S & T Results/Foreground

<u>WP3 – Bread production case study</u>

Preliminary assessment of MSD performances: The MSD was completed and configured for the bread dough application. Following further development work to address initial technical issues, all three sensors were operational by the end of the project. The DTS showed good performance for monitoring of prover temperature at multiple positions and the PAS was sensitive to CO_2, water vapor and ethanol. The QIVN provided NIR spectra for flour samples, but the performance characteristics were insufficient for the proposed application.

MSD Calibration: Although the MSD QIVN sensor was not suitable for monitoring of dough mixing, the MSD showed good potential for monitoring of dough proof. Laboratory trials were conducted for proving of bread doughs under a range of conditions.

The DTS was suitable for monitoring of prover temperature at multiple positions, revealing the temperature distribution at different locations, and was sensitive to periodic temperature variations due to the thermostatic control system. The use of purely optical sensors and optical fiber connections provides potential benefits for industrial use as an alternative to electrical sensors.

The PAS was capable of measuring 3 prover gases (water vapor, CO_2 and ethanol) simultaneously with a single sensor. Reference measurements demonstrated clear variations in ethanol concentration with proof, and sensitivity to temperature and the proof rate. Ethanol concentration is not currently measured in proof and has not been widely studied. The project demonstrated that this has exciting potential for industrial monitoring and control. The PAS had low sensitivity to ethanol concentrations in a batch laboratory prover, but work in WP8 showed better sensitivity under industrial conditions.

Matrix dataset and predictive models testing: Assessments made for preliminary NIR spectra obtained before correction of baseline drift showed potential for identification of absorbance bands due to water, expected to be relevant for assessment of dough mixing, and it was shown that the spectra were sufficient to enable discrimination between different groups of flour samples. Good potential was also shown for the other measurements made in T3.2. However, delays in achieving fully operational sensors meant that there was insufficient time for further work to develop predictive models for the measured CQAs.

WP4 – Potato chips frying case study

Preliminary assessment of MSD performances:

- The **DTS** unit was shown to be operating well under harsh condition during the frying process. A communication problem between the DTS and the MSD software was identified and took into account to apply the right calibration files in the MSD software.

- The **QIVN** measurements could be recorded directly by the MSD software. The QIVN dip probe seemed to discriminate between highly absorbing and highly reflective samples, even if no characteristic spectral peaks were observed. By using statistical analysis, such as partial least square (PLS) methods, spectra seemed to be useful to construct calibrations for sliced potatoes and oil attributes, oil volatile and mineral oil contamination. The use of the reflectance probe, to measure Vis/NIR spectra from fresh potatoes, required an external illumination, to obtain suitable signals and to record both Vis and NIR spectra at the same time.

- The **PAS** system still needs some refinements to work properly. Before carrying out the calibration it should be proved that gases from different oil qualities can be discriminated.

MSD Calibration:

- The **DTS** unit has been the easiest system to calibrate and have proven to be reliable for an online monitoring of the temperature during frying. For demonstration, the new corrective equation must be inserted in the MSD and a mobile mean should also be included to have data every 10 seconds.

- The **QIVN** unit have monitored our process in the Vis and NIR range. The number of CQAs was important and numerous spectral pre-treatments were applied in order to find the best combination. Table 2 summarizes the calibration results for some CQAs with a RPD >1.5. All others CQAS were eliminated due to a poor correlation.
  Therefore for the selected calibration, other statistical parameters, bias and the range error ratio (RER) were calculated to have an idea of the accuracy and performance of the models.

$$Bias = \frac{1}{M}\sum_{i=1}^{M}(\mathrm{y}_\mathrm{i}^{\mathrm{ref}} - \mathrm{y}_\mathrm{i})$$

$RER = \frac{y_{max}^{ref} - y_{min}^{ref}}{SEP}$ calculated on the validation samples set

Where $SEP \cong \sqrt{RMSEP^2 - bias^2}$

Table 2. Summary of the calibration models statistic for 8 CQAs.

