Vegetable oil speciation in processed foods

how legislation drives innovation

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legislation vs innovation
Food safety legislation is very strict
Food labelling: *the exemption*

*The labels are complex and yet informative*

IN THERE THE REGULATOR PUTS SOME STRICT RULES THAT COMPANIES MUST ADHERE BUT NOT ALWAYS THE RESEARCH EXIST TO POLICE THE LEGISLATION PROPERLY...

**INGREDIENTS**
- Water, Carrots, Onions, Red Lentils (4.5%) Potatoes, Cauliflower, Leeks, Paas, Cornflour, *Wheat* flour, Cream (*milk*), Yeast Extract, Concentrated Tomato Paste, Garlic, Sugar, *Celery* Seed, Sunflower Oil, Herb and Spice, White Pepper, Parsley

**ALLERGY ADVICE**
For allergens, see ingredients in **bold**

**The EU has the stricter legislation in the world**
New Regulation in place for vegetable oils sold as ingredients in processed foods

- EC Regulation 1169/2011, food businesses required to declare the composition of the oil mixture in the food product label. [Dec 2014: live]
- vegetable oils of interest: palm, sunflower, rapeseed; coconut oil
- Monitoring the compliance of the regulation is challenging for national bodies and other enforcers.
Shortcake fancies filled with buttercream (18%) and raspberry jam (11%).

INGREDIENTS
Wheat Flour, Vegetable Oil, Icing Sugar, Raspberry Jam (Glucose-Fructose Syrup, Raspberries, Humectant (Vegetable Glycerine), Gelling Agent (Pectin), Citric Acid, Acidity Regulator (Sodium Citrates), Flavouring, Colour (Anthocyanins)), Butter Invert Sugar Syrup, Salt, Raising Agents (Disodium Diphosphate, Sodium Bicarbonate), Humectant (Vegetable Glycerine), Flavouring, Sugar, Emulsifier (Polyglycerol Esters of Fatty Acids, Mono- and Diglycerides of Fatty Acids), Colour (Curcumin).

Suitable for vegetarians

Ingredients
Wheat Flour, Sugar, Vegetable Oil, Raising Agents (Calcium Phosphate, Potassium Bicarbonate), Salt.

Our promise
We are happy to refund or replace any Tesco product which falls below the high standard you expect. Just ask any member of staff.

Ingredients: Wheat flour, water, stabiliser (glycerol), vegetable oil, raising agents (sodium bicarbonate, sodium acid pyrophosphate), emulsifier (mono and diglycerides of fatty acids), dextrose, salt, preservative (potassium sorbate). Packaged in a protective atmosphere.

CONTAINS WHEAT INGREDIENTS.
because everyday foods shouldn't taste everyday

INGREDIENTS Wheatflour contains Gluten (with Wheatflour, Calcium Carbonate, Iron, Niacin, Thiamin) · Sugar · Palm Oil · Rapeseed Oil · Barley Malt Extract (contains Gluten) · Raising Agent: E503, Sodium Bicarbonate, E450 · Glucose Syrup · Salt · Preservative: E223 (Sulphites).

CRISP BISCUITS Ingredients: Wheat Flour (with Calcium, Iron, Niacin, Thiamin), Sugar, Vegetable Oil (Sunflower), Glucose Fructose Syrup, Barley Malt Extract, Raising Agents (Sodium Bicarbonate, Ammonium Bicarbonate), Salt.

For allergens, including cereals containing gluten, see ingredients in bold. May also contain Soya.
Can you find out what type of vegetable oil is present in processed foods?

analytical method capable to identify oil species in the vegetable oil blends?
What is the issue with palm oil?

- sustainable production?
  *production raised 500% during the last 20 years*
- Fair trade / fair wages?
- Deforestation

In supermarkets, 50% of all baked goods, confectionery, spreads, cosmetics, cleaning agents, air fresheners etc.

