Quality and Control Analysis of Wheat Fractions by Using Laser Induced Breakdown Spectroscopy (LIBS)

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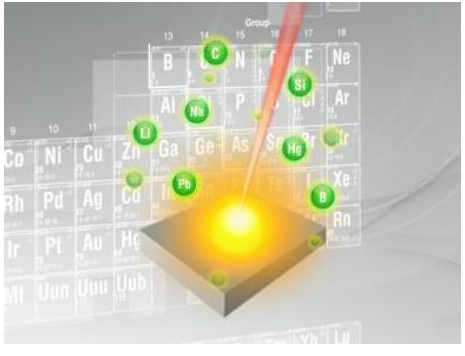
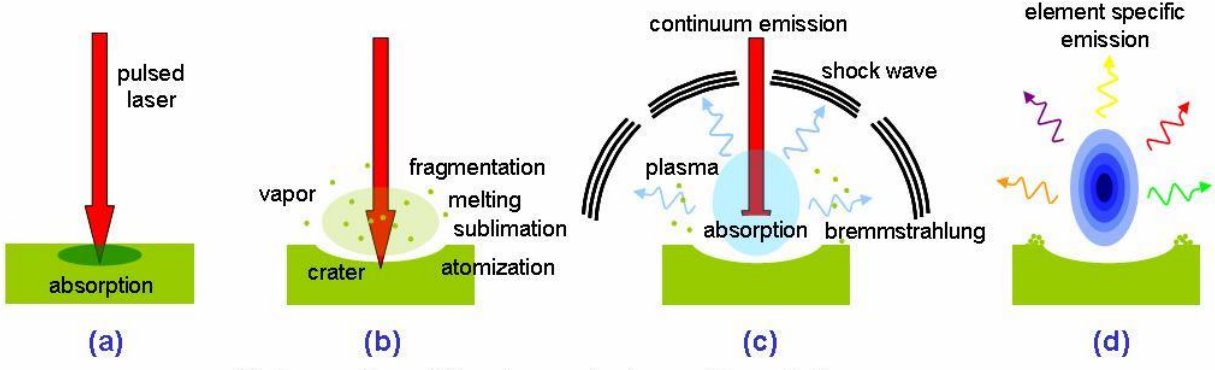
OUTLINE

- **Technical information about LIBS**
- **Applications**
  - NaCl determination in bakery products
  - Determination of Ca in wheat flour
  - Ash analysis in wheat fractions
  - Protein analysis in cereals
- **Results**
- **Conclusions**
- **Potential of LIBS**
- **Acknowledgements**

Laser Induced Breakdown Spectroscopy (LIBS)…

- LIBS is a laser based optical spectroscopy technique to detect atomic and molecular emission signals of elements. This technique has been used for qualitative and quantitative measurements of the elemental composition of different matrixes.
- The analysis by LIBS starts with focusing of laser energy in a small volume of material and within a short time period (5 to 20 nsec). This rapid energy deposition on the surface of the object being analyzed leads to material breakdown and generation of a characteristic microplasma.

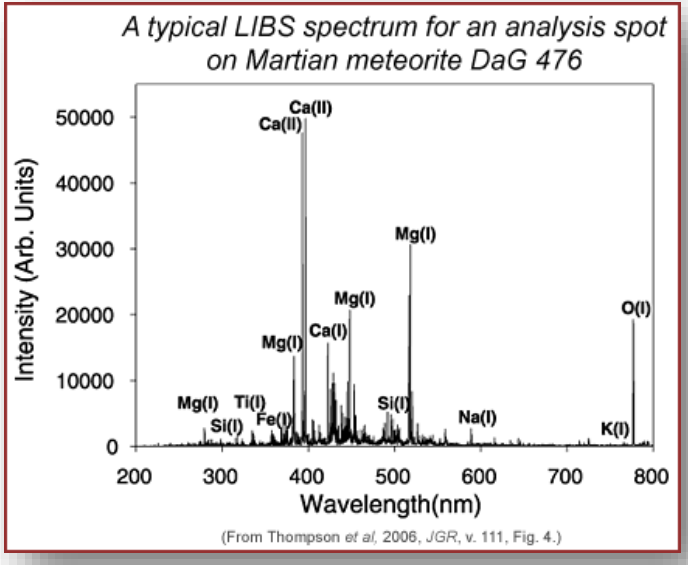




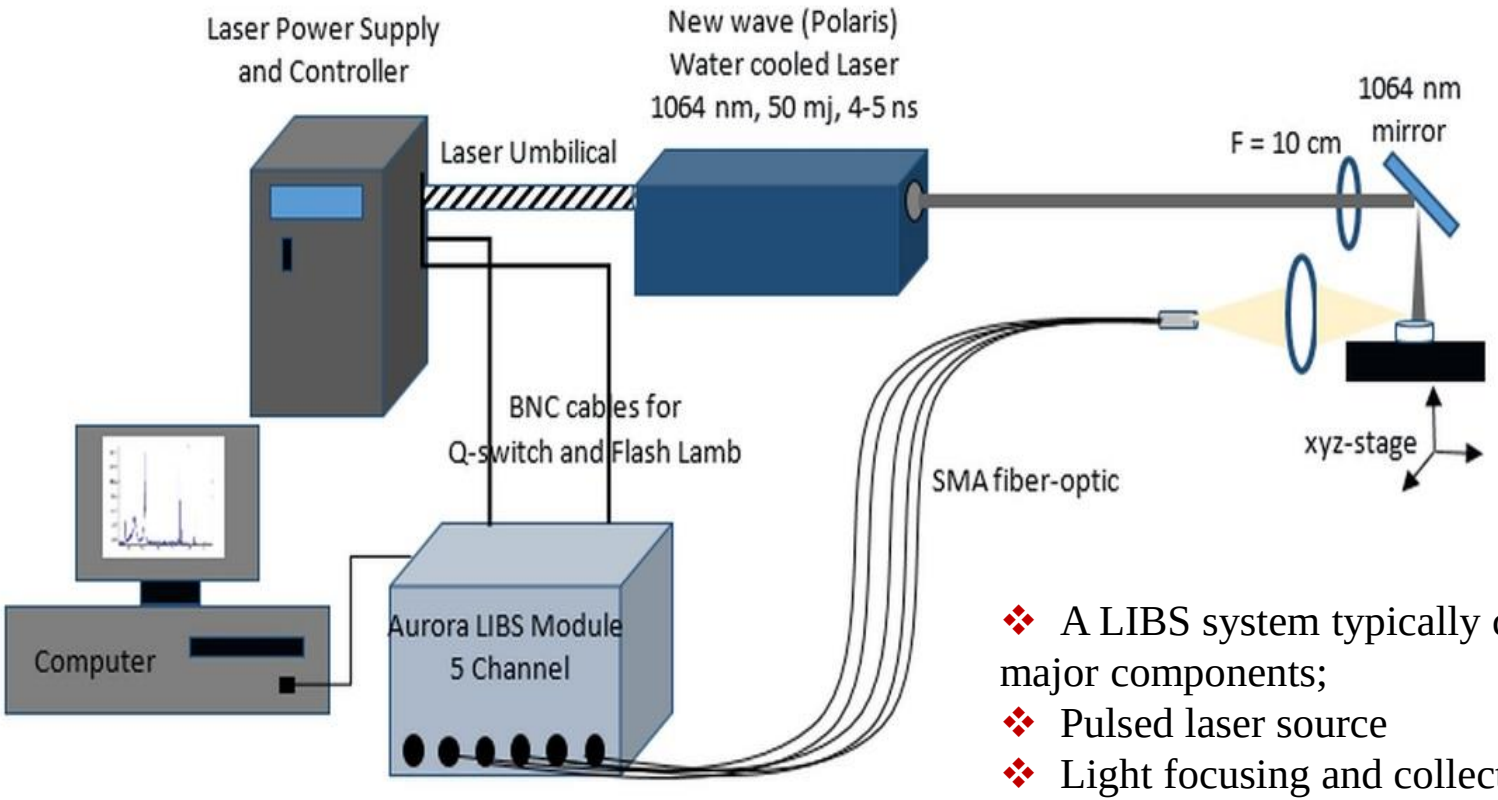
Schematic of the laser-induced breakdown process.

