Supplementary information file for

Dendrimer grafted nanoporous silica fiber for headspace solid-phase micro-extraction coupled to gas chromatography determination of solvents residues in edible oil

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Abstract

A recently prepared nanoporous G (1)-Dendrimer supported Santa Barbara Amorphous-15 (SBA-15) solid phase micro-extraction (SPME) fiber was successfully applied to the headspace solid-phase micro extraction of solvent residues such as hexane, benzene and toluene in edible vegetable oils followed by gas chromatography flame ionization detection (GC-FID). Experimental conditions such as extraction time and temperature, and GC parameters were optimized. In the optimized conditions, linear calibration curves were obtained in the ranges of 6 – 300 for hexane, and 8 - 250 mg kg^{-1} for both benzene and toluene. The detection limit was the concentration of the analyte having signal 3 times that of the noise and was in the range of 0.90-1.2 mg kg^{-1} for the three mentioned solvents. The relative standard deviations (RSD) for hexane, benzene and toluene at optimum conditions were 9.50, 6.70, and 7.30% for a certain fiber (repeatability, n=6) and 12.1, 9.30, and 14.90% between fibers (reproducibility, n=6), respectively. The method was successfully applied to the extraction and determination of the above-mentioned solvents in ten different vegetable oils collected from local markets. The results were in good agreement with those obtained by the commercial fibers.

Table 1S lists the maximum residual limit (MRL) for hexane in vegetable fat and oils. Information on the maximum concentration of hexane, benzene, and toluene that threaten the human life is also presented. MRL for hexane is reported from two source, European and Canadian health services. Canadian health introduce 10 mg kg^{-1} as the maximum residual limit. This indicates that our method quantify hexane in vegetable oils as well.

Table1S. Benzene, toluene and hexane level that threatens human health

Solvent	MRL in oil (mg Kg^{-1})	Concentration Limit (mg Kg^{-1})	Concern
Hexane	5[a]	290	toxic
	10[b]		
Toluene	NA	890	toxic
Benzene	NA	2	carcinogen

MRL stands for maximum residual limit; NA stands for not assigned for edible oils.[a] European standard and [b] reported by health service of Canada

Microscopic image of the fiber in Fig. 1S indicates that diameter of the coating for as prepared fiber is about 50 μm. Fig. 2S schematically present the whole procedure in the head space analysis of the three tested solvents residue in edible oil samples. The present head space GC/FID analysis of hexane, benzene, and toluene residue in edible vegetable oils was compared with previously reported head space methods from different point of view. As it is observed in Table 2S, present method is faster that other reported head space methods.

One of the method of accuracy evaluation is comparing the data obtained for a pair samples by newly introduced method and a reference or accepted one. Fig. 3S graphically shows the concentration of three tested solvents obtained by both PDMS/DVB and SBA-G (1) fibers for three randomly selected spiked vegetable oil samples (for more detail see main manuscript).