CQAs	Product	Range	Pre-treatments	R^2_{Val}	RMSEP	RER	Bias

Mineral oil (%)	Oil	NIR*	1st derivative	0.791	1.4	7.1	-0.07
Mineral oil (%)	Oil	NIR*	BGD+1st deriv	0.821	1.3	7.5	-0.13
b*$_{CIELAB}$	Potato	Vis	INT+BL+BGS+SNV	0.741	2.8	7.0	-0.27
Chroma	Potato	Vis	INT+BL+BGS+SNV	0.723	2.9	6.7	-0.11
TPM (%)	Oil	NIR	1st derivative	0.715	1.9	6.4	-0.44
Acidity (%)	Oil	NIR	NCR+2nd deriv	0.550	0.14	5.2	0.020
p-anisidine value	Oil	NIR	1st derivative	0.621	8.8	4.9	-0.12
Pentilfuran (10^{6}area)	Oil	NIR	1st derivative	0.660	0.8	6.6	-0.15
2,4 decadienal (10^{6}area)	Oil	NIR	NCR	0.854	0.85	8.7	0.01

*reduced range to 1100 -1285 and 1365 – 2195 nm

In order to implement the calibration different criteria have been evaluated, such as the need to use a background correction or the amount of calculation on the resulting spectra.

For the CQAs b* and chroma measured with the QIVN-Visible, a white plate reference must be measured each sampling say and later several spectral pre-treatments should be applied.

For the other CQAs measured with the QIVN-NIR, spectral pre-treatments are simple to implemented and do not required a background correction. This is important because to do the measurement of the background, the dip probe have to be taken out from the oil and cleaned. The main drawback with the dip probe is the possible presence of micro-bubbles or thin potatoes particles in the optical path of the probe.

The AACC Method 39-00.01 (1999) provides quality thresholds for model performance based on the RER values: For RER ≥ 4 – the calibration is acceptable for sample screening; for RER ≥ 10 – the calibration is acceptable for quality control; and for RER ≥ 15 – the calibration is good for quantification.

In our case RERs range from 4.9 to 8.7 and are all superior to 4.0, therefore the QIVN predictions will be acceptable for screening and maybe for process control, where usually decision making is taken on the basis of threshold values.

- **The PAS unit** was evaluated as a stand-alone unit for the on-line assessment of oil quality at IRTA pilot plant. Our results seem to indicate that PAS cannot specifically detect single target volatiles released by oil during frying. However, the profile of the PAS spectrum progressively changes during frying, and a correlation with oil degradation and TPM increase was observed. As TPMs of the oil increased, the ratio between the intensity of the peaks in the PAS spectra at 1090 nm and 1030 nm also increased, ranging from a value of 1.39 at 5.5 TPM, 2.15 at 11.25 TPM and 2.40 at 16.25 TPM, respectively. So, ratio of the peak intensities at 1090 nm and 1030 nm in the PAS spectra is proposed as a potential indicator of the overall quality of the frying oil (see Supplementary information at the end of this document).

Matrix dataset and predictive models testing: Results from the pilot plant experiments were organized and a matrix dataset was constructed (D4.3), which included:

- NIR air measurements (probe outside the oil) and light OFF measurements (dark measurements).
- NIR spectra & reference values for the CQAs of frying oil samples obtained from the 100 frying independent experiments (DoE).
- Vis-NIR spectra & reference values for the CQAs of raw sliced potatoes samples used during the 100 frying independent experiments (DoE).
- Reference values for the target CQAs (physicochemical and organoleptic) of the potato chips obtained during the 100 frying independent experiments (DoE).

The dataset was used by USTR to obtain calibrations and predictive models for the WP4.