Laser Induced Breakdown Spectroscopy (LIBS)…

- Solids, liquids and gasses can be analyzed by using LIBS free from the state of sample because when the sample is excited with high temperature, elements emit characteristic plasma light.
- All elements can be analyzed due to type of spectrometer, energy of laser source, sensitivity of the dedector and wavelength range



Laser Induced Breakdown Spectroscopy (LIBS)…



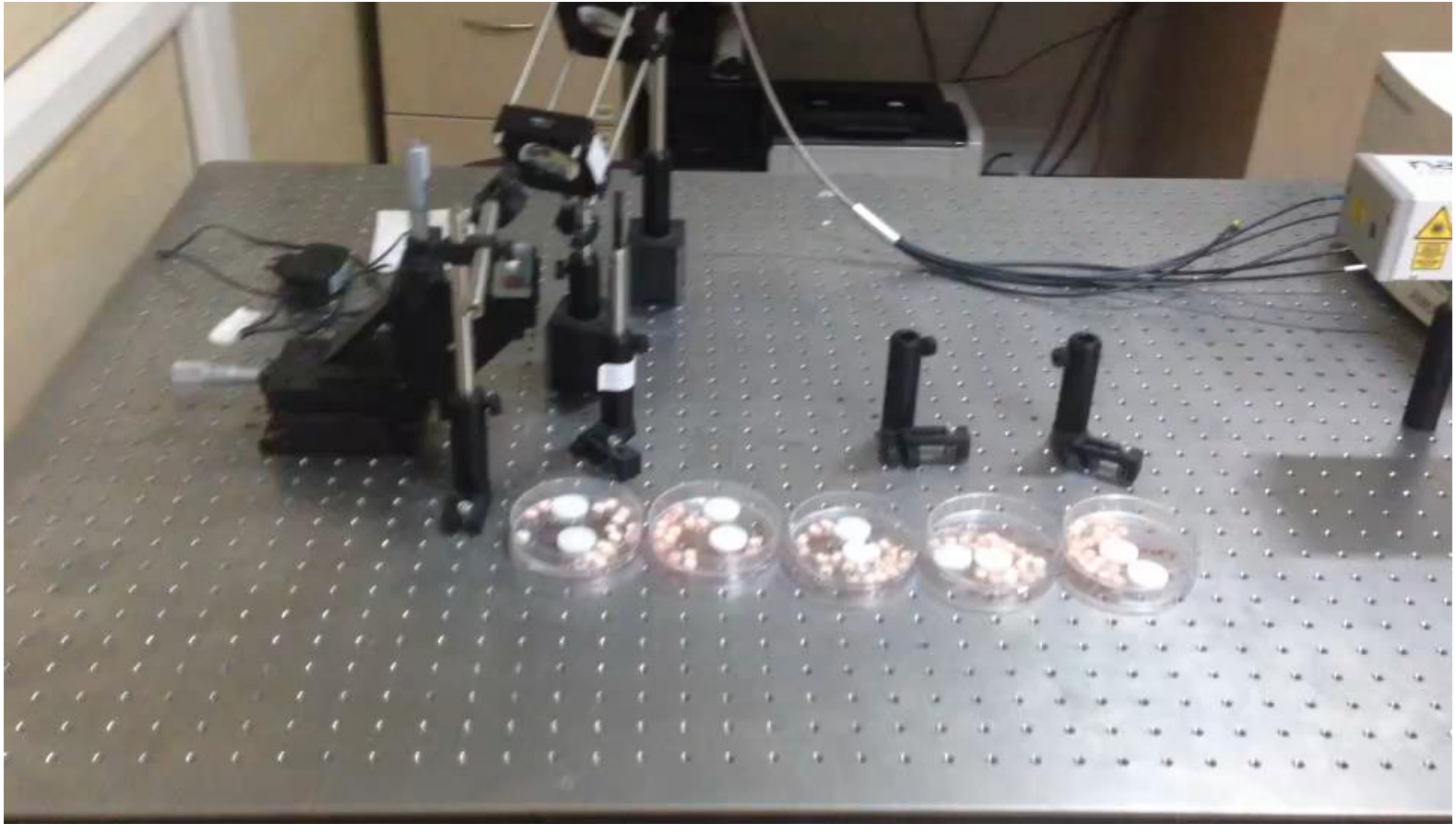
- A LIBS system typically consist of 4 major components;
- Pulsed laser source
- Light focusing and collection optics
- Spectrometer
- Computer

Laser Induced Breakdown Spectroscopy (LIBS)…

Main advantages of LIBS systems;

- Offer rapid analysis
- Require minimum or no sample preparation
- Relative experimental ease
- Different sampling protocols; fast measurement of the sample surface or depth profiling
- Thin-sample analysis
- Sensitive to all elements
- Require no contact with the sample
- Portability/stand-off

Laser Induced Breakdown Spectroscopy (LIBS)…



Applications by Using LIBS…

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Food Chemistry

Volume 181, 15 August 2015, Pages 186-190

Analytical Methods

Analysis of bakery products by laser-induced breakdown spectroscopy

Gonca Bilge [a], İsmail Hakkı Boyacı [a, b], Kemal Efe Eseller [c], Uğur Tamer [d], Serhat Çakır [e]

European Food Research and Technology

October 2016, Volume 242, Issue 10, pp 1685–1692 | Cite as

Determination of Ca addition to the wheat flour by using laser-induced breakdown spectroscopy (LIBS)

Authors | Authors and affiliations

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Journal of Cereal Science

Volume 78, November 2017, Pages 33-38

A novel method for ash analysis in wheat milling fractions by using laser-induced breakdown spectroscopy

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JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

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Laser-Induced Breakdown Spectroscopy Based Protein Assay for Cereal Samples

Banu Sezer, Gonca Bilge, and Ismail Hakki Boyaci*

Laser Induced Breakdown Spectroscopy (LIBS) Applications

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Analysis of bakery products by laser-induced breakdown spectroscopy

Gonca Bilge [a], İsmail Hakkı Boyacı [a,b,*], Kemal Efe Eseller [c], Uğur Tamer [d], Serhat Çakır [e]

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[c] Department of Electrical and Electronics Engineering, Atilim University, 06836 Ankara, Turkey
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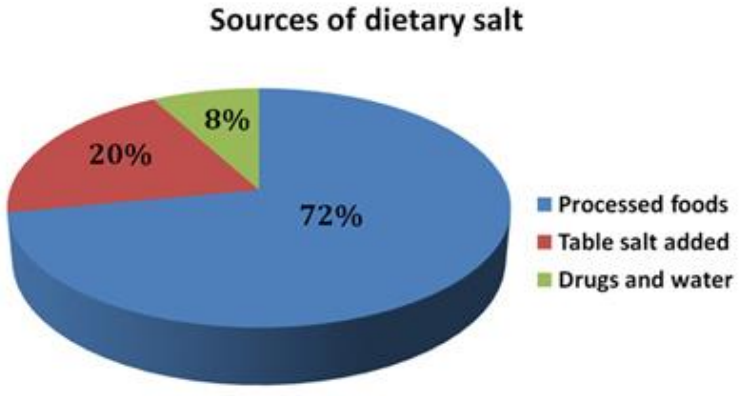
Laser Induced Breakdown Spectroscopy (LIBS) Applications

- Out of the total daily sodium chloride (NaCl) intake in the human diet, 70–75% is obtained from processed foods, out of which cereal and cereal products constitute approximately 30%.
- Na also is an important ingredient in bakery products because it plays a technological role in the dough-making process by regulating the fermentation rate, strengthening the dough and adding to the taste of the bread.



Conventional methods are

- Time consuming,
- Complex
- Requirement of sample preperation method
- Unsuitable for in situ and point detection analyses.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

- **In this study**, detection of Na in bakery products is conducted by the LIBS technique to quantify Na concentration
- To demonstrate the applicability of LIBS to the analysis of Na in bakery products, standard bread samples are chosen as the model system.
- In addition, **commercial bakery products, including crackers, biscuits and different types of breads**, are included in this study.
- Further, we use atomic absorption spectroscopy methods to confirm Na concentrations in the samples.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

Standard bread samples were produced according to American Association of Cereal Chemists (AACC) Optimized Straight-Dough Bread-Baking Method No. 10-10.03.