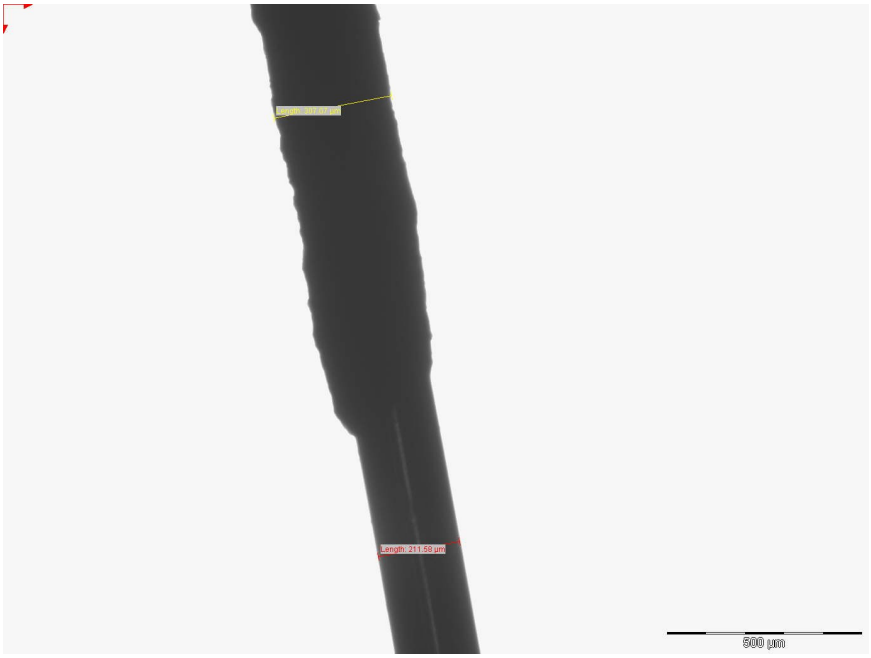

Fig. 1S microscopic image of as prepared fiber

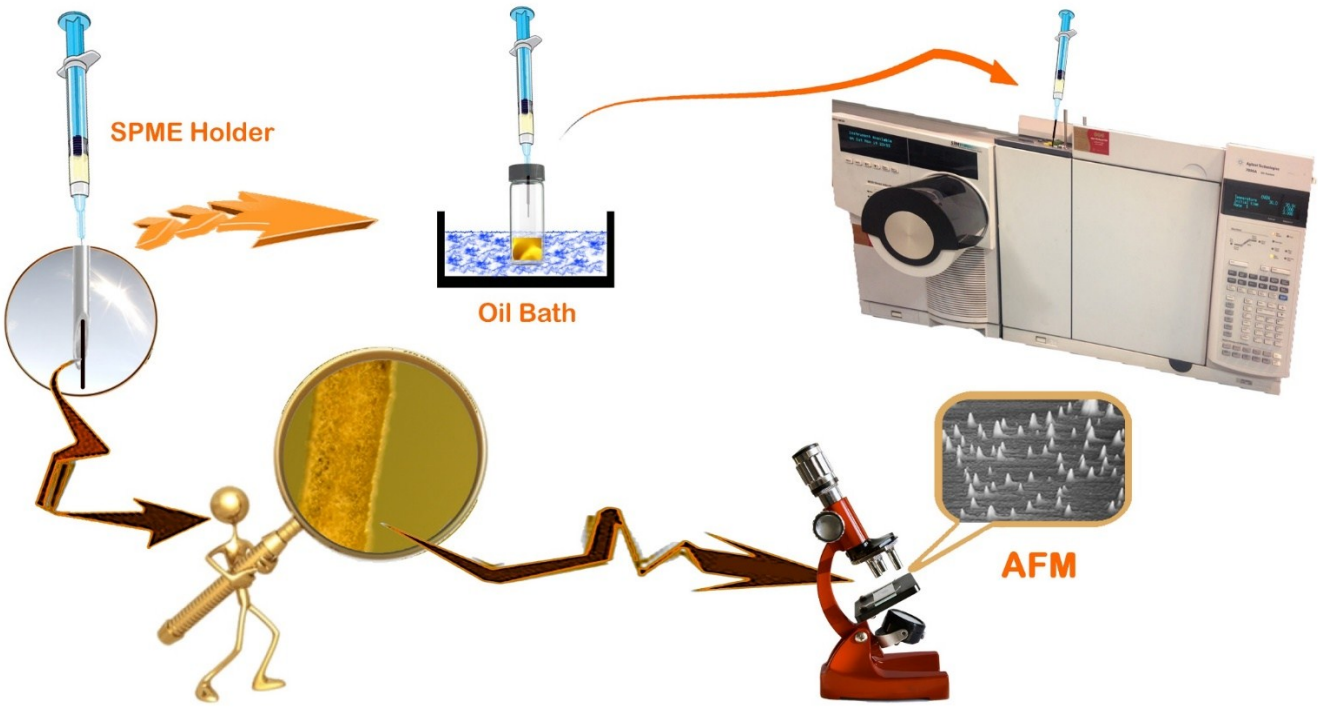

Fig. 2S Schematic representation of the system set up used in separation, pre-concentration and determination of solvent residues in edible oil.