WP5 – Brewing case study

Preliminary assessment of MSD performances:

- *The PAS sensor:* PAS spectra of selected model substances (methanol, acetone) qualitatively corresponded to the published IR absorption spectra and relevant response was also obtained for dimethyl sulphide. The PAS system was shown to be functional in the process conditions, however, the sampling procedure needs to be improve to avoid problems with hot wet vapors.
- *NIR sensor in the mash tun:* Direct measurement with immersion probe in the mash tun during the mashing process has been proved to be extremely difficult. The mash is too dense, particles of grist are too big and the slit in the top of the probe head (which has to be of the order of 1-2 mm due to high absorption of water in the used NIR region) was very quickly clogged. Therefore this type of measurement was abandoned.
- *VIS-NIR transmission – at line during mashing*: Because it was impossible to use optical probes directly in the mash tun, a special dual optical path length chamber (**DOPC**) chamber was designed. It was proved to be usable for at-line simultaneous measurements of VIS and NIR transmission spectra during mashing. Only simple sampling and filtration was necessary to prepare mash for the measurements.
- *VIS sensor in the copper:* Optical absorption spectra in VIS region were measured during hop boiling directly in the copper. The quality of the spectra was poor due to the presence of multiple phenomena influencing the light propagation, such as changes in the flow, microbubbles, vortexes and the presence of particles of different shapes and sizes. A gradual soiling of optical parts of the probes (windows, mirrors) in contact with the brewing media was also found.

- *QIVN sensor with reflection probe:* Reflection probe showed an appropriate response with simple model samples but it lacked the sensitivity (and/or stability) to be ready for use for continuous monitoring of input raw material (barley malt or grist) in practice. Fluctuation of signal response was about +/-1% whereas better stability was necessary.

MSD calibration: PAS spectra obtained with selected model substances (methanol, acetone) qualitatively corresponded to the published IR absorption spectra. The PAS sensor showed relevant response also for DMS (but not so clear for linalool). PAS spectra of hot vapours from the copper during the boiling process were analysed. The most of sharp narrow peaks in the used spectral region between 970 and 1330 cm^{-1} were assigned to water vapours. No signal which could be selectively attributed to DMS or linalool during hop boiling was found. Even so, a broad band between 970 and 1120 cm^{-1} was observed in the spectra of wort and hopped wort. It probably reflected some IR continuous absorption of multiple volatiles. Its amplitude changed during boiling and was dependent on the variety of wort used. Due to the fluctuations of signals and very frequent failures of measurement, it was not possible to verify this point. On the other hand a strong significant response of the PAS response to ethanol in the vapour phase was revealed.

No usable correlations of CQAs reference values with NIR reflection spectra of malt measured by QIVN-NIR unit with VTT reflection probe were found.
VIS spectra recorded by QIVN unit with immersion probe(s) during wort boiling did not match the spectra recorded by the laboratory spectrometer and it was not possible to track the changes in colour during hop boiling. A big decrease of transmission nearly at all wavelengths was observed during the hop boiling. One can speculate that this effect was related to the creation of particles due to coagulation of some proteins and formation of protein-polyphenol precipitates. But further experiments would be necessary to check this hypothesis.
On the contrary, the data treatment performed by USTR on NIR and VIS transmission spectra recorded with the DOPC chamber in DOE mashing, showed some significant correlations with most of measured CQAs. An algorithm for control of mashing was suggested.

Thanks to the DTS sensor was find out that significant temperature differences may occur in a lauter tun, even in small tanks like in the case of the VUPS pilot plant. The DTS was demonstrated to be useful in the future to better control and adjust the processes a brewhouse to ensure both a perfect homogenization in the lauter tun during mash pumping in decoction mashing, and to exactly control the temperature level during sparging in decoction as well as in infusion mashing.

