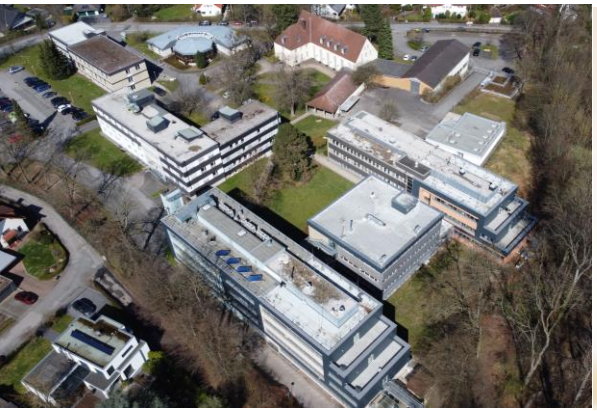


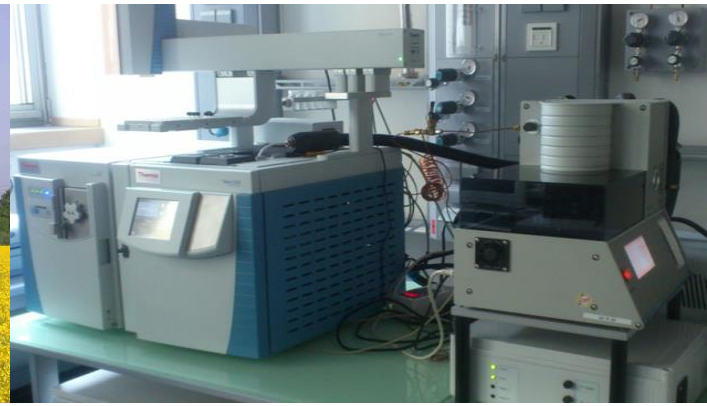

Authenticity and contaminants - Challenges for edible oils

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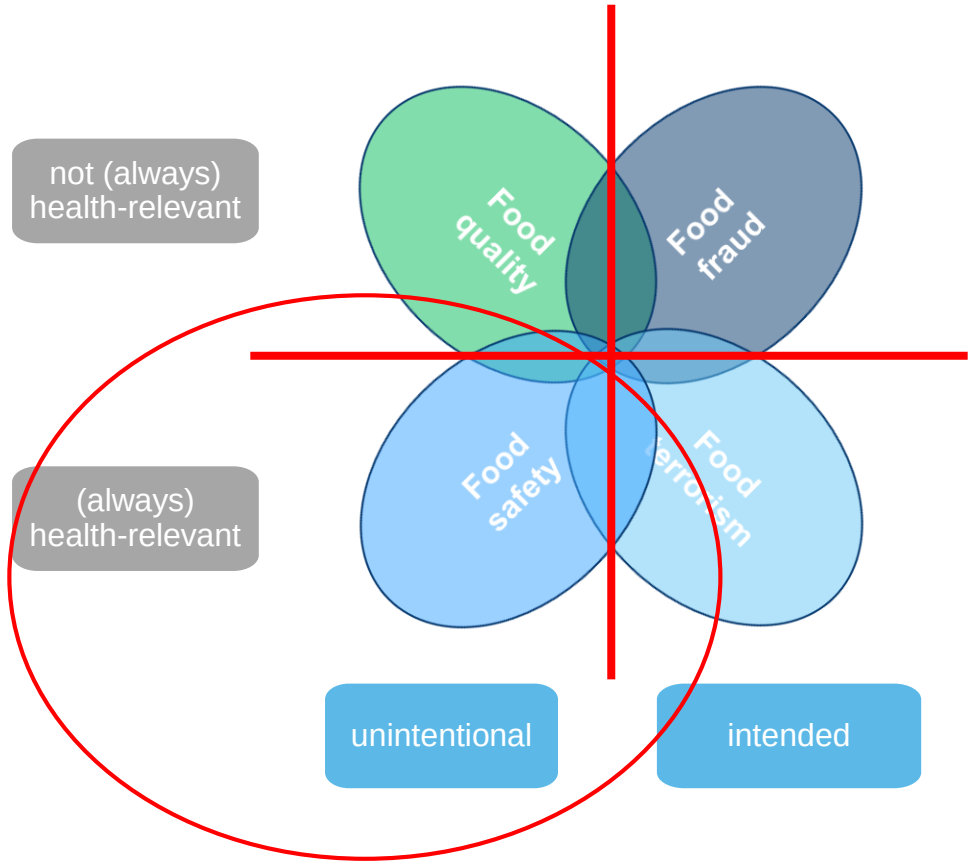
Max Rubner-Institut; Federal Research Institute of Nutrition and Food;
Institute of Safety and Quality of Cereals, Detmold

What are contaminants?