Twelve standard bread samples were produced by this method at various salt concentrations of 0.03–3.5%.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

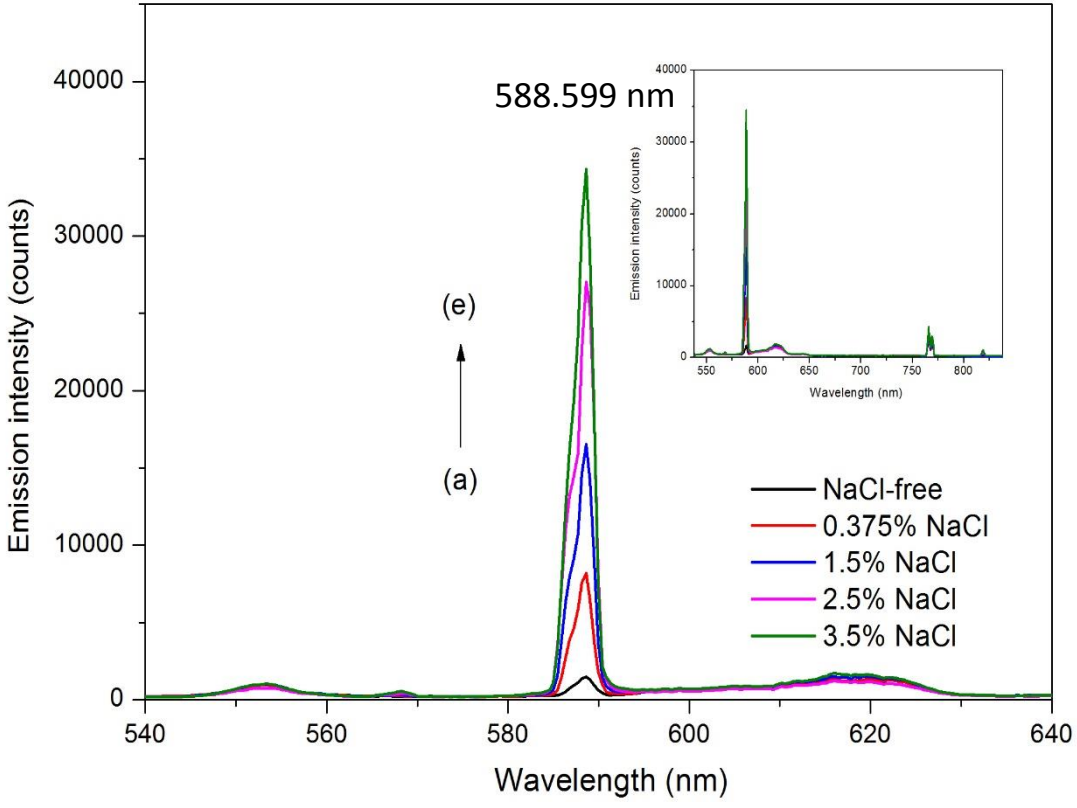


Fig 1. LIBS spectra of standard bread samples at various salt concentrations

Laser Induced Breakdown Spectroscopy (LIBS) Applications

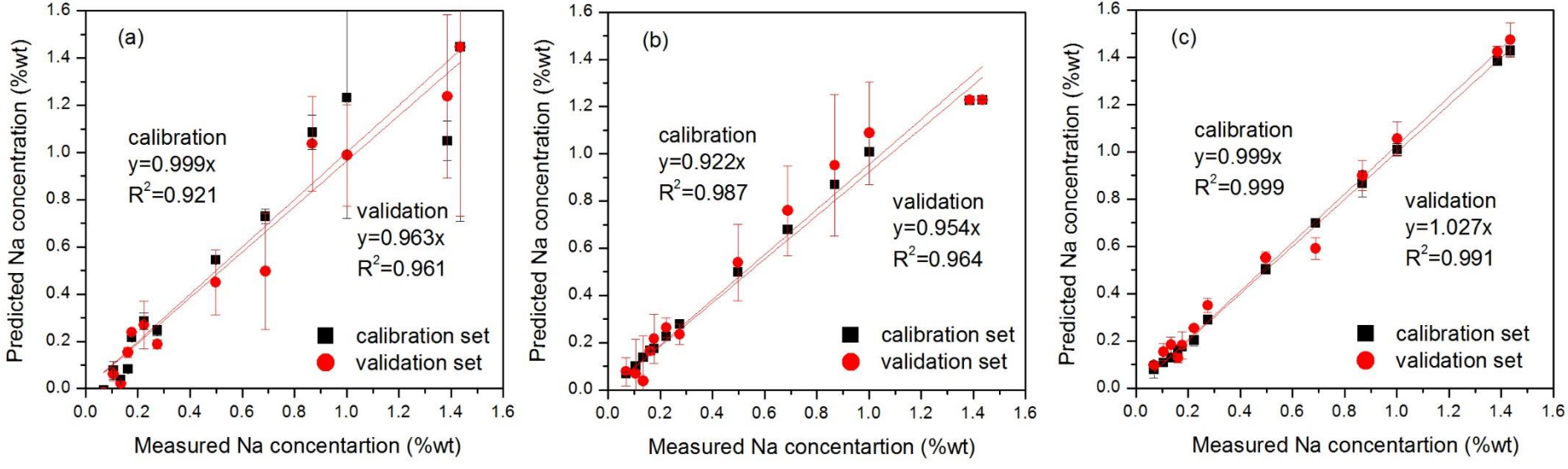


Fig. 2. Calibration and validation plots developed with SC (a), ANN (b), PLS (c) data analysis techniques

Laser Induced Breakdown Spectroscopy (LIBS) Applications

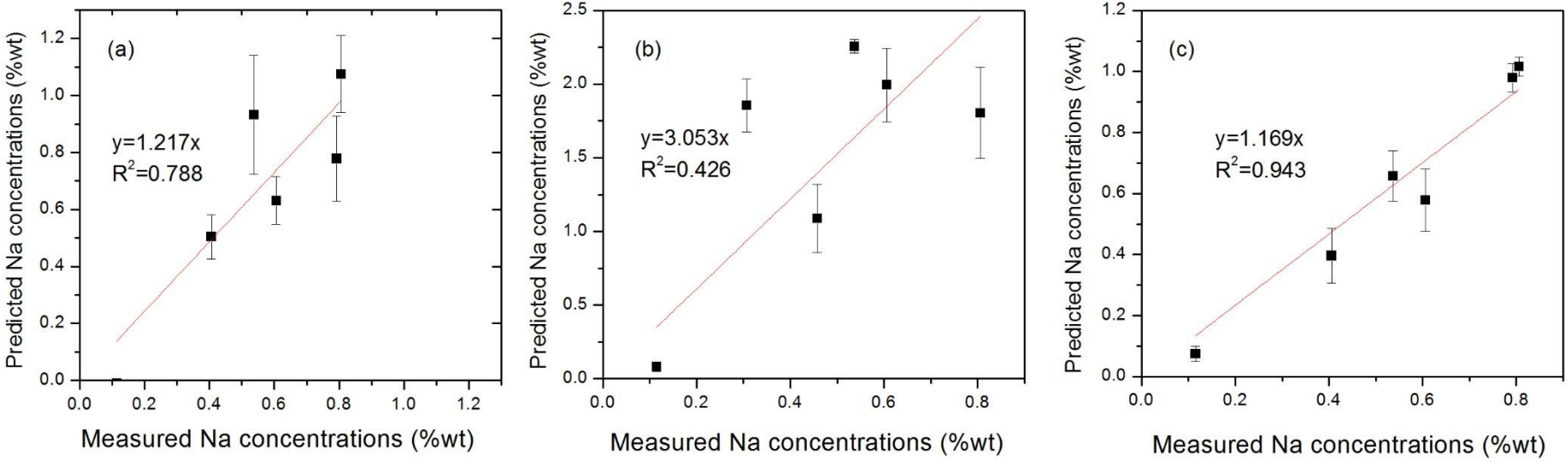


Fig. 3. Correlation between AAS and LIBS method for commercial products with SC (a), ANN (b), PLS (c) data analysis techniques.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

