An Roinn Talmhaíochta,
Bia agus Mara
Department of Agriculture,
Food and the Marine

14F866 - Process Analytical Technologies for Dairy and Infant Formula powder manufacture (DairyPAT)

Final Report

This project was funded under the Department of Agriculture, Food and the Marine Competitive Funding Programme.

SUMMARY

The overall project objective is to develop and characterise novel PAT technologies for control and optimisation of dairy powder and infant formula manufacturing. Specifically the project will:

- Develop and characterise new PAT tools, namely Laser Induced Breakdown Spectroscopy (LIBS) and Guided Microwave Spectroscopy(GMS), for dairy processing.
- Validate LIBS and GMS PATs for stand-alone use in industrially relevant dairy processing applications.
- Investigate sensor and data fusion opportunities, combining new and existing state-of-the-art sensors and data analytics, for enhanced product characterisation and process control

The results demonstrate the feasibility of LIBS and Raman with multivariate analysis as a rapid process analytical techniques for the discrimination of milk samples contaminated with alternative nitrogen sources such as melamine, urea and whey protein. FT-IR spectroscopic method with multivariate analysis cannot clearly determine different contaminant groups. Presented results indicate that more efforts and costs have to be allocated in order to establish robust technique, based on LIBS, for microbial detection. The performed experiments also revealed that multipoint NIR could be a powerful tool for monitoring blending process of dairy ingredients. Raman and FT-IR with chemometrics also hold strong potential to determine multiple mineral contents e.g. Ca, K, Mg, Zn, Mn, Fe, Cu, Na in milk powder or aqueous milk products. All these spectroscopic techniques can be implemented further for the development of process analytical tools for on-line use in the dairy industry.

These results demonstrate the potential impact of the project to improve competitiveness in dairy processing. More real time data from LIBS and Raman has the potential to improve quality assurance in dairy processing.

KEYWORDS

PAT, Dairy, Processing

ACRONYM	DAIRYPAT
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Section 1 - Research Approach & Results

Start Date

01 December 2014

End Date

30 April 2019

Research Programme

Food Institutional Research Measure

TRL Scale

TRL 5: Technology validated in relevant environment

NRPE Priority area

Sustainable Food Production and Processing

Total DAFM Award

€549,590.00

Total Project Expenditure

€485,250.34

Rationale for undertaking the Research

With the planned abolition of milk quotas from March 2015, it is a priority that a large proportion of the increased dairy output is linked to added value products such as infant formula. Irish dairy processors will be required to demonstrate that they implement systems to enable control of and confidence in the specifications and properties of the powdered products they produce for the infant formula industry. This is a major challenge considering the high degree of variation and influencers in dairy processes. Through the introduction of a process analytical technology (PAT) approach which facilitates real-time process monitoring capabilities with spectroscopic sensors, the industry can move from inferential monitoring and control towards continuous measurement of core quality parameters.

Methodology

The project was executed under the following tasks:

1. Technology development: Laser-induced breakdown spectroscopy (LIBS) and Guided Microwave Spectroscopy (GMS) PAT technologies
2. PAT technologies (LIBS, Microwave, NIR, MIR and Raman spectroscopy systems) for raw milk quality and safety characteristics.
3. PAT technologies (Microwave spectroscopy system and NIR process sensor) for monitoring milk concentrates.
4. PAT technologies (LIBS and multi-point NIR) for milk powder composition and safety.
5. Data analytics: chemometric model development and data fusion.

Project Results

Task 1

- LIBS system was configured.
- LIBS laboratory platform was built, delivered, installed and tested.
- LIBS parameters were optimized and its performance to test milk samples was tested.

Task 2

- Protocols to analyse mineral composition of powdered milk by LIBS have been developed and established.
- Protocols to analyse protein, crude fat, fatty acids and mineral content with GMS and FT-IR have been developed and established.
- LIBS system coupled with chemometrics was able to detect toxic amount of Fe and Cu in powdered milk samples.
- LIBS coupled to PCA was able to distinguish between whole milk samples and samples contaminated with melamine, urea and whey powder, however LIBS was not able to distinguish between contaminated samples.
- Raman spectroscopic method with multivariate data analysis can determine whole milk from contaminated samples with 100% accuracy of correct classification. The melamine group and the whey group can be accurately classified with 100% accuracy. While the melamine group and the urea group cannot be identified from each other.
- FT-IR spectroscopic method with multivariate analysis cannot clearly determine different contaminant groups.