EFSA
Chemical substances that are not intentionally added to food or feed. Contaminants can pose a risk to human and animal health..

natural toxines	alkaloids or mykotoxins
Environmental pollutants	polychlorinated biphenyls (PCBs), dioxins, persistent chlorinated compounds, brominated flame retardants, PFAS, heavy metals, mineral oil components
Process-induced contaminants	acrylamide, 3-MCPD- and glycidyl ester, 4-hydroxy nonenal, Furan

Examples of intentional addition of undesirable substances:
- Spanish oil syndrome → Denaturing of olive oil with aniline, 1981
- Melamine scandal due to (baby) milk stretched with nitrogen-containing synthetic resin bases, 2008, China
- Processed horse meat in beef products, 2013
- Detection of fipronil in eggs, 2017



Components of food integrity

Why is it important to take contaminants into consideration?

Important aspect of consumer protection:

- Can pose a significant health risk to consumers
  - General toxicity (immediate death or illness)
  - Accumulation → long-term toxicity
  - Carcinogenic
  - Mutagenic
  - Teratogenic
  - Endocrine disruptors (hormones)
  - microbial pathogens

- Consumers must be able to rely on food being safe and contaminated as little as possible
- Transparency and information about possible contaminants strengthen confidence in food safety.

Sources for contaminants in edible oils

food processing

refining

oil processing

storage

Cultivation
(pesticides, mineral oils, mycotoxins)

Processing
(PAH, mineral oil components, trans-fatty acids, plasticizer, 3-MCPD and glycidyl ester, toxic aldehydes)

Environment
(heavy metals, dioxins, PAH, PAH, PFAS chloroparaffins, mineral oil components

Transportation and storage
(plasticizer, mineral oil components, mycotoxins)

environment

cultivation

harvest

transportation

Example: 3-MCPD- and glycidyl ester

October 2006: scientific paper on 3-MCPD fatty acid esters in edible fats and oils(Z. Zelinková et al.: Fatty acid esters of 3-chloropropane-1,2-diol in edible oils; Food Additives and Contaminants 2006, 1-9)


Food Additives and Contaminants, December 2006; 23(12): 1290–1298

Fatty acid esters of 3-chloropropane-1,2-diol in edible oils

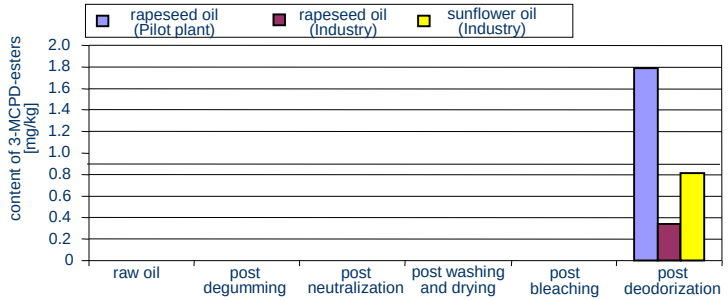
Z. ZELINKOVÁ, B. SVEJKOVSKÁ, J. VELÍŠEK & M. DOLEŽAL

Department of Food Chemistry and Analysis, Institute of Chemical Technology Prague, Technická 1905, 166 28 Prague, Czech Republic

(Received 22 May 2006; revised 21 June 2006; accepted 29 June 2006)

November 2007: Statement of CVUA Stuttgart and Max Rubner-Institut

Formation of 3-MCPD-FE and related compounds during refining and modification of fats and oils: 1–15 **mg/kg**



Statement Nr. 047/2007 des Federal Institut for Risk Assessment vom 11. December 2007

Toxicological importance of 3-MCPD-Esters is not clear → worst-case assumption: 100 % transfer into free 3-MCPD

Toxicological assessment of 3-MCPD

- Carcinogenic in high doses in animal trails with rats
- SCF does not assume genotoxicity
- IARC classifies 3-MCPD as a possible human carcinogen (2B)
- Limit 20 µg/kg for soybean souces und HVP (VO (EG) 1881/2006)
- TDI: 2 µg/kg BW(JECFA, EU, SCF)