	SCC	ANN	PLS
R^2 for calibration	0.921	0.987	0.999
R^2 for validation	0.961	0.964	0.991
RSD	26.3%	25.3%	11.2%

Limit of detection (LOD): 0.028%

Limit of quantification (LOQ): 0.093% for PLS.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

European Food Research and Technology
October 2016, Volume 242, Issue 10, pp 1685–1692 | Cite as

Determination of Ca addition to the wheat flour by using laser-induced breakdown spectroscopy (LIBS)

Authors | Authors and affiliations

Gonca Bilge, Banu Sezer, Kemal Efe Eseller, Halil Berberoğlu, Hamit Köksel, İsmail Hakkı Boyacı

Laser Induced Breakdown Spectroscopy (LIBS) Applications

- Calcium is an essential nutrient for healthy bones, teeth and critical for various tissues in human body.
- All of the Ca needed by human body is supplied from diet.
- Milk and milk products are major sources for Ca but bread and other cereal products, vegetables and hard water are also important Ca sources.
- Recently, Ca has been added into the flour mainly for Ca fortification in flours and breads.
- The aim of the study is a new method development for determination of Ca content in wheat flour by using LIBS

Laser Induced Breakdown Spectroscopy (LIBS) Applications

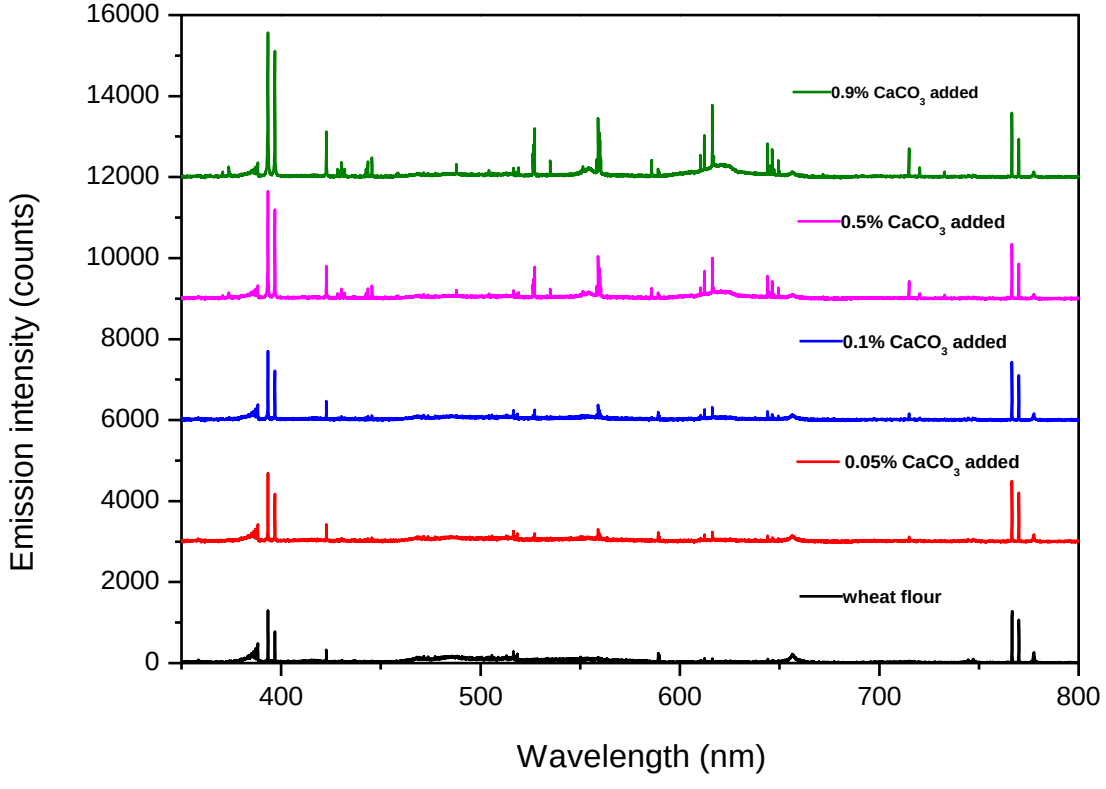
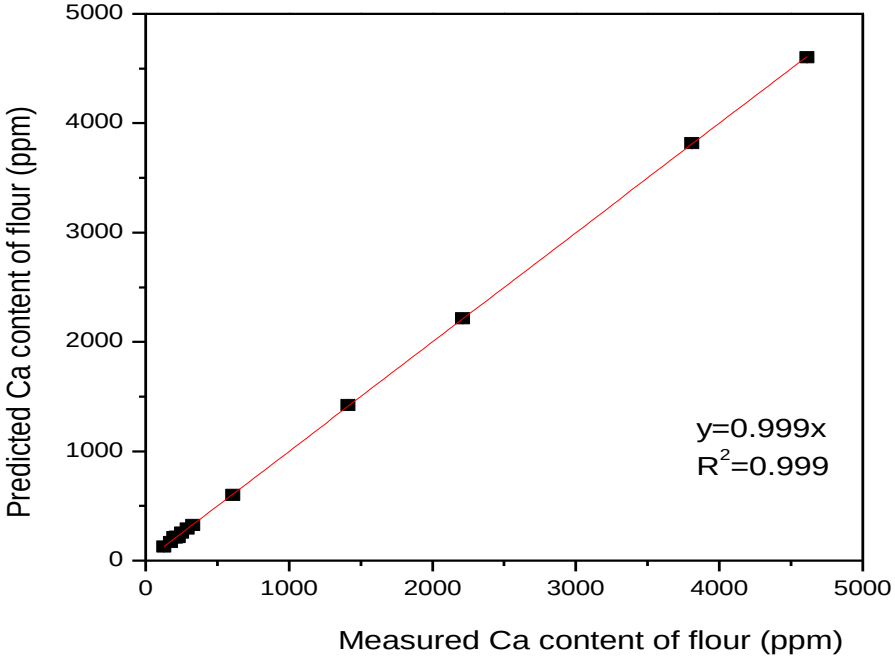


Fig. 1. LIBS spectra of the different Ca containing samples.

Laser Induced Breakdown Spectroscopy (LIBS) Applications



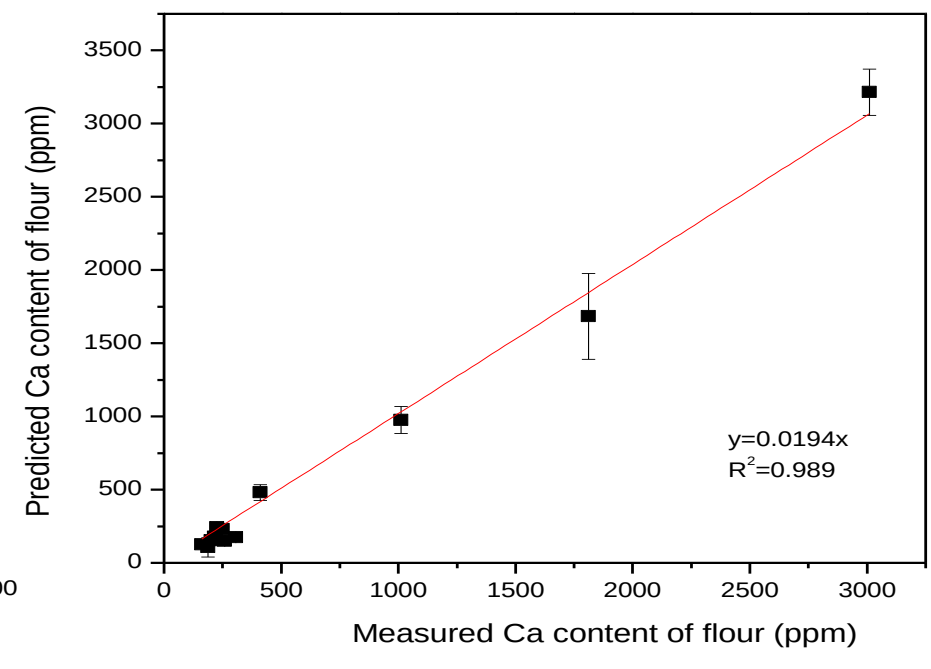


Fig. 2. PLS model of Ca added and natural wheat flours, calibration, validation models

