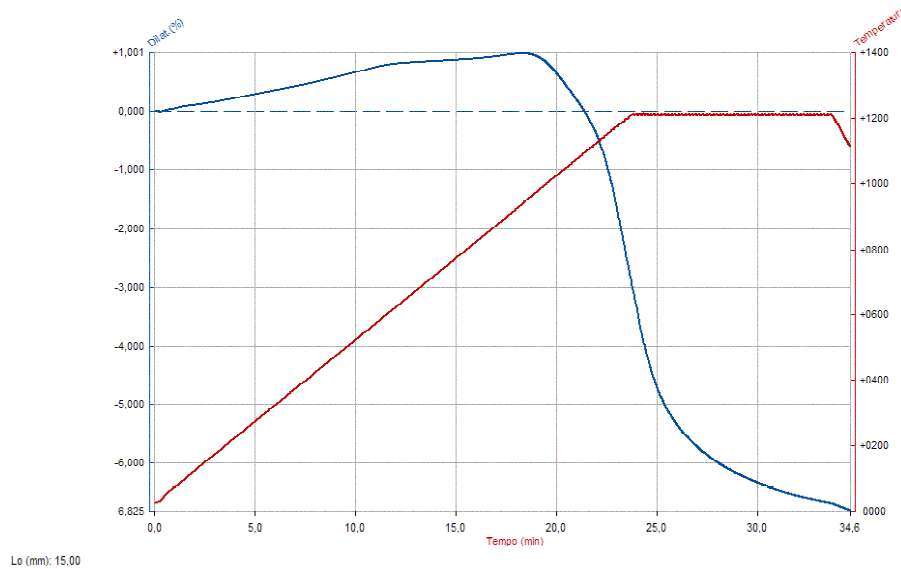
**Graph 10: constant gradient sintering curve of clay for enamelled porcelain**



The next test is carried out setting the same temperature gradient to 1215 °C, maintaining a constant temperature for 10 minutes to control the behaviour of the material during the sintering phase.

This is a sample of glazed porcelain body and shows a smooth behaviour during the sintering phase.

**Graph 11: Kinetics of sintering with constant temperature of the clay for glazed porcelain**



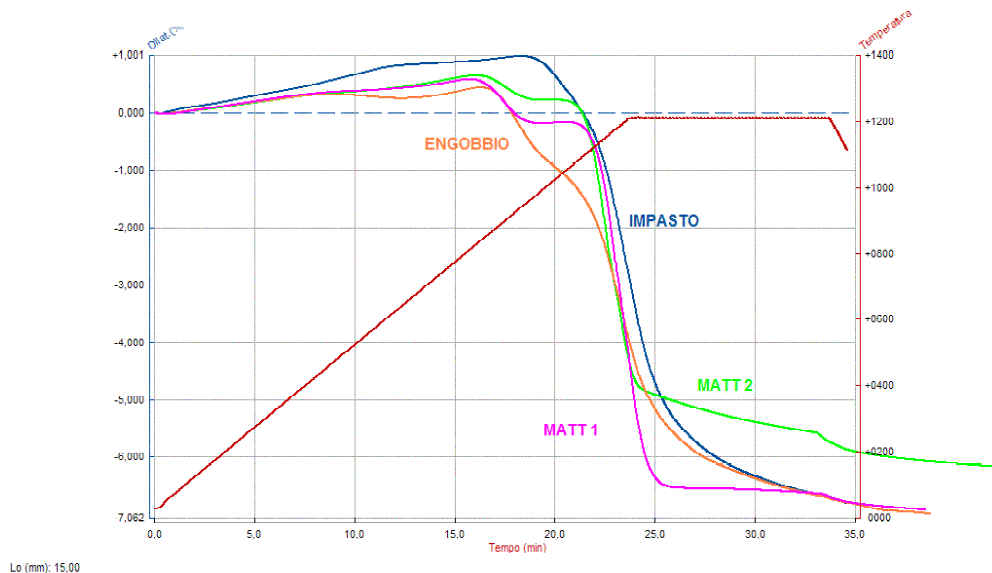
The tile made with this clay has the following behavioural characteristics:

- the tile without engobe and without enamel is perfectly flat;
- with the engobe is perfectly flat
- application of a type of matt enamel results in concave tiles
- application of another type of matt enamel (matt 2) results in convex tiles

The reason for this behaviour becomes clear looking at Graph 12, which sums up the behaviour of all the components of the system during the sintering obtained with a uniform heating treatment.

- It is clear that the engobe (orange curve) at the end of the firing cycle has the same dimensions as the clay and the sintering course is similar. In fact, in these conditions the application of the engobe does not cause any deformation to the piece.
- The matt enamel (lilac curve), which causes concavity, sinters much more quickly than the body and is much faster at reducing in size than the body. At the end of the firing cycle its size is identical to that of the body but at the beginning of the sintering phase it has shortened significantly compared to the body and has become convex. This matt glaze is very consistent and behaves like clay: it sinters without ever reaching a full and proper fusion. If the glaze behaves in a vitreous manner and reaches a fairly low viscosity its behaviour at sintering has little influence, in as much as above its temperatures of glass transition it releases all its tension. In the case of a crystallised matt glaze this did not happen, as the glaze was stiff and this shrinkage affects the flatness of the support.
- The second matt glaze behaves differently: it sinters in a fairly similar way to the clay but, after crystallising, the sintering process stops, while the body underneath continues to sinter. Therefore, by the end of the firing cycle, this material becomes convex because the clay has contracted faster than the glaze. This can be one of the reasons for the difficulty in obtaining flat sintered material.