Task 3

- The potential of guided microwave spectroscopy (GMS) for on-line prediction of chemical compositions in dairy products was explored. GMS with chemometrics hold strong potential for prediction of crude fat and total solids and major minerals such as Ca, Mg in infant formula products /milk concentrate.
- Raman firbre optics and FT-IR spectroscopy with chemometrics hold strong potential for determination of multiple trace mineral elements in infant formula products/milk concentrate which were in the aqueous status.
- A new ICP-AES analytical method was developed to determine trace mineral elements in aqueous dairy samples.
- PLSR models were developed using spectral data and chemical references for the evaluation of prediction performance using these spectroscopic techniques. High values of R_cv^2 and R_p^2 and lower values of the corresponding RMSECV and RMSEP confirmed good prediction performance of models developed.

Task 4

- Protocols for mineral analysis of milk powders by LIBS has been established. Calibration models were developed using partial least squares regression (PLS), correlating the LIBS spectral data with reference Ca, Mg, K, Na, Cu and Fe contents previously established by atomic absorption spectroscopy (AAS).
- The efficacy and detection limits of LIBS for microbial detection has been tested. After applying PCA no clustering of samples contaminated with certain bacteria was observed. Further improvements of LIBS device are needed in order to achieve satisfactory results.
- The ability of NIR multipoint to monitor blending has been tested. Multipoint NIR can effectively determine homogeneity of the blends of dairy powders.

Task 5

- LIBS combined with chemometrics can be a rapid and low-cost method for mineral quantification in the dairy industry.
- Raman and MIR spectroscopy combined with multivariate data analysis hold the potential to indirectly quantify mineral cations in a chemical complex via directly determination of their corresponding anions. To achieve more accurate prediction results, PLSR models were also developed based on complementary

information of both Raman and FT-IR spectral variables and features. Data fusion strategies were studied and compared.

Section 2 - Research Outputs

Summary of Project Findings

The project results shows that LIBS and GMS technology are feasible for composition analysis of dairy products, offering rapid, at- and on-line response for quality control purposes due to various reasons:

- They can be portable what makes these systems suitable to all kind of scenarios where spaces might be reduced.
- Their high speed analysis provides real-time information of key quality attributes of milk samples.

Summary of Staff Outputs

Research Output	Male	Female	Total Number
PhD Students	2	1	3
Post Doctorates	0	2	2
Other/Temporary	2	0	2

Summary of Academic Outputs

Research Outputs	Total Number	Details
Publications in Peer Reviewed Scientific Journals	9	1. Kang, R., Zhao, M. and O'Donnell, C., 2017. Explorations of guided microwave spectroscopy (GMS) features for infant milk formula detection. BIOSYSTEMS AND FOOD ENGINEERING RESEARCH REVIEW 22, p.85. 2. Zhao, M., Markiewicz-Keszycka, M., Beattie, R.J., Casado-Gavalda, M.P., Cama-Moncunill, X., O'Donnell, C.P., Cullen, P.J. and Sullivan, C., 2020. Quantification of calcium in infant formula using laser-induced breakdown spectroscopy (LIBS), Fourier transform mid-infrared (FT-IR) and Raman spectroscopy combined with chemometrics including data fusion. Food chemistry, 320, p.126639. 3. Cama-Moncunill, X., Markiewicz-Keszycka, M., Cullen, P.J., Sullivan, C. and Casado-Gavalda, M.P., 2020. Direct analysis of calcium in liquid infant formula via laser-induced breakdown spectroscopy (LIBS). Food chemistry, 309, p.125754. 4. Cama-Moncunill, X., Markiewicz-Keszycka, M., Cama-Moncunill, R., Dixit, Y., Casado-Gavalda, M.P., Cullen, P.J. and Sullivan, C., 2018. Sampling effects on the quantification of sodium content in infant formula using

