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TP 266

Fast quantification of polychlorinated alkanes in cooking oil by quadrupole Time-Of-Flight Mass Spectrometry

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1. Introduction

- Chlorinated Paraffins (CPs) are industrial chemicals containing persistent organic pollutants (POPs), mainly polychlorinated alkanes (PCAs). CPs have been utilized since World War I, with large-scale production beginning in the U.S. in 1932.[1)]
- PCAs are a product of radical chlorination of n-alkane feedstocks, i.e. extremely complex mixtures of isomers which cannot be separated by liquid chromatography (LC)[2)]
- PCAs are among the most challenging POPs to monitor, mostly due to their poor ionization and the complexity of mixtures containing numerous unresolved isomers.[2)]
- This study addresses these challenges by developing a rapid quantification method for PCAs in cooking oils derived from nuts and seeds, enhancing detection capabilities through advanced ionization techniques forming chloride adducts ($C_xH_zCl_y \rightarrow [C_xH_zCl_y+Cl]^-$) to aid ionization of the PCAs (Fig. 1).

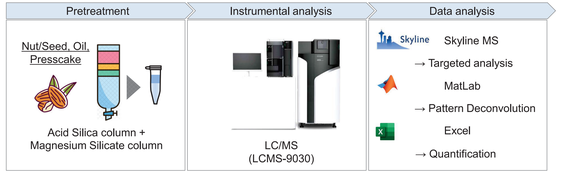

Fig. 1 Workflow of this research

2. Methods

A direct infusion method to quantify PCAs in the range C10-C20 from cooking oil samples using a Shimadzu LCMS-9030 quadrupole time-of-flight mass spectrometer (Q-TOF). A heated Electron Spray Ionization (ESI) probe was utilized with $P(Ph)_4Cl$ as an additive to facilitate the formation of $[M+Cl]^-$ ions.

Oil/Oilseed/Presscake/QC samples were homogenized using an Ultra-Turrax® blender, followed by extraction with dichloromethane/n-hexane (1:1, V/V). An acid silica column was used for matrix removal, followed by further purification on a magnesium silicate column. The 3 QC samples consisted of olive oil, black cumin and coconut oil, all used in and compared to earlier studies.

Two mixtures of PCAs with carbon chain lengths from 10 to 20 carbons (C10-C20) served as quantification standards. One contained only PCAs with 40-50%Cl (low) and the other only PCAs of 50-60%Cl (high).

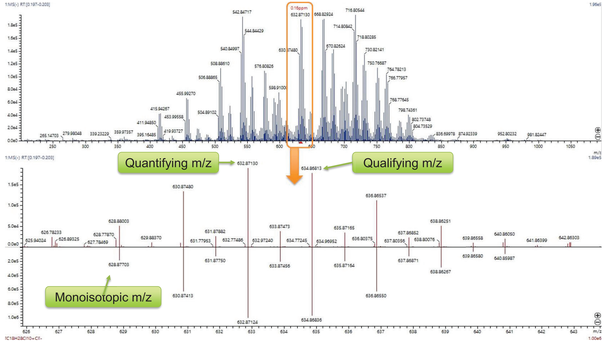

Fig. 2 Comparison theoretical vs measured isotopic distribution of $C_{18}H_{28}Cl_{10}$

The theoretically most abundant isotope per PCA homologue group is used as quantifying ion, the second most abundant isotope is used as qualifying ion and the ratio between them is used for scoring of matches. An example of theoretical pattern for $C_{18}H_{28}Cl_{10}$ compared to measured pattern can be seen in Fig. 2

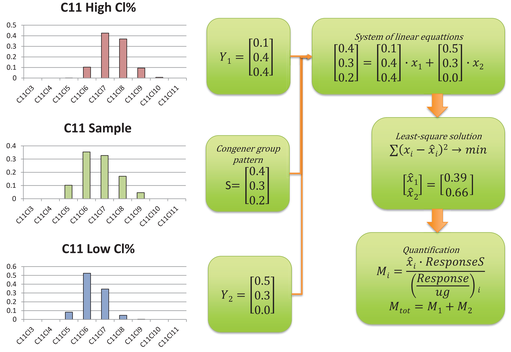

Fig. 3 Pattern deconvolution and quantification procedure

Quantification followed a procedure similar to Bogdal et al.[3)]: PCA patterns of the samples were deconvoluted into a linear combination of PCA patterns of quantification standard mixtures using a mathematical algorithm to obtain weighted results from quantification. An example is shown in Fig. 3.

3. Results

- Short chain PCAs (C_{10}-C_{13}) were found in all 5 oil samples, 4 out of 5 nut/seed samples and all 5 presscake samples. The average contributions of the homologue groups of decanes, undecanes, dodecanes and tridecanes were 40%, 3%, 9%, 48% respectively (Fig. 4)
- Medium chain PCAs (C_{14}-C_{17}) were found in all samples. The average contributions of the homologue groups of tetradecanes, pentadecanes, hexadecanes and heptadecanes were 53%, 19%, 21%, 6% respectively (Fig. 4)
- Long chain PCAs (C_{18}-C_{20}) were found in 2 out of 5 oil samples, 3 out of 5 nut/seed and all 5 presscake samples. The average contributions of the homologue groups of octadecanes, nonadecanes, and eicosanes were 20%, 43%, 36% respectively (Fig. 4)

Fig. 4 PCA levels per oil/seed/presscake and average contribution by chain length per combined seed, oil and presscake

A simple indicator of directionality can be seen in Fig. 5, showing that there is no significant enrichment or depletion of PCA levels in the oils during the pressing process. As rule of thumb, a value smaller than ±0.3 can be considered an insignificant change in concentration and a value larger than ±0.3 might indicate enrichment (+) or depletion (-).

Even though the value for MC-PCAs in Apricot is slightly larger than ±0.3 (-0.31), it's not likely to indicate a significant enrichment since there is no clear trend over PCA-groups or over samples pointing towards enrichment which should be expected since all seeds are processed in the same mill.

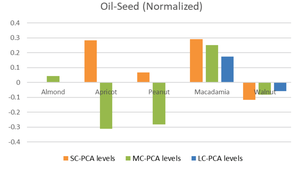

Fig. 5 Relative Enrichment of PCAs after oil pressing across seed types

4. Conclusion

- Preliminary results indicate that concentrations of PCAs in the C_{10}-C_{20} range are accurately quantified with high sensitivity using the developed method
- The use of P(Ph)4Cl as an ionization enhancer results in enhanced signal intensity for PCAs, facilitating the detection of low concentration levels
- The results show that PCAs can be found in various cooking oils
- Walnut and macadamia oil contain higher levels of total PCAs, especially LC-PCAs, whether this is due to higher fat content or these being the only true nuts included in this study is not clear
- This method presents a promising approach for routine monitoring of PCAs in food-related matrices, contributing valuable data for environmental and health assessments

Reference

1) The Handbook of Environmental Chemistry, (1980) Vol. 3, p. 149-156, Zitko *et al.*
2) The Handbook of Environmental Chemistry, (2010) Vol. 10, p. 84-86, Boer *et al.*
3) Anal. Chem. (2015) 87, 5, 2852–2860, Bogdal *et al.*

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Jonatan Nygren, Jakob Hauns, Franz Hansert, Sicco Brandsma, Pim Leonards, Jeroen Kool and Alexander Schächtele declare no competing financial interest.

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