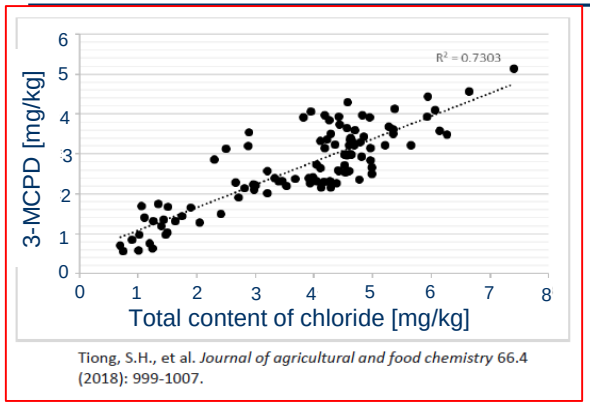
⇨ As low as reasonable achievable ALARA

Säuglingsanfangs- und Folgenahrung kann gesundheitlich bedenkliche 3-MCPD-Fettsäureester enthalten

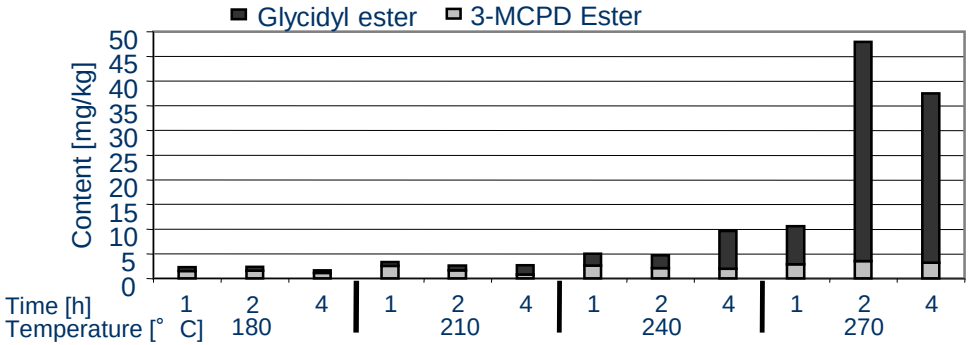
Stellungnahme Nr. 047/2007 des BfR vom 11. Dezember 2007

Need for action to reduce the content of 3-MCPD esters in edible fats and fatty foods

Options for mitigation of 3-MCPD- and glycidyl esters



Tiong, S.H., et al. *Journal of agricultural and food chemistry* 66.4 (2018): 999-1007.



Selection of raw oil with low contents of precursors (e.g. DAG < 4%)

Fast processing of raw material

Avoidance of lipophilic organochlorines

Low lipase varieties

Optimal time of harvest

Raw material

Adjustment of temperature and time during deodorization

Washing the crude oil with water, alcohol, ionic liquid

Bleaching
-neutral BE
- Amount of BE

Short-path distillation

Two-step deodorization

Refining

Enzyms
Adsorbents

Product

- Degumming, neutralization and bleaching reduce the potential of fats and oils to form 3-MCPD and glycidyl esters
- The critical point for the formation of esters is the deodorization step → The lower the temperature during deodorization, the lower the ester content
- With regard to the formation of esters, chemical refining is preferable to physical refining
- Introduction of new refining steps

Challenges in the determination of contaminants in edible oils

- good fat solubility
- similar structure as triacylglycerols
- only contained in very low concentrations

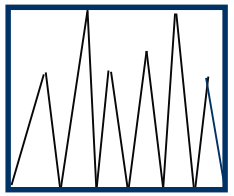
➡ sophisticated analytics

3-MCPD- und glycidylester

direct methods

Matrix removal

SPE+LC-MS^2



7 FS → 105 Analyts

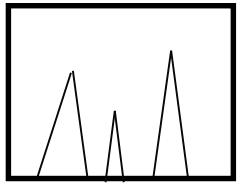
indirect methods

splitting of the esters (alkaline, acidic, enzymatic)

Removal of matrix material

Derivatisation

GC-MS



AOCS Cd 29 a,b,d,e,f-13/19/21
ISO 18363-2 & 4 18363-3
DGF C-VI 17 & 18A (10)