Table 2S. The results obtained for the analysis of different edible oil obtained by the proposed method, before and after addition of 12 mg kg^{-1} hexane and 16mg kg^{-1} benzene and toluene under the optimized conditions

Sample Code	Before the addition (mg kg^{-1})		After the addition	Recovery (%)
NO.1 (semi-solid oil)	Hexane	6.46 (0.88)[a]	20.22 (1.60)	109.53
	Benzene	9.00 (0.87)	26.86 (0.70)	107.44
	Toluene	N.D[b]	18.76 (0.77)	117.25
NO.2 (frying liquid oil)	Hexane	N.D	10.89(1.42)	90.75
	Benzene	N.D	15.01 (0.87)	93.81
	Toluene	N.D	15.75 (1.07)	98.43
NO.3 (frying liquid oil)	Hexane	8.42 (0.60)	22.43 (3.65)	109.84
	Benzene	N.D	17.42 (1.22)	108.87
	Toluene	N.D	17.53 (1.12)	109.56
NO.5 (cooking liquid oil)	Hexane	N.D	10.20 (1.02)	85.00
	Benzene	N.D	14.70 (1.50)	91.87
	Toluene	N.D	15.10 (0.87)	94.37
NO.5 (cooking liquid oil)	Hexane	12.47 (3.26)	26.07 (2.97)	106.54
	Benzene	N.D	17.04 (1.52)	106.50
	Toluene	N.D	16.73 (1.28)	104.56
NO.6 (frying liquid oil)	Hexane	11.10 (2.29)	25.01 (3.02)	108.27
	Benzene	N.D	17.23 (0.80)	107.69
	Toluene	N.D	17.05 (0.79)	106.56
No.7 (frying liquid oil)	Hexane	N.D	14.24 (1.47)	118.66
	Benzene	N.D	16.99 (1.21)	106.19
	Toluene	N.D	16.35(0.75)	102.18
No.8 (cooking liquid oil)	Hexane	N.D	10.70(0.96)	89.17
	Benzene	N.D	15.40(0.97)	96.25
	Toluene	N.D	14.20(1.08)	88.75
No.9 (semi-solid oil)	Hexane	9.00	19.3(1.36)	91.90
	Benzene	N.D	15.46(1.10)	96.62
	Toluene	N.D	16.75(0.84)	104.68
No.10 (semi-solid oil)	Hexane	10	24.1(1.96)	109.54
	Benzene	N.D	16.8(1.18)	105.00
	Toluene	N.D	15.84(0.97)	99.00

[a]The figures within parentheses are standard deviations of three replicates.
[b]N.D. stands for not detected

Area ratio to show the optimum value for time and temperature is listed in Table 3S. In this table initial peak area are divided by the peak area at any different time or temperature. Therefore, this ratio becomes lower as the difference between the two signals increases.

Table 3S Area ratio for some points reported in Fig. 2 (See the main manuscript)

Compound	Bp (° C)	Time(A_i/A_5)	(A_i/A_6)	(A_i/A_7)	(A_i/A_8)	(A_i/A_{10})	T(A_i/A_{70})	T(A_i/A_{80})	T(A_i/A_{100})
Hexane	**69**	0.767582	0.774116	0.779346	0.78458	0.804427	0.255284	0.260978	0.260978
Benzene	**80**	0.458571	0.434041	0.424172	0.439553	0.447459	0.434041	0.433813	0.472444
Toluene	**110**	0.554899	0.539656	0.515966	0.510801	0.554899	0.643774	0.510801	0.567024

T and Bp stand for temperature and boiling point, respectively.

Reference

Health Canada (www.hc-sc.gc.ca), Food and Nutrition, List of permitted carrier and extraction solvents (list of permitted food additives) date issued: 2016-06-29