Problems arising when sensors were used under real brewing conditions and which need to be tackled were identified and described. Some solutions or directions of further development were suggested to overcome obstacles observed and to enable the industrial implementation, *e.g.*:

- A gradual blinding of optical immersion trasflection probe in the copper due to soiling of its window during boiling; (Difficult to solve – maybe an external probe, windows from another less adhesive material - e.g. sapphire, or developing some special cleaning system - e.g. ultrasonic cleaning, thin pulsed water jet)
- Oversaturation effects of PAS, failures of measurements due to high content of hot water vapours in the sampled gas; (Auto-ranging of the PAS system or hardware/software adjustments).
- Frequent failures of PAS system sampling due to water condensation in the pump tubes; (A possible solutions could be to carry out a quick flush of the PAS chamber with the built-in system or by filling it with dry clean air or nitrogen).
- Wavelength dependent time instability of the VIS sensor unit; (Could be solved by modifying the hardware/software and the reference channel).

Matrix dataset and predictive models testing: The data gathered during DOE mashing experiments suggests that the models built can effectively predict the CQAs, which are important for mashing control.
The models built with the MSD NIR measurements can provide useful information to access the fermentable sugar concentration and the α-aminonitrogen concentration (D5.3). The NIR wavelength region is less affected by scattering effects, and this is the region of the N-H(s) and C-H(s) chemical bond peaks, explaining the better performance of these models (D5.4).
The models built with MSD UV-VIS measurements can provide some useful information about the fermentable sugar concentration. However for the maltose, maltotriose and dextrin CQAs, the models have a lower performance. One possible explanation is that these molecules have no colour (no absorption peaks in the UV-Vis region).
The potential for the MSD to realise predictive models for several CQAs for the mashing process (D5.3 and D5.4) have been clearly identified. The performance of the models built with these strategies and their usefulness can be determined by the user.

WP6 – Software developments

Developing the software and operator interface: The software and Operator Interface have been developed to provide an interface to the data fusion software developed in WP 7. In the initial installations a basic operator functionality was described in response to the definition of task 6.1 and the developing requirements of the operators. This was then developed and modified over the coming months leading to the final version.
Developing the software and operator interface involved working with beneficiary 5 (USTR) to develop the software to allow the algorithms (developed by USTR) to be run on the MSDs *in-situ*. PTL was task leader for this task.
The initial requirements for the software were previously established in Task 6.1. A basic structure and functionality was designed and captured in internal documents. These formed the basis of discussions between all parties and requirements were gradually refined. At the midway point, (M18), the Subtask 6.2.1 (*Developing an interface to the fusion software*) developed to a level suitable for this stage of the project *i.e.* a basic functionality has been built in to the software with basic operator interface.
In order to interface with the data fusion software developed in WP7, early discussions were held with USTR to establish the most suitable data formats to make this task easier.

The interface developed at this stage comprises 4 main modules: the Instrument Capture Module, the Data Fusion Module, the Data Output Module and the Data Collection Module. These are all fairly well defined at the midway point and were designed in such a way as to be well defined but easily adapted for future requirements. Work continued on this right up to the end of the project with the algorithms being developed in USTR to allow for changing user requirements and the result of the initial data coming from the labs and from the sites in the mid - late second half of the project (again work carried out at USTR).
The initial intention was to develop the algorithms in Matlab (more flexible for development but with increased runtime in an industrial system) and for PTL to then code them in C++, python or some suitable means. This would provide a compiled version which would run parallel code very much more quickly for real-time use. As the development of the algorithms was taking longer than forecast (due to late data from the industrial partners as a consequence of sensor problems), it was decided to use a compiled version of the Matlab code for expediency. In the last weeks of the project, this could not be done as a third party licence was required for the compiler and the procurement of this was delayed. The structure of the Matlab software and the two versions of the operator interface are shown in figures 1-3.