Laser Induced Breakdown Spectroscopy (LIBS) Applications

Wheat flour samples	Ca content (ppm)	K content (ppm)	Ca/K ratio
Sample 1	210.52	934.08	0.2478
Sample 2	249.15	1218.04	0.2484
Sample 3	305.76	2248.04	0.2034
Sample 4	227.66	2548.87	0.1357
Sample 5	127.02	1243.40	0.1234
Sample 6	187.88	1384.97	0.1644
Sample 7	259.05	1239.58	0.2515
Sample 8	198.59	1054.06	0.2111
Sample 9	160.50	1264.60	0.1500
Sample 10	173.16	948.66	0.2135
Sample 11	225.89	1045.79	0.2495
Sample 12	200.73	1470.26	0.1705
Sample 13	216.39	1270.42	0.2089
Sample 14	218.21	1156.91	0.2220

Laser Induced Breakdown Spectroscopy (LIBS) Applications

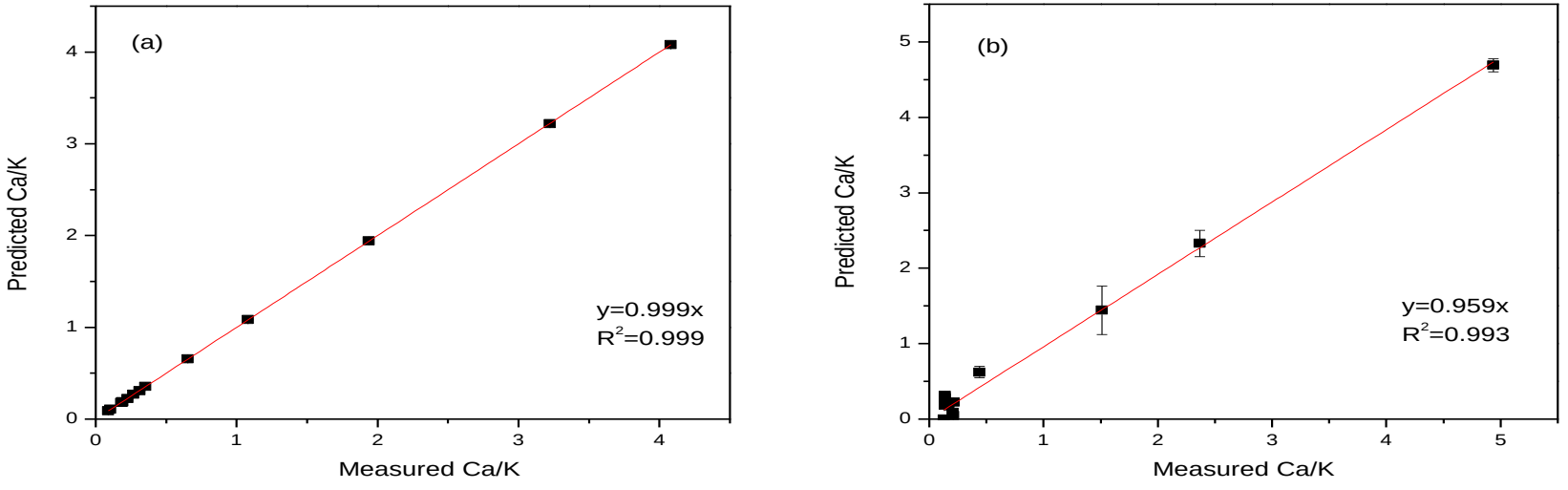


Fig. 3. PLS model of Ca/K ratio for Ca added and natural wheat flours, calibration model, validation model

Laser Induced Breakdown Spectroscopy (LIBS) Applications

- Limit of detection (LOD) values for Ca and Ca/K analysis was calculated as 25.9 ppm and 0.013 respectively.
- The results were found to be consistent with the data from atomic absorption spectroscopy (AAS) method as reference method for flour samples.
- The developed method is a rapid and reliable for determining Ca content in wheat flour quantitatively and for determining Ca addition.
- By looking at the Ca/K ratio, it can be determined if it is a natural flour or Ca salt added flour.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

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Journal of Cereal Science

Volume 78, November 2017, Pages 33-38

A novel method for ash analysis in wheat milling fractions by using laser-induced breakdown spectroscopy

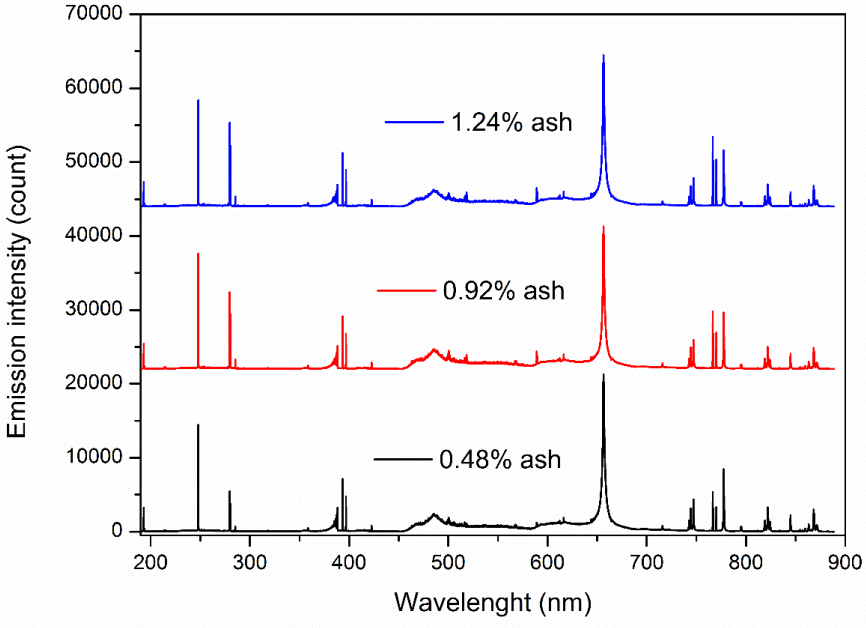
Banu Sezer [a] ✉, Gonca Bilge [b] ✉, Turgay Sanal [c] ✉, Hamit Koksel [a] ✉, Ismail Hakki Boyaci [a] ✉

Laser Induced Breakdown Spectroscopy (LIBS) Applications

- The inorganic part of the food that remains after burning at high temperatures is called ash.
- Affects the technological properties of food.
- Determines nutritional quality of foods.
- Used as an index,
  - ❖ especially for refinement of foods such as wheat flour
  - ❖ good indicator to understand the separation/discrimination of bran and germ from the wheat kernel during flour milling.

- **Basic ash method;**
- **Muffle furnace; 550°C for soft wheat flours or 575–590°C for hard wheat flours,**
- **Incineration; until light gray ash or constant weight,**
- **Cooling,**
- **The sample is weighed and ash content is calculated on dry basis.**
- **<u>This procedure is time consuming (5-6 hours) and causes power waste</u>.**

Laser Induced Breakdown Spectroscopy (LIBS) Applications



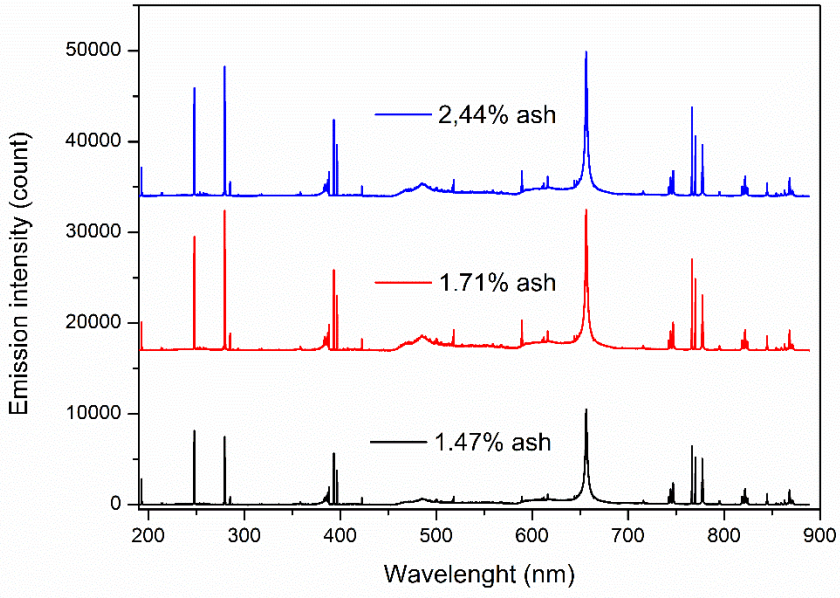


Fig. 1. LIBS spectra of wheat flour and whole meal.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