		laser-induced breakdown spectroscopy (LIBS). International Dairy Journal, 85, pp.49-55. 5. Cama-Moncunill, R., Casado-Gavalda, M.P., Cama-Moncunill, X., Markiewicz-Keszycka, M., Dixit, Y., Cullen, P.J. and Sullivan, C., 2017. Quantification of trace metals in infant formula premixes using laser-induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 135, pp.6-14. 6. Cama-Moncunill, X., Markiewicz-Keszycka, M., Dixit, Y., Cama-Moncunill, R., Casado-Gavalda, M.P., Cullen, P.J. and Sullivan, C., 2017. Feasibility of laser-induced breakdown spectroscopy (LIBS) as an at-line validation tool for calcium determination in infant formula. Food Control, 78, pp.304-310. 7. Markiewicz-Keszycka, M., Zhao, M., Cama-Moncunill, X., El Arnaout, T., Becker, D., O'Donnell, C., Cullen, P.J., Sullivan, C. and Casado-Gavalda, M.P., 2019. Rapid analysis of magnesium in infant formula powder using laser-induced breakdown spectroscopy. International dairy journal, 97, pp.57-64. 8. Markiewicz-Keszycka, M., Cama-Moncunill, X., Casado-Gavalda, M.P., Dixit, Y., Cama-Moncunill, R., Cullen, P.J. and Sullivan, C., 2017. Laser-induced breakdown spectroscopy (LIBS) for food analysis: A review. Trends in food science & technology, 65, pp.80-93. 9. Markiewicz-Keszycka, M., Cama-Moncunill, R., Casado-Gavalda, M.P., Sullivan, C. and Cullen, P.J., 2019. Laser-induced breakdown spectroscopy for food authentication. Current Opinion in Food Science, 28, pp.96-103.
PhD Theses	3	1. Cama Moncunill, X. (2019) Laser-Induced Breakdown Spectroscopy (LIBS): a Potential Quality Tool for Infant Formula Manufacture, Doctoral Thesis, Technological University Dublin. DOI: 10.21427/dcm0-fn22 2. Jiani Luo (2021) Development and validation of rheological process analytical technology tools for dairy processing. PhD Thesis | University College Dublin. 3. Eva Maria Achata Gonzales (2020) Development and validation of hyperspectral imaging process analytical technology tools for food processing applications. PhD Thesis, University College Dublin.
Peer Reviewed Conference Papers	3	1. O'Donnell C, (2018) Development of PAT solutions for dairy processing applications. 32nd International Forum on Process Analytical Technology IFPAC 2018, February 11 – 14 2018, Washington DC, USA. 11 Feb 2018 2. O'Donnell, C (2017) Prediction of heat treatment temperature of selected dairy ingredients using Vis-NIR spectroscopy and chemometrics American Society of Agricultural and Biological Engineering (ASABE) Annual

	International Meeting, Washington, USA, 16 Jul 2017 - 19 Jul 2017. 16 Jul 2017 3. Maria Markiewicz-Keszycka (2018) Laser induced breakdown spectroscopy for quantification of minerals in powdered infant formula. Innovation in food science and human nutrition. Rome, September 13-15, 2018.

Potential Impact related to Policy, Practice and Other Impacts

Impact	Details
Industry	Quality assurance is an essential part of the of Irish dairy production. Irish dairy processors will be required to demonstrate that they implement systems to enable control of and confidence in the specifications and properties of the powdered products they produce for the infant formula industry. This project has further develop the integration of state of the art PAT tools in the dairy industry and has tested this implementation to the industrial stage. Project PIs were lead PIs in the Enterprise Ireland funded Dairy Processing Technology Centre (Phase 1 and 2). Technology updates were presented to the 8 dairy industry partners at regular intervals. Also results from this DAFM project underpinned industry trials at higher TRL levels in DPTC. The UCD PI were funded partners in a large EU framework project directly related to this project. https://ditect.eu/. Nov 2020 to April 2024. UCD amount 250,008 Euro. In addition Glanbia were in receipt of EU funds to trial PAT tools directly related to this DAFM project 131k Euro. Project PIs were lead PIs in the Enterprise Ireland funded Dairy Processing Technology Centre (Phase 1 and 2). Total funding awarded to UCD >1 million euro for follow-on PAT related research.

Knowledge Transfer Activities

Identify knowledge outputs generated during this project.	Project PIs were lead PIs in the Enterprise Ireland funded Dairy Processing Technology Centre (Phase 1 and 2). Technology updates were presented to the 8 dairy industry partners at regular intervals. Also results from this DAFM project underpinned industry trials at higher TRL levels in DPTC.

Section 3 - Leveraging, Future Strategies & Reference

Leveraging Metrics

Type of Funding Resource	Funding €	Summary
Exchequer National Funding	€1,000,000.00	Project PIs were lead PIs in the Enterprise Ireland funded Dairy Processing Technology Centre (Phase 1 and 2). Total funding awarded to UCD >1 million euro for PAT related research.
EU R&I programmes	€250,008.00	UCD were funded partners in a large EU framework project directly related to this project. https://ditect.eu/ N1 Nov 2020 to April 2024. UCD amount 250,008 Euro. In addition Glanbia were in receipt of EU funds to trial PAT tools directly related to this DAFM project 131k Euro.