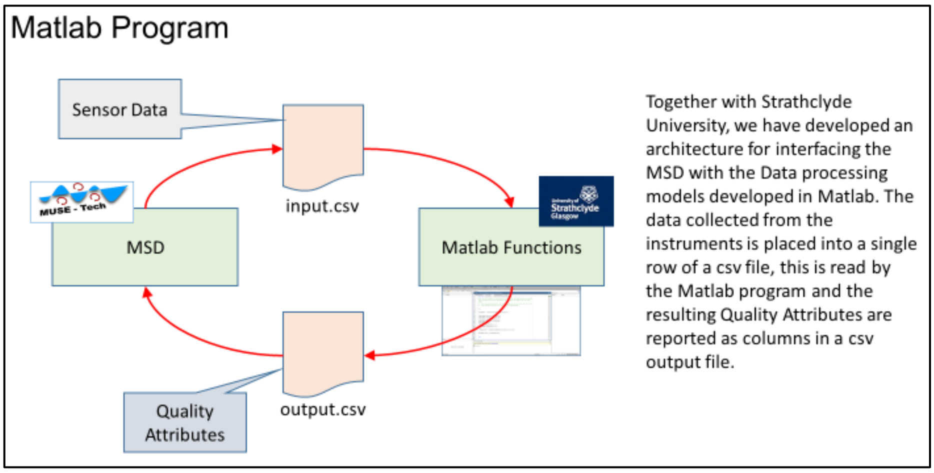

Figure 1 - Structure of the Data Processing Architecture

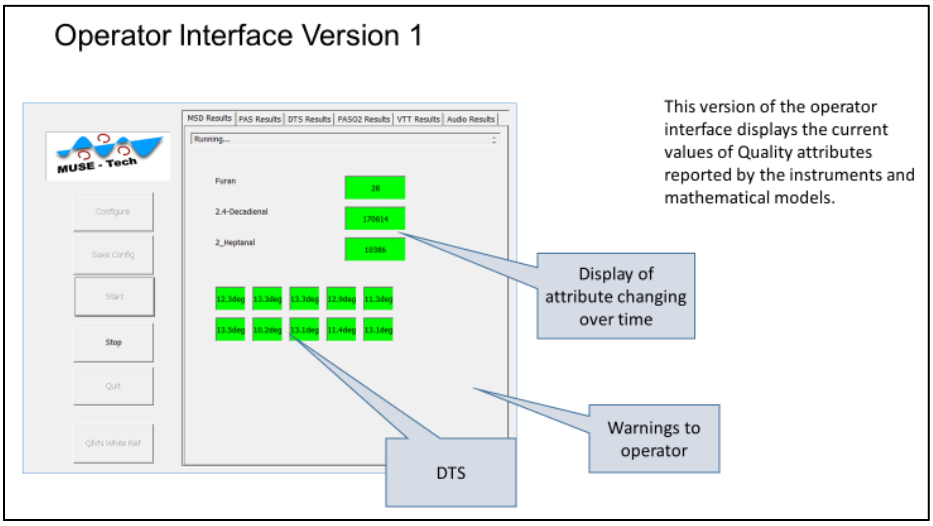

Figure 2 - Operator Interface Version 1

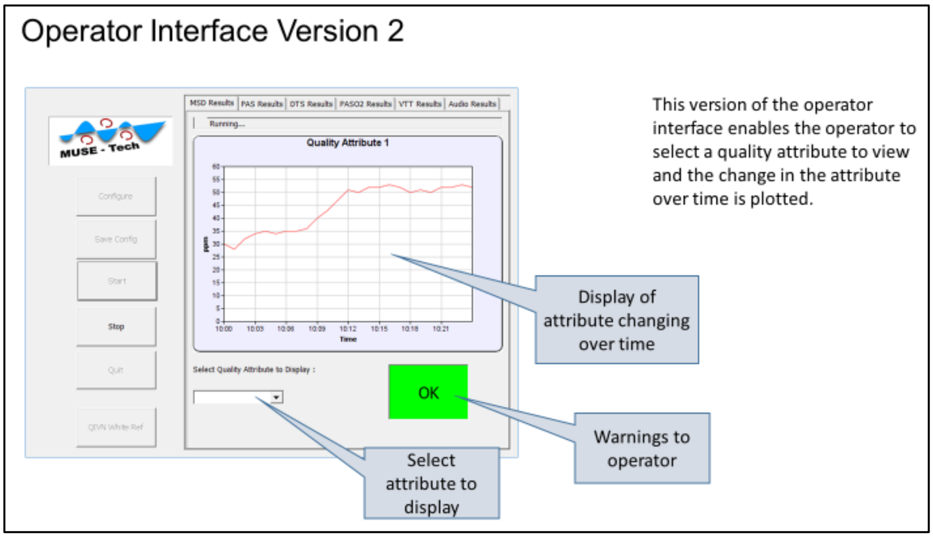

Figure 3 - Operator Interface Final Version

Demonstration of Industrial Application: The MSD was installed at the three industrial sites. This was the result of excellent cooperation between the installer, the site operators and the sensor makers. Milestones 6.1 and 6.2 were achieved.
Demonstration of Industrial applications and the related work described above, much work was carried out by beneficiary 9 (PTL) with multiple visits to all the sites, both industrial and lab-based. As expected with such delicate scientific instruments, there were many issues with all 3 sensors and much interplay between the partners developing these instruments, the lab or site owners and PTL. PTL visited each site several times in the latter half of the project and worked with the other partners to resolve these difficulties. This added some delay to the installation in some areas but, on the whole, this was successful and the MSD started to produce results from both lab and industrial sites.

The Milestones for this half of the work were:

- MS18: *Systems running at offices of partner PTL (M22)*. MS18 was late due to issues with the instrument reliability, and occurred at M32.
- MS19: *Systems installed at production plants (M30)*. MS19 was slightly late as a result of the above. However, the team managed to minimize any delay by making short term visits to the sites and through very effective collaboration between the partners who ran the industrial lines, the labs and the instrument designers. Thus many issues were sorted out quickly and effectively by working in parallel. The milestone was succeed in M35.

Photos of the installation at the three sites are shown in figure 4.

Figure 4 – MSD installation at the three demonstration sites.