Mineral oils

ISO 20122:2024

Fat oil
EtOH/ hexane

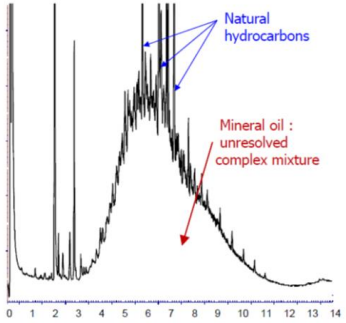
clean up column for impurities

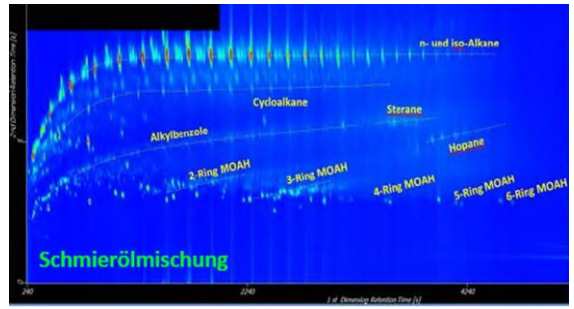
Epoxidation *m*CPBA in EtOH
20 min/ 40 °C

LC-GC

Removal of long chaines n-alkanes
10 g Al_2O_3 + 3 g silica gel

LC-GC





lubricant

Food adulteration - Need for reliable analytics

Problem: most analytical methods

- may be limited in range, sensitivity or reproducibility
- are targeted
- can be levered out by "elaborated" frauds
- are too expensive to be practized on a grand scale

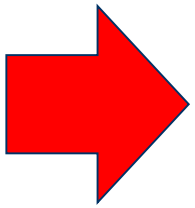
Food fraud hints can find expression in single compounds within the complex mixture, or can be entangled in subtle matrices effects.

The search for (Cost-)effective and reliable analytical methods dealing with both tasks simultaneously is an ongoing story

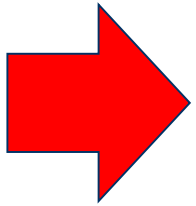
Prerequisite for minor compounds to be good markers

Ideal markers should be

- typical and unique for the oil or fat
- not influenced by other factors
- easily to be determined



- The natural variability of natural occurring minor compounds
- Markers are often influenced not one-dimensional

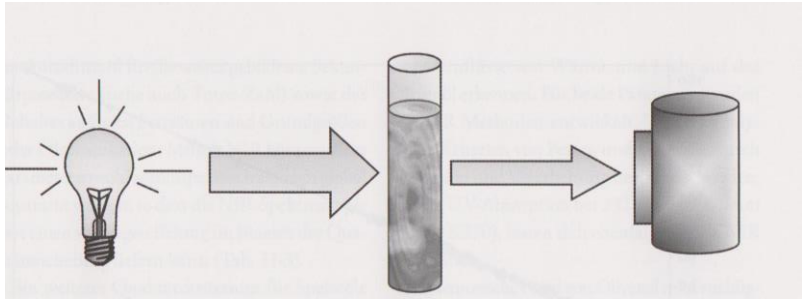


The combination of different parameters with the help of statistical methods allows the network to be tightened to prevent falsification.

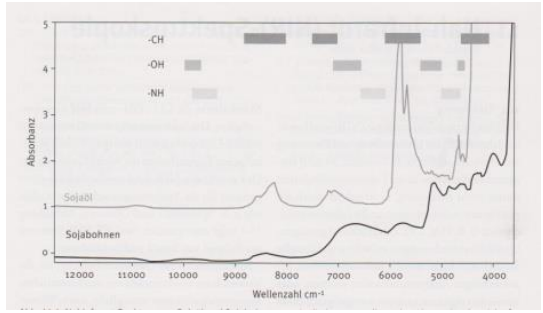
FT-NIR Measurement of oils

Benefit of NIR Spectroscopy

- Very fast analysis method (< 30 s)
- No use of chemicals, solvents or gases
- Untrained staff can carry out analyses
- Operator independent results
- Applicable in the production area



Source of light Sample Detector



Detection of a „Soft-Deodorization“ of virgin olive oil

Problem

- „Soft Deodorization“
- Aim: Removal of undesired aroma components
- Prozess:
  - → Low temperature (< 120° C)
  - → High vacuum (2-5 Torr)
  - → Short time (10-60 min)

Virgin olive oil
With unpleasant aroma

Virgin olive oil extra

FRAUD!