**The average first-world citizen consumes at least 10kg of palm oil each year!**
Fusion of **spectroscopy** and *chromatography*

Is to extract information about the whole of the sample product by analysing a wealth of variables that defines it which on their own they might not mean much but in systematically viewing them all together do supply an overview of the unique “character” (fingerprint) of the sample.
Refined palm (12), sunflower (12), rapeseed (12)

Pure palm (n=36)

Pure PO, SUN and RO and admixtures on PO-RO, PO-SO oil (n=30 pure oils + 48 admixtures)

Different oils are mixed in clearly defined binary mixtures

INDEPENDENT
Pure oils and admixtures (n=22 pure oils + 36 admixtures of these pure oils)

Calibration set (n=58)

INDEPENDENT
Pure oils and admixtures (n=8 pure and 12 admixtures)

Prediction set (n=20)

Commercial biscuits with unique oil sources (21) and with blends (4) [as declared in the label]

Validation set (n=25)

IDENTIFICATION OF VEGETABLE OIL SPECIES IN BISCUITS
the use of vegetable oils in bakery products

A “crust” that has a “hard” oil like palm stearin
A “creamy” sauce that has a “soft” vegetable, fat, for example, palm olein, rapeseed oil or coconut oil

pastry Crust: Hard fraction → Palm Stearin
filling: Soft fraction → Palm Olein
Bakery/pastry products

biscuits

plain (no filling)

with filling

rich tea

digestive

all butter

other

cocoa filling

cream filling

bourbon
In biscuits with fillings:
Common fillings include chocolate, bourbon and white cream (vanilla).

In biscuits without fillings:
- 79% palm oil
- 12% sunflower oil
- 9% ropo

Oil species applied in chocolate biscuits:
- 92% Palm
- 42% cocoa
- 42% butter
- 8% coconut
- 17% rapeseed

Cream fillings:
- 52% Palm oil
- 3% palm oil, palm kernel oil, palm fat
- 13% veg oil (Palm)
- 6% veg oil (Palm); veg oil (palm olein, palm)
- 19% palm kernel oil, palm oil, rapeseed oil
- 7% vegetable oil (palm, coconut)
Key features of the study

• 36 authentic vegetable oil samples
  – 12 palm, 12 sunflower, 12 rapeseed oils
  – trusted sources from the industry
  – in house chemical analysis with official methods

• 48 admixtures of oils
  – (ROPO, SOPO)

• 5 oil classes (PO, SO, ROPO, SOPO, RO) trained with supervised discriminative algorithms

• 3+ layers of validation
Baking of biscuits

Extraction of fat from biscuits

FTIR

Spectra collection

Raman

Data analysis

RESULT: What oil your biscuit has?

Classification algorithms
In-house baking
solvent extraction
spectra acquisitions

**Raman**
- 1064 nm laser frequency
- 200 - 2000 cm\(^{-1}\) range
- 10 cm\(^{-1}\) resolution

**FTIR**
- 400 - 4000 cm\(^{-1}\) range
  - DTGS detector on d-ATR
- number of scans: 32
- resolution: 4.0
Changes in the intensities of spectral bands of different oils are related to the composition of molecular bonds absorbing at those regions.

FTIR spectra on pure oils

PKO: Palm Kernel Oil; PO: Palm oil; RO: Rapeseed oil; SO: Sunflower oil
Pre-processing steps

Raw data → SNV → 1st der → S-Golay → Pareto scaling → Pretreated data

Raman

\[ \times 10^4 \]

Absorbance

0 500 1000 1500 2000

FTIR

Absorbance

0 1000 2000 3000 4000 5000

0 1000 1500 2000 2500 3000

Absorbance

0 0.1 0.2

0 -0.1 0.2
Model and class development and validation

FTIR and RAMAN DATA

TRAINING of the MODEL using calibration set

VALIDATION

SIMCA

- Soft Class Model of Class Analogy
- Creates a PCA space for each class and determines DtModel

PLS-DA

- Partial Least Square – discriminant analysis
- Supervised classification
PCA scores plot of FTIR data of different vegetable oils
PCA FTIR from oils of in-house and commercial products
Classification results: for in-house samples

<table>
<thead>
<tr>
<th>TARGET GROUP</th>
<th>SIMCA</th>
<th>PLS-DA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SENSITIVITY (%)</td>
<td>SPECIFICITY (%)</td>
</tr>
<tr>
<td></td>
<td>RAMAN</td>
<td>FTIR</td>
</tr>
<tr>
<td>PO</td>
<td>66.7</td>
<td>83.3</td>
</tr>
<tr>
<td>PORO</td>
<td>66.7</td>
<td>83.3</td>
</tr>
<tr>
<td>POSO</td>
<td>83.3</td>
<td>66.7</td>
</tr>
<tr>
<td>SO</td>
<td>83.3</td>
<td>83.3</td>
</tr>
<tr>
<td>RO</td>
<td>50.0</td>
<td>100.0</td>
</tr>
<tr>
<td>TOTAL (%)</td>
<td>19/26</td>
<td>21/26</td>
</tr>
</tbody>
</table>

for SIMCA we accept samples with Pconf>0.05 and for PLD-DA with Pconf >0.5; if no limits are applied, correct classification is at 100% at all cases
Gas Chromatography/Mass Spectroscopy
test fti pca with cal+perd + val.M29 (PCA-X)
Colored according to classes in M29