WP7 – Predictive models

Initial data collection and analysis:

- Best Practice and Standard Operating Procedures disseminated to all partners to optimise the data collection for maximum information content;
- Strategies to deal with unexpected features in NIR spectra including large baseline shifts and irregular data repetitions, demonstrating how useable information can be extracted even from poor quality data;
- Liaison with VTT to discuss improvements to the data acquisition quality that were subsequently implemented in the firmware;
- Filters to improve the DTS signal.

Novel pre-processing methods:

- A standard workflow has been developed which can be used with the MSDs at any of the case study, pilot or demonstrations sites;
- The software for model development is complemented by a model selection strategy to allow optimal selections to be made;
- Candidates for more detailed exploration are identified and pursued for the deliverables D3.4, D4.4 and D5.4

Data fusion through Augmentation and Multi-block Methods: The most significant conclusion for this project is that data fusion approaches do not enhance the predictive capabilities of the MSD tools for our particular processes; instead, the development of robust models based on regular PLS but with bespoke pre-processing, as described in D7.1 and D7.2, is the most viable way forward for the MSD implementation.

Process Predictive Models: the potential for the MSD to realise predictive models was identified for several potato chip CQAs including Flavour, Colour and acrylamide content.

Model Refinement:

- The predictive software can run with the MSD computational resources in usable time;
- The predictive models for potato chip frying have potential for monitoring sensory qualities (flavour, odour), food safety (acrylamide content) and oil degradation (volatiles such as hexanal);
- The MSD technology has potential for the monitoring of brewing processes in particular.