Future Strategies

This project outcomes have allowed the researchers to leverage further funding in the area of dairy process control and the researchers are focusing now in furthering up the TRL level of the work by participation in the Dairy Process Technology Centre, an Enterprise Ireland and industry funded platform that ensures the impact of research into the dairy industry. The collaborations developed with industry in this project (ie Carbery) will be leveraged to increase the relevance of the research.

Further to this, the researchers plan to diversify the research to develop new applications for PAT tools in the dairy sector (e.g. organic milk producers and fresh food chains) developing further collaboration in Ireland and abroad.

Project Publications

1. Kang, R., Zhao, M. and O'Donnell, C., 2017. Explorations of guided microwave spectroscopy (GMS) features for infant milk formula detection. BIOSYSTEMS AND FOOD ENGINEERING RESEARCH REVIEW 22, p.85.
2. Zhao, M., Markiewicz-Keszycka, M., Beattie, R.J., Casado-Gavalda, M.P., Cama-Moncunill, X., O'Donnell, C.P., Cullen, P.J. and Sullivan, C., 2020. Quantification of calcium in infant formula using laser-induced breakdown spectroscopy (LIBS), Fourier transform mid-infrared (FT-IR) and Raman spectroscopy combined with chemometrics including data fusion. Food chemistry, 320, p.126639.
3. Cama-Moncunill, X., Markiewicz-Keszycka, M., Cullen, P.J., Sullivan, C. and Casado-Gavalda, M.P., 2020. Direct analysis of calcium in liquid infant formula via laser-induced breakdown spectroscopy (LIBS). Food chemistry, 309, p.125754.
4. Cama-Moncunill, X., Markiewicz-Keszycka, M., Cama-Moncunill, R., Dixit, Y., Casado-Gavalda, M.P., Cullen, P.J. and Sullivan, C., 2018. Sampling effects on the quantification of sodium content in infant formula using laser-induced breakdown spectroscopy (LIBS). International Dairy Journal, 85, pp.49-55.
5. Cama-Moncunill, R., Casado-Gavalda, M.P., Cama-Moncunill, X., Markiewicz-Keszycka, M., Dixit, Y., Cullen, P.J. and Sullivan, C., 2017. Quantification of trace metals in infant formula premixes using laser-induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 135, pp.6-14.
6. Cama-Moncunill, X., Markiewicz-Keszycka, M., Dixit, Y., Cama-Moncunill, R., Casado-Gavalda, M.P., Cullen, P.J. and Sullivan, C., 2017. Feasibility of laser-induced breakdown spectroscopy (LIBS) as an at-line validation tool for calcium determination in infant formula. Food Control, 78, pp.304-310.

7. Markiewicz-Keszycka, M., Zhao, M., Cama-Moncunill, X., El Arnaout, T., Becker, D., O'Donnell, C., Cullen, P.J., Sullivan, C. and Casado-Gavalda, M.P., 2019. Rapid analysis of magnesium in infant formula powder using laser-induced breakdown spectroscopy. International dairy journal, 97, pp.57-64.
8. Markiewicz-Keszycka, M., Cama-Moncunill, X., Casado-Gavalda, M.P., Dixit, Y., Cama-Moncunill, R., Cullen, P.J. and Sullivan, C., 2017. Laser-induced breakdown spectroscopy (LIBS) for food analysis: A review. Trends in food science & technology, 65, pp.80-93.
9. Markiewicz-Keszycka, M., Cama-Moncunill, R., Casado-Gavalda, M.P., Sullivan, C. and Cullen, P.J., 2019. Laser-induced breakdown spectroscopy for food authentication. Current Opinion in Food Science, 28, pp.96-103.

Conference Publications

10. O'Donnell C, (2018) Development of PAT solutions for dairy processing applications. 32nd International Forum on Process Analytical Technology IFPAC 2018, February 11 – 14 2018, Washington DC, USA. 11 Feb 2018
11. O'Donnell, C (2017) Prediction of heat treatment temperature of selected dairy ingredients using Vis-NIR spectroscopy and chemometrics American Society of Agricultural and Biological Engineering (ASABE) Annual International Meeting, Washington, USA, 16 Jul 2017 - 19 Jul 2017. 16 Jul 2017
12. Maria Markiewicz-Keszycka (2018) Laser induced breakdown spectroscopy for quantification of minerals in powdered infant formula. Innovation in food science and human nutrition. Rome, September 13-15, 2018.