- → stigmastadiene
- → trans-fatty acids
- → polymere triacylglycerols
- → fatty acid alkyl esters
- → pyropheophytin A
- → K270/K232

Individual parameters give no distinct detection of a soft thermal treatment

Cooperation between Maxfry GmbH and Max Rubner-Institut

Detection of a „Soft-Deodorization“ of virgin olive oil

Olive oil samples (n=2188)
for method development

- No heat treatment (EVOO)
- Soft heat- treatment (80 - 110°C, 60-120 min)
- Refined olive oil (ca. 220°C)

NIR measurement
Simultaneous analysis of several parameters

- free fatty acids (FFA)
- K232/K270
- pyropheophytin A (PPP)
- 1,2-Diacylglycerols (DG)
- total polar compounds (TPC)
- iodine value (IV)
- peroxide value (PV)
- monomere oxidized triacylglycerols

Logit Regression
Binary logistical regression model

heat treatment?

yes (1) | no (0)

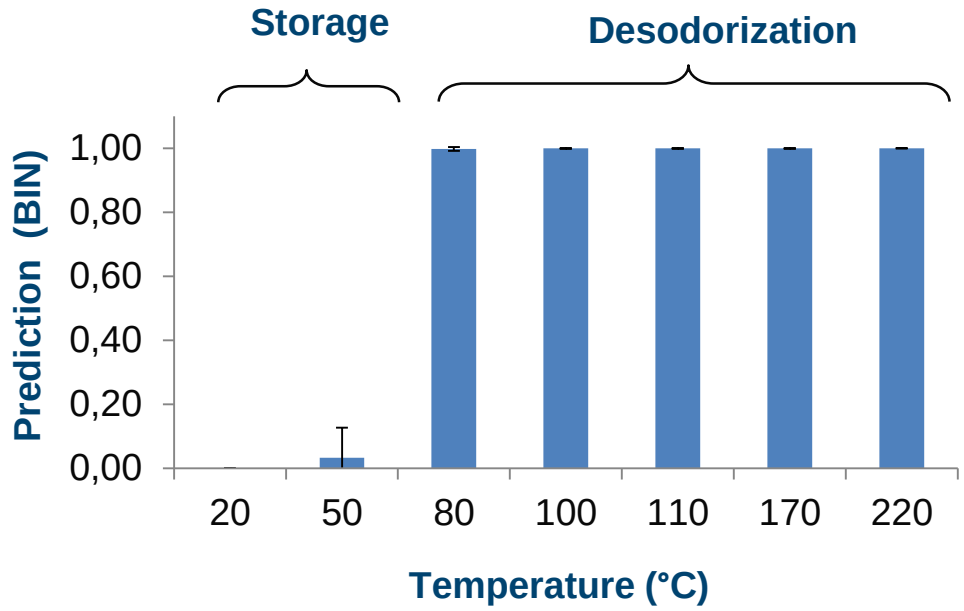
→ Calculation of the probability of a heat treatment

Detection of a „Soft-Deodorization“ of virgin olive oil

Optimized logit model

Used parameters:

- free fatty acids(FFA)
- K232 (> hydroperoxide)
- K270 (> Conjugene fatty acids)
- iodine value (IV)
- anisidine value (AnV)
- Monomere oxidized TG
- total polar compounds (TPC)



Confusion matrix

from\to	0	1	n	correct %
0	2034	10	2044	99.51
1	13	131	144	90.97
Total	2047	141	2188	98.95

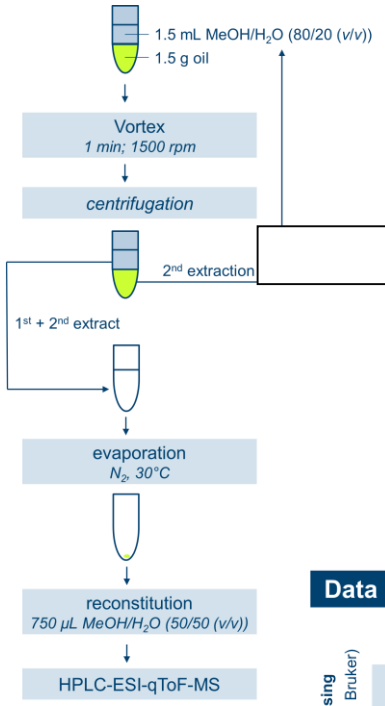
binary Code:

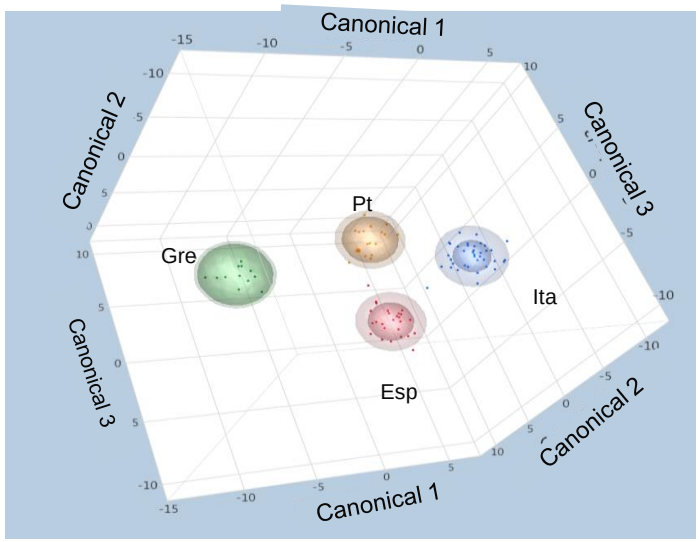
0 → No Fraud

1 → Fraud

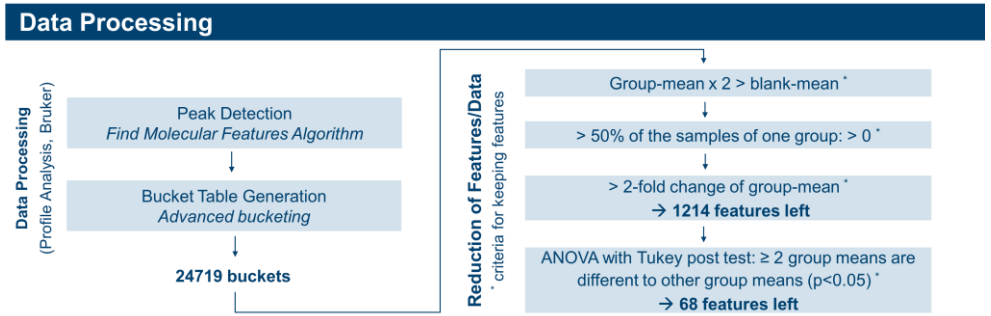
Origin of Olive oil virgin extra by polar compounds

Extraction of polar compounds





Data Processing



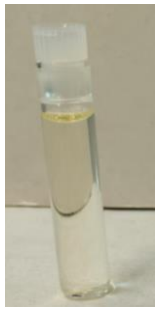
Oil Authenticity of cactus seed oil – A machine learning approach

Cactus seed oil authenticity is crucial and challenging

Background

– A high quantity of seeds is needed, making the oil very expensive (≈600 €/L), which drives adulteration risk.

– Data set is limited due to high analysis effort



Sunflower Oil (SO)
3 €/L

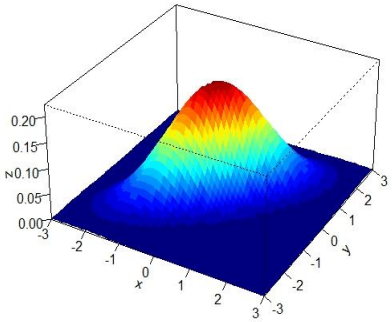
Cactus Oil (CO)
600 €/L

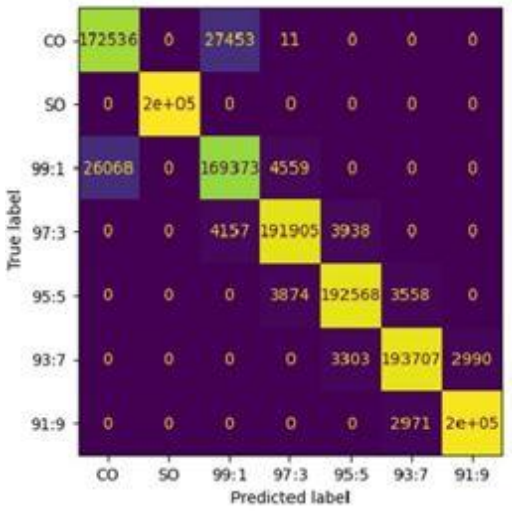
Adulterated Cactus Oil (9%)

Results

– Lab data of 27 Cactus seed oils and 10 sunflower oils

- Monte-Carlo simulation for the underlying probability distribution





– Classification of oils:
  - Random forest (RF)
  -> 90% accuracy
  - Neural networks (NN)
  -> 80% accuracy

– Adulteration of 3% and higher are clearly identifiable
– detection of 1% is possible but associated with higher uncertainty

Summary

- Current contaminants oil are numerous like MOH, 3-MCPD
- There are practical mitigation and minimization strategies

  -> best practices

- Authenticity: fingerprints getting harder to fraud

- Overall analytical challenges remain
- The analytical instrumentation getting more complex, but more user friendly

Thank You for your attention

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