<u>WP8 – Demonstration at industrial scale</u>

Scale up and adaptation of the MSD to the industrial conditions:

- *<u>Bread production case study</u>:* MSD and the different probes were installed easily in the industrial plant and showed to be very robust and resistant to the, sometimes aggressive, industrial environment. It was installed in that environment up to two months without any problem. It resisted standard cleaning procedures of the industrial line. MSD did not suffer any damage during the industrial demonstration and technology worked properly.
- *<u>Potato chips frying case study:</u>* MSD was able to be installed easily in the industrial plant, in spite of it was a gluten-free factory. The different probes and sensors were able to be integrated, after slight modifications, in the production line and installed in the industrial fryer. The MSD and the probes showed to be very robust and resistant to the industrial environment. They were installed inside the factory for almost four months and did not suffer any damage. MSD hardware and software were able to work properly.
- *<u>Brewing case study</u>*: MSD was able to be installed easily in the brewing house. Flexibility of the sensors and the simple installation simplified the procedure. Although some slight modifications of the brew house were needs, the different probes and sensors were able to be integrated.

Preliminary trials & models adaptation:

- *<u>Bread production case study</u>:* DTS technology was successfully installed inside the industrial prover. Connections resisted the temperature and humidity conditions inside the chamber during the whole experimental period, demonstrating that this technology can be applied to control this industrial process. Preliminary results were, in general terms, concordant with the data acquired by reference probes. PAS technology was able to detect and measure ethanol, CO_2 and humidity concentration in the prover during the industrial production of bread. Preliminary results were, in general terms, concordant with those acquired by reference probes. MSD software worked properly, recording and showing data from every probe connected.
- *<u>Potato chips frying case study</u>:* DTS technology was successfully integrated in the industrial fryer, resisting the industrial process, high temperatures-long time, without any problem. It worked properly, giving useful information about temperature changes in the oil bath, coherent with the results given by reference probes. QIVN technology was able to give spectral information from raw materials. It was also able to give spectral information from the oil bath in the industrial fryer. However, no models were installed in the MSD software, so it

was impossible to perform a direct validation of the spectral measurements taken under industrial conditions. MSD software worked properly, recording and showing data from every probe connected.

- *Brewing case study:* When we attempted to commission the MSD at Nutfield we found that none of the sensors were functioning. Delays of the project meant a very tight timetable and with no extensions allowed it was not possible to repair the sensors before the project ended. Because of this we were not able to obtain any results for the brewing case study at Nutfield.

Validation and demonstration:

- *Bread production case study:* DTS technology was tested during several industrial trials and bread production to validate the measurements obtained. Data were registered during the starting up of the prover and during more than 30 hours of bread production. DTS sensed the same temperature variation than reference probes and showed good results. The results showed, in general terms, the same temperature distribution inside the proving chamber than reference probes. DTS is a very sensitive technology for monitoring the temperature distribution, directly applied to industrial environments. PAS technology was able to detect and measure ethanol, CO_2 and humidity concentration in the prover during the industrial bread production. Changes in those concentrations due to production gaps or stops were properly monitored. Results were satisfactory and it can be concluded that PAS is a technology able to be applied for controlling proving processes by measuring ethanol and CO_2 concentration.
- *Potato chips frying case study:* DTS technology was validated and demonstrated in several standard industrial productions of fried potatoes. Additionally, an experimental trial was carried out monitoring the temperature variations during the starting up of the industrial fryer and the beginning of production. Different stages of heating and cooling were defined during this trial. Probes reflected quite well the temperature changes, compared with the reference probes installed in the fryer. A constant deviation was detected in some probes but it could be easily corrected by a recalibration. Spectral measurements of raw potatoes were taken with QIVN technology. There were no models to apply and validate those data, but QIVN operation was demonstrated under industrial conditions. QIVN was able to acquire spectral information directly from the industrial oil bath. Some problems were identified to acquire a good noisy-less signal, but it was possible obtain useful spectral data on line.

  Oil spectra were acquired under different industrial conditions, different fryers and different degradation levels, in order to have enough variability in the spectral data for a further external validation with the results obtained by reference chemical analysis of the oil samples. Also quality parameters of the final product were analyzed, in order to correlate that information with the spectral information from the oil samples.
- *Brewing case study:* Since none of the sensors of the MSD was operational at Nutfield, no validation trials could be performed.