R2X[1] = 0.604
R2X[2] = 0.29
R2X[3] = 0.0333

Ellipse: Hotelling's T2 (95%)
## Fatty acids profiles

<table>
<thead>
<tr>
<th>Oil species</th>
<th>OIL SOURCES</th>
<th>C14:0</th>
<th>C16:0</th>
<th>C18:0</th>
<th>C18:1c</th>
<th>C18:2c</th>
<th>C20:0</th>
<th>C22:0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In-house biscuits</td>
<td>1.3 ± 0.1</td>
<td>44.9 ± 0.5</td>
<td>4.2 ± 0.1</td>
<td>36.9 ± 0.6</td>
<td>11.1 ± 0.4</td>
<td>0.3 ± 0.0</td>
<td>0.1 ± 0.0</td>
</tr>
<tr>
<td>PO</td>
<td>Commercial bisc.</td>
<td>1.3 ± 0.1</td>
<td>45.3 ± 2.0</td>
<td>4.1 ± 0.2</td>
<td>36.2 ± 1.5</td>
<td>11.0 ± 1.6</td>
<td>0.3 ± 0.0</td>
<td>0.1 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>Untreated oils</td>
<td>1.1 ± 0.1</td>
<td>43.4 ± 0.9</td>
<td>4.8 ± 0.2</td>
<td>34.8 ± 0.9</td>
<td>8.2 ± 0.4</td>
<td>0.4 ± 0.1</td>
<td>0.0 ± 0.0</td>
</tr>
<tr>
<td>SO</td>
<td>In-house bisc.</td>
<td>0.1 ± 0.0</td>
<td>7.1 ± 0.2</td>
<td>3.3 ± 0.2</td>
<td>28.6 ± 2.2</td>
<td>59.1 ± 2.2</td>
<td>0.1 ± 0.0</td>
<td>0.7 ± 0.0</td>
</tr>
<tr>
<td></td>
<td>Commercial bisc.</td>
<td>0.1 ± 0.0</td>
<td>5.5 ± 1.3</td>
<td>2.9 ± 0.2</td>
<td>78.0 ± 2.5</td>
<td>11.2 ± 1.4</td>
<td>0.2 ± 0.0</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Untreated oils</td>
<td>0.1 ± 0.0</td>
<td>6.1 ± 0.2</td>
<td>3.6 ± 0.2</td>
<td>26.8 ± 1.8</td>
<td>55.9 ± 1.9</td>
<td>0.1 ± 0.0</td>
<td>0.7 ± 0.0</td>
</tr>
<tr>
<td>RO</td>
<td>Untreated oils</td>
<td>0.0 ± 0.0</td>
<td>4.5 ± 0.2</td>
<td>1.7 ± 0.1</td>
<td>55.9 ± 2.3</td>
<td>17.5 ± 0.8</td>
<td>0.5 ± 0.0</td>
<td>0.3 ± 0.0</td>
</tr>
<tr>
<td>OO</td>
<td>Untreated oil (lit.)</td>
<td>0.0 ± 0.0</td>
<td>13.8 ± 6.2</td>
<td>2.7 ± 2.2</td>
<td>69.0 ± 14.0</td>
<td>12.2 ± 8.7</td>
<td>0.4 ± 0.4</td>
<td>0.1 ± 0.1</td>
</tr>
</tbody>
</table>
Fat extraction with solvent (hexane, ethyl acetate)

Analysis (screening, confirmation)

Palm components:
- Confectionary fats
- Cocoa butter replacers (CBR)
- Cocoa butter equivalents (CBE)

Further challenge: to identify the type of oils used in confectionery products
An interlaboratory trial with 14 participants having different brands of Fourier-transform infrared spectrometers for the identification of oil species in mixtures of oils.

VALIDATION
9 oil samples
(Pure oils and admixtures)

14 Participants

FTIR spectra

Pre-processing

Classification model

an instrument agnostic FTIR method
a different approach to model transfer
Data augmentation in food authenticity: synthesizing spectroscopic data of vegetable oils for performance enhancement
the team

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