**Graph 12: the kinetics of the clay's sintering, engobe and two matt enamels**

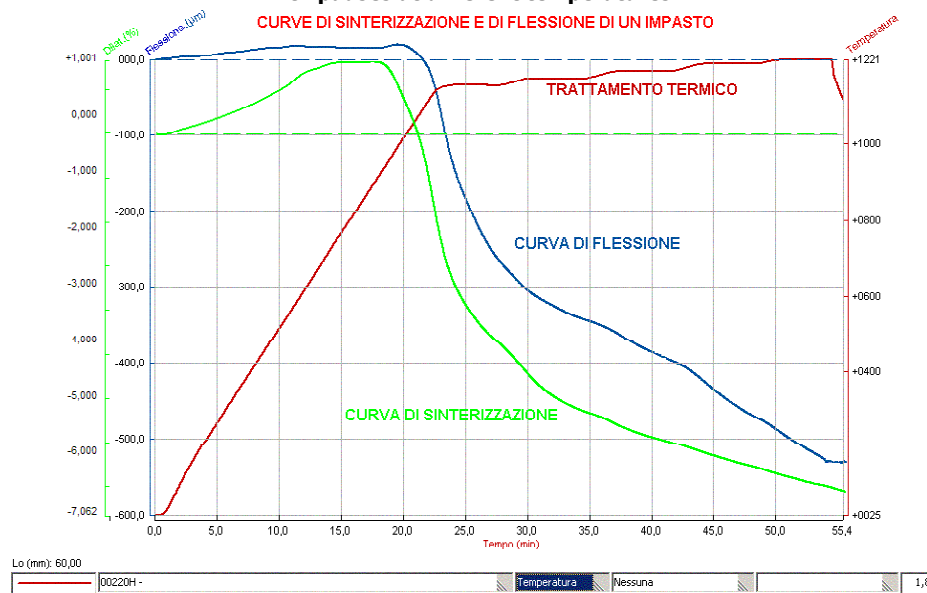


Study of the deformations caused by the pyroplastic behaviour on non-glazed, completely sinterised products (technical porcelain)

The sintering process of the traditional ceramic body is due to the formation and flow of vitreous phases. The driving force of the process is the surface tension of the liquid phase, made up by vitreous phases resulting from the fusion of the alkaline components of the body. The surface tension of the vitreous phases remains quite constant when the temperature increases, while the viscosity drops exponentially in accordance with the law of Arrhenius. The quantity of vitreous phases increases progressively during the sintering phase, but its composition does not remain constant because it continually incorporates new mineral components of the raw materials. The effect of increased temperature is not therefore uniform. In the case of a clay with a high degree of kaolin, the vitreous phase absorbs alumina and silicon. This characteristic of composition increases the viscosity, despite the increase in temperature. In the case of a body with a high degree of feldspar, the first vitreous phase formed is certainly rich in alkalis and this reduces surface tension and lowers viscosity. If the temperature is increased and the sintering proceeds, the vitreous phase absorbs alumina and silicon, while reducing rapidly the porosity of the product. All these variations happen simultaneously, reduce the pyroplasticity and increase resistance to flexion at high temperature. This is the situation described in Graph 13, which carries results of two tests carried out on the same material.

The red curve represents the thermal treatment: the material is heated up on a gradient of 50 °C/minute until 1150 °C. There followed five intervals at constant temperature of five minutes each at the following temperatures: 1150 °C, 1170 °C, 1190 °C, 1210 °C, 1220 °C. The green curve represents the sintering trend and has been measured with a vertical optical dilatometer MISURA HT. It is worth noting that at the end of the treatment the sample contracts by more than 7% at 1210 °C, which corresponds to about 8% of the material once it has cooled. Under these conditions the absorption of water equals zero. The blue curve represents the trend of flexion of a sample 6mm wide and 85mm long suspended on two supports with an inter-axis of 70mm. This curve has been measured with an optical fleximeter MISURA FLEX, using as always the heat treatment of the preceding test. As will be noted, flexion reaches 500 micron, more than half of which occurred during the first interval of constant temperature at 1150 °C. This result confirms the theory described earlier: at the beginning of the sintering phase there may be a poor result caused by low density of the material and by the formation of highly fluid vitreous phases with low surface tension.

**Graph 13: Sintering curve and flexion of clay for technical porcelain, with pauses at different temperatures.**



## Conclusions

The instruments for the thermo-mechanical analysis have been created by Expert System Solutions to understand the transformations that occur in the ceramic materials during the industrial heating treatments. The analytical options created with the introduction of the two latest models, MISURA LT and MISURA FLEX, permit a depth of investigation resulting in an understanding of and solutions to highly complex problems that before now were not measurable with laboratory instruments. The range of thermo-mechanical analysers available in a ceramics laboratory has never been so complete and so useful.