Rapid Analytical Methodology for Bio-monitoring of Cooking Oil Fume's based VOCs in Lung Tissue Samples using micro-QuEChERS method coupled with UHPLC-MS/MS technique

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Abstract

Cooking methods (deep-frying and pan-frying) release carcinogens like PAHs, aldehydes, ketones, and alcohols by oxidizing fatty acids from cooking oils. Among which aldehydes like 4-hydroxy-hexenal (4-HHE), 4-hydroxy-nonenal (4-HNE) and trans,trans-2,4-decadienal (tt-DDE) are most commonly emitted Volatile Organic Compounds (VOCs) from Cooking oil fumes (COFs) and its exposure is directly associated with lung adenocarcinoma cells in humans leading to lung cancer. In this study, we developed a novel analytical method for determination of VOCs in rat lung tissue using a micro-QuEChERS technique combined with Ultra high-performance liquid chromatography/ tandem mass spectrometry (UHPLC-MS/MS). Three toxic VOCs were chosen as target analytes and determined by UHPLC-MS/MS with positive ion mode electrospray ionization and multiple reaction monitoring (MRM). Separation of target analyzes was carried out using Atlantis T3 C18 (2.1×150 mm) column with 0.1% FA in water and acetonitrile as mobile phase solvents and the column flow rate of 0.30 mL/min. The reasonable limit of detection and quantification values at sub ppb levels were measured by the method. The linear coefficients were found to be greater than 0.99 for all VOCs. The extraction recoveries were ranged from 85~110%. This presented method is proven to be a simple, highly selective, efficient, and sensitive analytical method that can be applied for biomonitoring of VOCs and determine the in-door COFs exposure levels in humans to predict the health risks.

Keywords: Volatile Organic Compounds, Cooking Oil Fumes, Lung tissue, Micro-QuEChERS, UHPLC–MS/MS

Highlights

- Rapid analytical procedure for biomonitoring and analysis of VOCs in lung tissue samples
- An improved Micro-QuEChERS technique combined with UHPLC–MS/MS
- The matrix effect is negligible with higher extraction recoveries were achieved
- Method is simple, fast, sensitive, eco-friendly and efficient

1. Introduction

Cooking oil fumes (COFs) are important volatile organic compounds (VOCs) sources of indoor air, which are released into the room air as lipid peroxidation products during cooking methods (deep-frying and pan-frying). Cooking oils are rich in saturated and polysaturated fatty acids which undergoes chemical change when heated at higher temperatures. Figure 1 shows the mechanism of polysaturated fatty acids from cooking oils undergoing lipid peroxidation to form toxic aldehydes. The oxidative radicals generated in the water-oil system facilitate oxidation of fatty acids producing carcinogenic aldehydes like trans, trans-2,4-decadienal (tt-DDE), 4-hydroxy-hexenal (4-HHE), and 4-hydroxy-nonenal (4-HNE). Therefore, it is essential to measure toxic VOCs levels in people exposed to long-term cooking conditions to predict the health risk assessment.

Pathways involved in formation of aldehydes from cooking oil

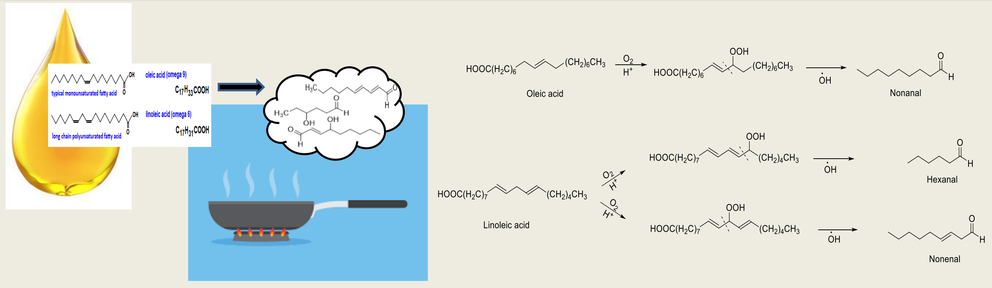

Fig 1: Mechanism of polysaturated fatty acids from cooking oils undergoing lipid peroxidation to form toxic aldehydes

1.1 Aim of the Study

To quantify three major toxic VOCs (tt-DDE, 4-HHE, and 4-HNE) in rat lung tissue samples using a novel micro-QuEChERS technique combined with UHPLC-MS/MS for bio monitoring and toxicology studies