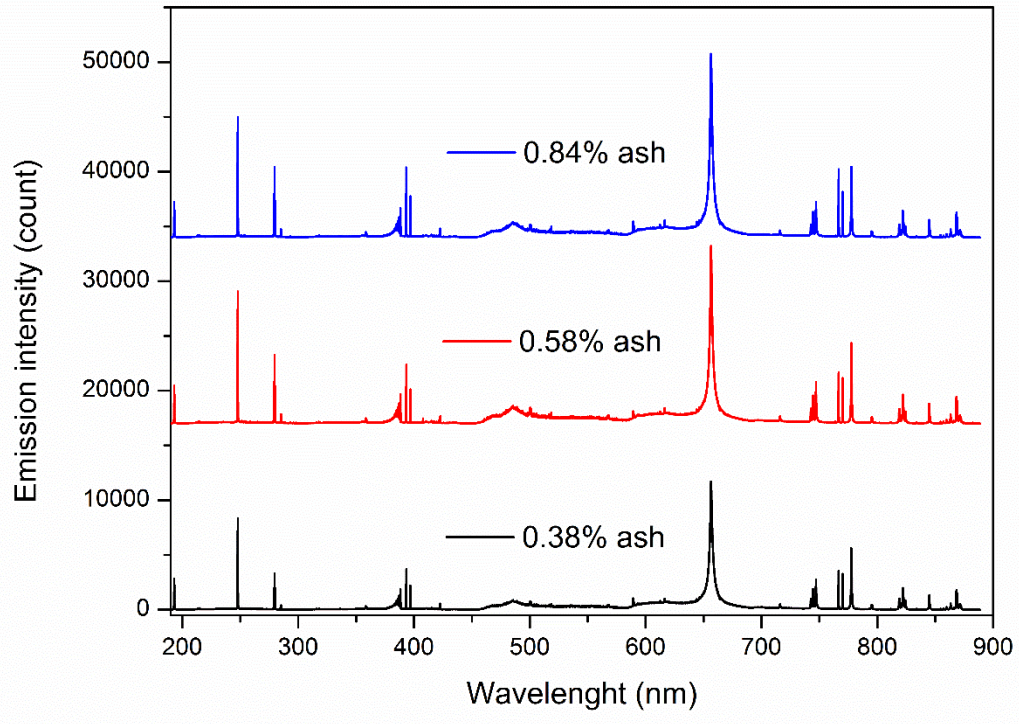


Fig. 2. LIBS spectra of semolina.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

Central wavelenght (nm)	Possible element	Central wavelenght (nm)	Possible element
247.769	Fe I (247.978)	589.031	Na I (588.995)
279.500	Mg I (279.553)	610.298	Ca I (610.272), S II (610.226), Zn (610.249)
388.205	Fe I (388.327)	612.231	Ca III (612.011), Ca I (612.221), Fe (612.790)
393.360	Ca II (393.366), Ca I (393.529)	616.260	Ca I (616.217)
396.821	Ca II (396.469)	643.982	Ca I (643.907), Fe I (643.875)
422.700	Ca I (422.672), Ca II (422.815)	645.040	Na II (645.076)
443.548	Ca I (443.569)	646.268	Ca I (646.258)
445.517	Ca I (445.478)	656.230	Fe II (656.220)
471.388	Ca III (471.626)	714.785	Ca I (714.815), Na IV (714.200), Fe I (714.814)
473.598	Ca III (473.668)	747.328	Zn II (747.877)
516.528	Fe I (516.748), Mg I (516.732)	766.568	K I (766.489)
518.950	Ca I (518.885), Na II (518.715), Mg I (518.360)	769.893	K I (769.896)
527.096	Fe I (527.035), Na II (518.715), S I (527.899)	777.224	Ca III (777.710)
558.909	Ca III (557.908), P II (558.327)		

Laser Induced Breakdown Spectroscopy (LIBS) Applications

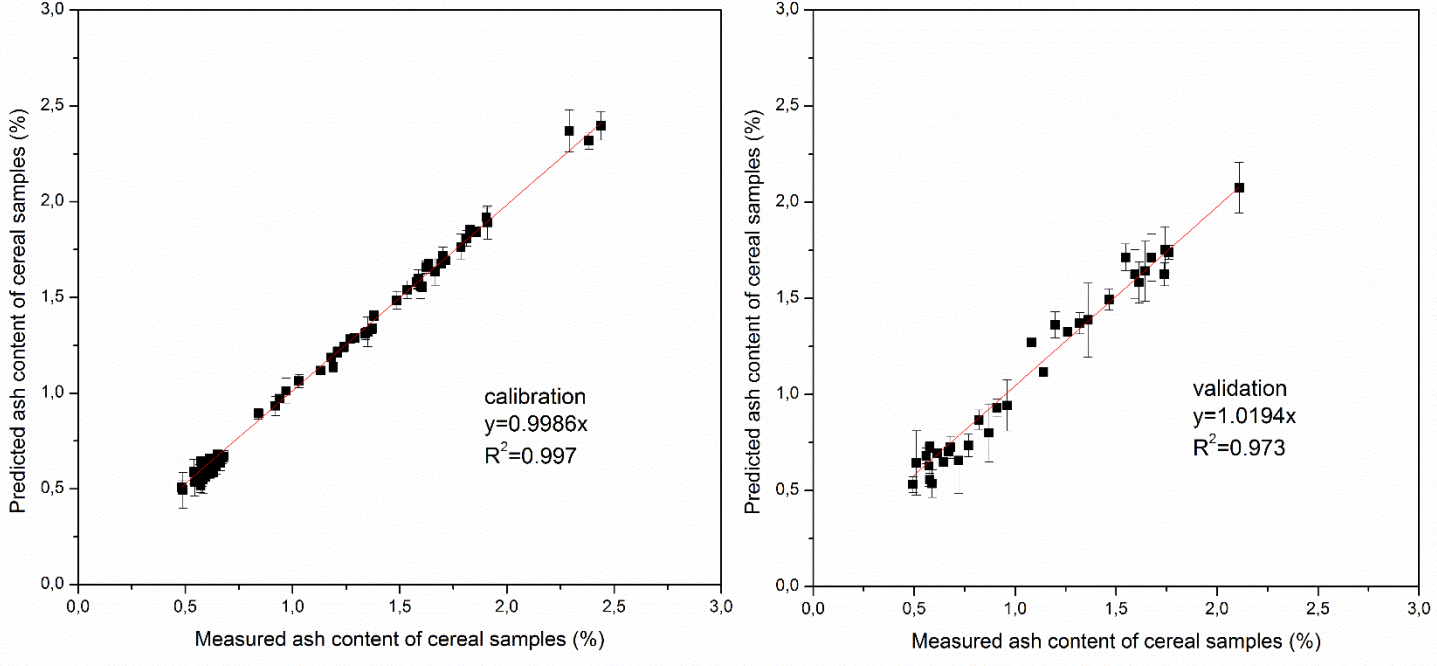


Fig. 2. PLS calibration models of wheat flour, whole meal and semolina together.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

- RSD, REP and LOD values are calculated as 8.01%, 9.53% and 0.073%
- R^2_{cal} and R^2_{val} were calculated as 0.997 and 0.973, respectively.
- Due to that LIBS is a reliable and sensitive method for ash analysis in flour samples and has good prediction ability.
- Conventional ash analysis method is based on gravimetric analysis in which the mass of analyte is weighed, and it provides information only about total mineral content, while LIBS offers data on both total mineral content and mineral composition.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