2. Experimental

2.1.List of chemicals structure and their properties

Chemical	Formula	MW	BP (°C)	Structure
trans,trans-2,4-Decadienal	$C_{10}H_{16}O$	152.23	280	
4-Hydroxyhexenal	$C_6H_{10}O_2$	114.1	233.5±23.0	
4-Hydroxynonenal	$C_9H_{16}O_2$	156.2	275.6±23.0	

Table 1: Structures and Chemical properties of VOCs

2.2. Sample preparation procedure

100 mg lung tissue was homogenized using liquid N_2 and was grind thoroughly to powder

↓

1 mL ACN and 500 mg NaCl +200 mg $MgSO_4$ were added and tube was vortexed (3 min)

↓

Transfer extractant to solid-phase extraction (SPE)cartridge tube filled with PSA+C18+ $MgSO_4$ and vortex 3 minutes

↓

Finally the sample solution was taken into vial for UHPLC-MS/MS analysis

2.3. Instrument conditions

Ultra High performance liquid chromatography (UHPLC)	
Model	Shimadzu Nexera -i
Column	Atlantis T3 C18 (3µm, 250 x 2.1 mm
Column Temp.	40°C
injection volume	10 µL
column flow rate	0.3 mL/min
Mobile phase	Eluent A : 0.1% FA in water Eluent B : ACN
Total Run Time	10 Minutes
Tandem mass spectrometry(MS/MS)	
Model	LCMS-8045
ESI	Positive mode
Interface temperature	250°C
DL line temperature	300°
Heat block temperature	350°C

Analyte	Ion mode	Mol wt.	Precussor m/z	Product m/z	Q1 Pre Bias (V)	CE	Q3 Pre Bias (V)
4-HHE	Positive	114.0	115.1	69	-36	-32	-30
			115.1	97	-38	-21	-19
4-HNE	Positive	156.1	157	69.0	-16	-30	-27
			157	83.1	-17	-21	-25
tt-DDE	Positive	152.33	153.3	251.1	-24	-19	-28
			153.3	83.1	-12	-14	-18
4-HHE-D3	Positive	117	118	95	-18	-37	-21
			118	100	-19	-39	-28
4-HNE-D3	Positive	159.2	160.2	83.2	-30	-50	-23
			160.2	142.1	-28	-25	-28

Table 2:Optimized Instrument Conditions for VOCs

3. Results and Discussion

Parameters affecting the extraction efficiency including type of solvent volume and effect of salt addition, clean-up sorbents and extraction time are systematically studied. The method showed good between 10 to 1000 $ngmL^{-1}$ with linear coefficients greater than 0.99 with limit of quantification as 10 $ngmL^{-1}$ for all the analytes. Table 3 shows the analytical performance of VOCs

No	Name	Calibration Curve (ng/mL)	Linear Equation	R^2	LLOQ (ng/mL)
1	**4-HHE**	10-1000	y = 0.0014x + 0.0383	**0.9981**	10
2	**4-HNE**	10-1000	y = 0.002x + 0.065	**0.9949**	10
3	**tt-DDE**	10-1000	y = 0.0061x + 0.0827	**0.9924**	10

Table 3: Analytical method performance of VOCs

UHPLC/ESI-MS/MS chromatogram of VOCs by this method

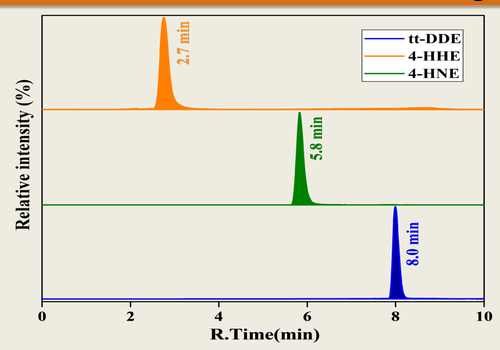

Fig 2: LC-MS/MS Chromatogram obtained from Spiked (100 $ngmL^{-1}$)- rat lung tissue, by the developed method.

4. Conclusion

A novel micro-QuEChERS based UHPLC-MS/MS method for the quantification of VOCs in rat lung tissue was reported. This process is simple, fast, low-cost, low-organic solvent consumption, and eco-friendly nature. The analytical method validation studies indicated that the developed technique achieved good extraction recoveries, showed good linearity, higher sensitivity, and selectivity with minimal matrix effect compared to previously reported methods. Therefore, experimental results indicate that the presented method can be used for biomonitoring of VOCs in lung tissue to predict the human health risks.

References

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