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Laser-Induced Breakdown Spectroscopy Based Protein Assay for Cereal Samples

Banu Sezer, Gonca Bilge, and Ismail Hakki Boyaci*

Department of Food Engineering, Hacettepe University, Beytepe 06800, Ankara, Turkey

Laser Induced Breakdown Spectroscopy (LIBS) Applications

- Protein content is an important quality parameter in terms of price, nutritional value, and labeling of various cereal samples.
- Conventional analysis methods, namely, Kjeldahl and Dumas, have major drawbacks such as long analysis :
  - time,
  - titration mistakes,
  - carrier gas dependence with high purity.
- For this reason, there is an urgent need for rapid, reliable and environmentally friendly technologies for protein analysis

Laser Induced Breakdown Spectroscopy (LIBS) Applications

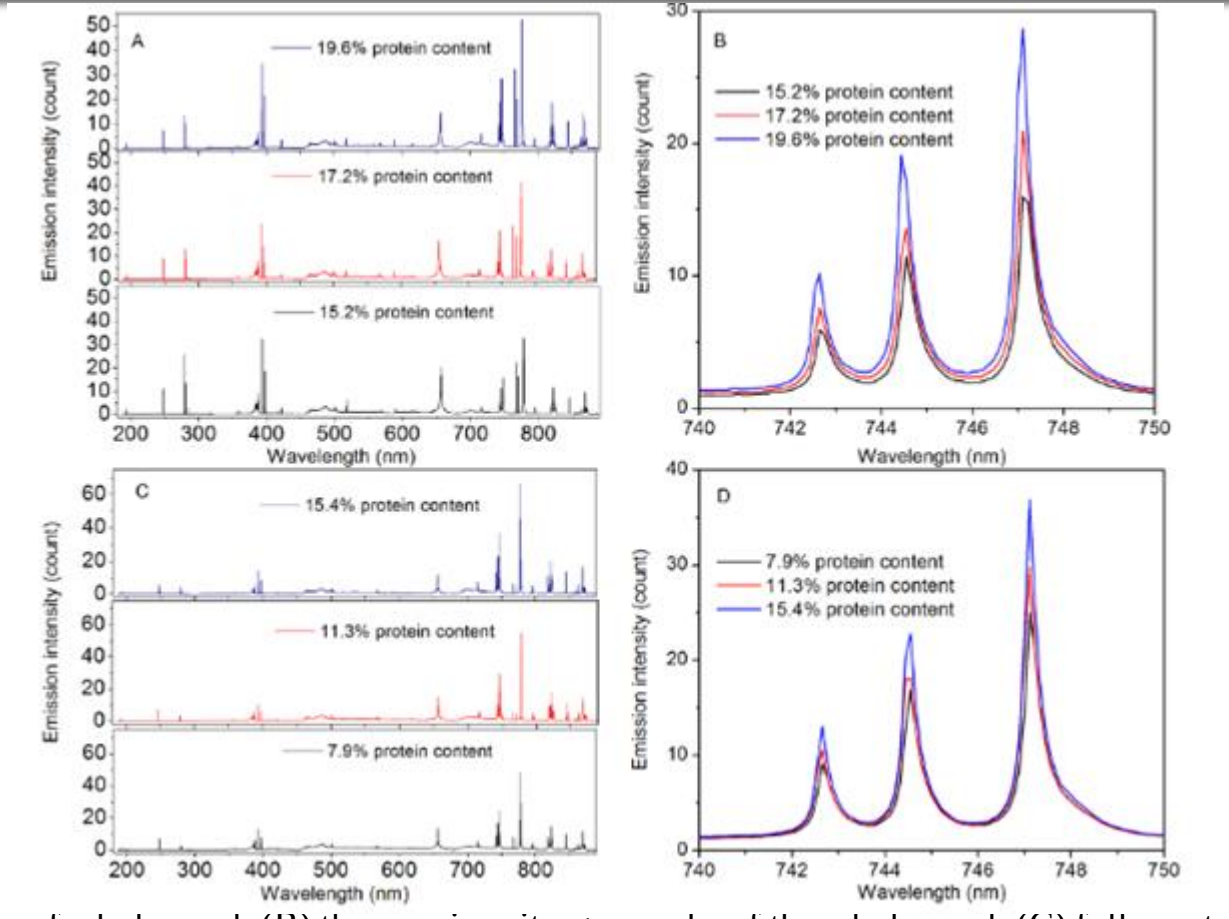


Fig. 1. (A) Full spectra of whole meal, (B) three major nitrogen peaks of the whole meal, (C) full spectra of the wheat flour, and (d) three nitrogen peaks of the wheat flour

Laser Induced Breakdown Spectroscopy (LIBS) Applications

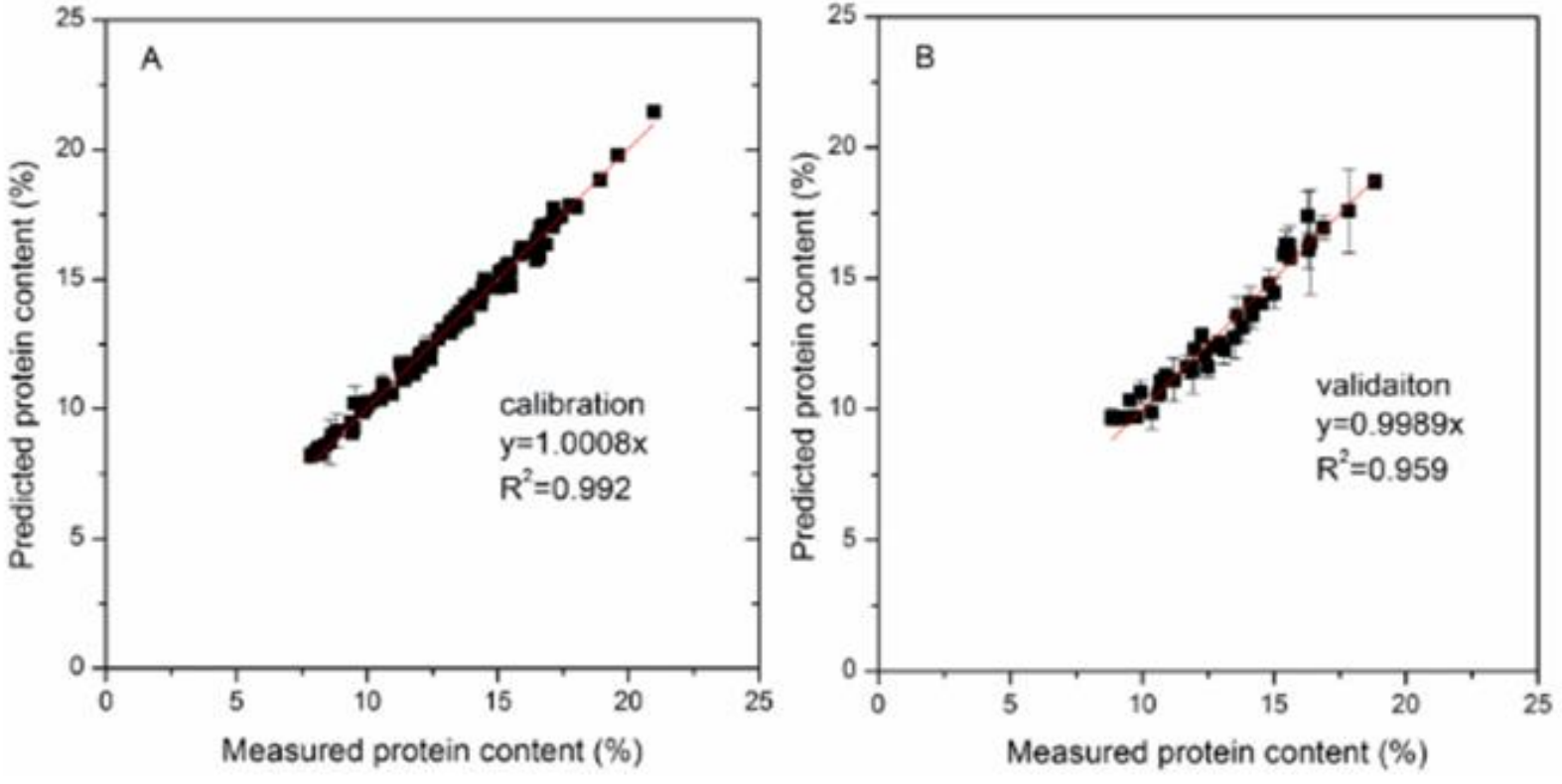


Fig. 2. (A) PLS calibration and (B) validaiton models of wheat flour and whole meal.

Laser Induced Breakdown Spectroscopy (LIBS) Applications

- To evaluate measurement sensitivity and precision, RSD, REP, LOD, and LOQ values were calculated as 4, 4.5, 0.26, and 0.77%, respectively; these values indicate that LIBS is a reliable and sensitive method for protein analysis in wheat flour and whole meal samples and has good prediction ability.

- LIBS is a quite acceptable technique for protein measurement in wheat flour and whole meal.

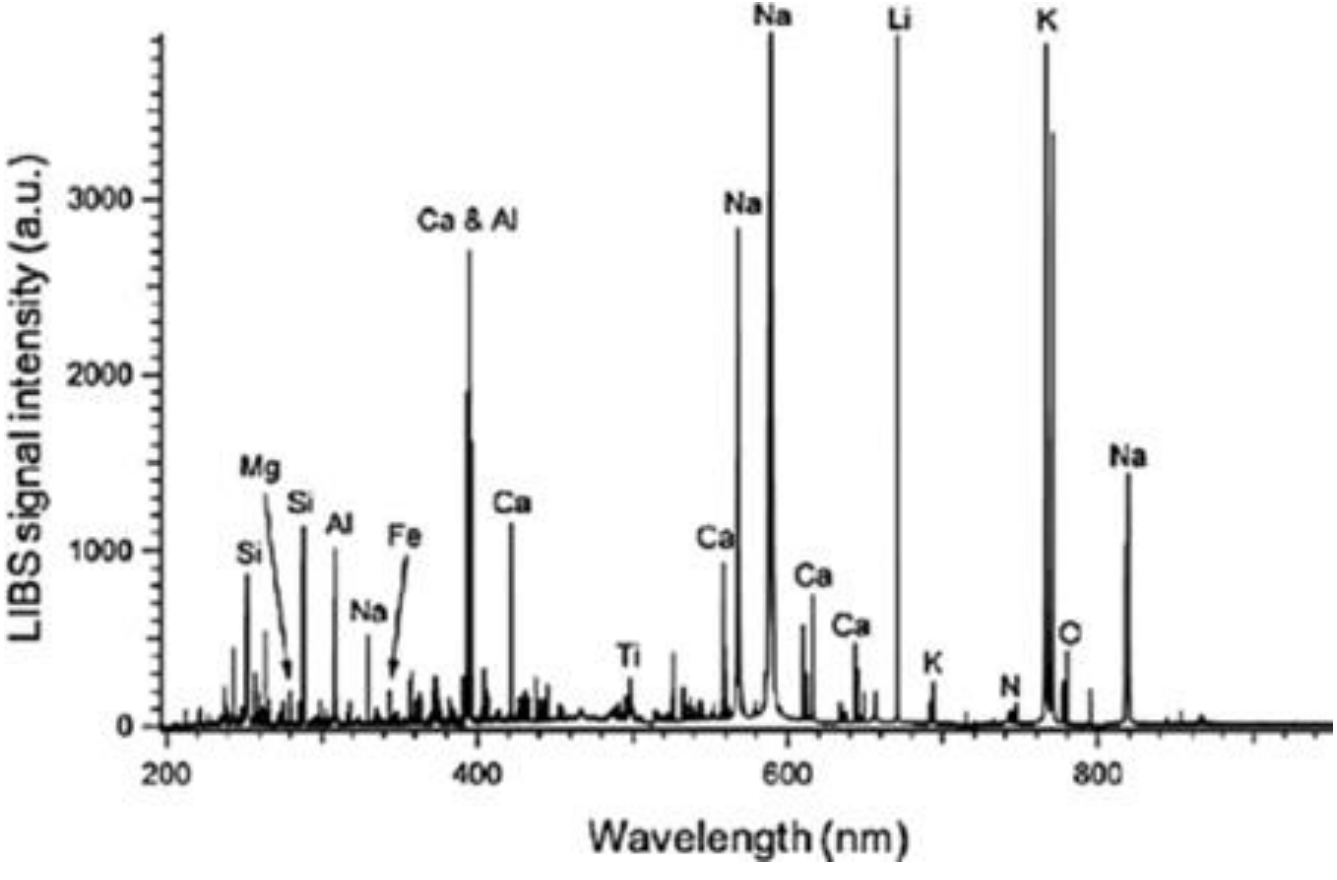
CONCLUSION…

Overall advantages of LIBS applications in cereal analysis:

- No or minimum sample preparations,
- Complete analysis within seconds,
- No additional chemical or hazardous reactants,
- Potential of multi-parametric analysis,
- Easy to use.

CONCLUSION…

- LIBS can be provide information about:



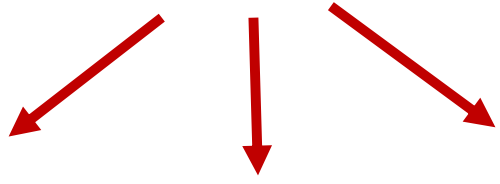
- Ca,
- Mg,
- Si,
- Al,
- Fe,
- Na,
- K,
- N,
- O
- P,
- Zn,
- Cu,
- Se,
- S,
- H,
- C_2 Swan band
- CN violet band

FUTURE APPLICATIONS…

- Potential of multi-parametric analysis
- Determination chemical quality control parameters namely;
  - Salt,
  - Total ash,
  - Total protein,
  - Moisture,
  - Dry matter,
  - Major and minor elemental content,
  - pH,
  - Acidity,
  - Ripening,
  - Geographical location,

From a Single LIBS Spectrum

- Cereal Industry (wheat, bread etc.)
- Dairy Industry (milk, cheese etc.)
- Beverage Production (fruit juice, wine, olive oil, coffee etc)
- Meat Industry



Raw Material Quality Control | **Production Process Control** | **Final Product Quality Control**

CONCLUSION…

Detection of meat adulteration

Meat Science 119 (2016) 118–122

Contents lists available at ScienceDirect

Meat Science

journal homepage: www.elsevier.com/locate/meatsci

Identification of meat species by using laser-induced breakdown spectroscopy

Gonca Bilge [a], Hasan Murat Velioglu [b], Banu Sezer [a], Kemal Efe Eseller [c], Ismail Hakki Boyaci [a,d,*]

Detection of milk powder adulteration

Food Chemistry 212 (2016) 183–188

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Determination of whey adulteration in milk powder by using laser induced breakdown spectroscopy

Gonca Bilge [a], Banu Sezer [a], Kemal Efe Eseller [b], Halil Berberoglu [c], Ali Topcu [a], Ismail Hakki Boyaci [a,d,*]

Detection of TiO_2

Food Chemistry 240 (2018) 84–89

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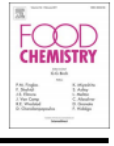

Analytical Methods

A rapid tool for determination of titanium dioxide content in white chickpea samples

Banu Sezer[a], Gonca Bilge[b], Aysel Berkkan[c], Ugur Tamer[c], Ismail Hakki Boyaci[a,*]

Detection of $LiCl_2$

Meat Science 135 (2018) 123–128

Contents lists available at ScienceDirect

Meat Science

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Detection and quantification of a toxic salt substitute (LiCl) by using laser induced breakdown spectroscopy (LIBS)

Banu Sezer[a], Hasan Murat Velioglu[b], Gonca Bilge[c], Aysel Berkkan[d], Nese Ozdinc[b], Ugur Tamer[d], Ismail Hakkı Boyaci[a,*]

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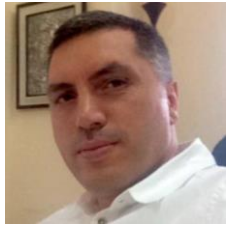

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