A novel sample preparation procedures for assessement of canola oil quality

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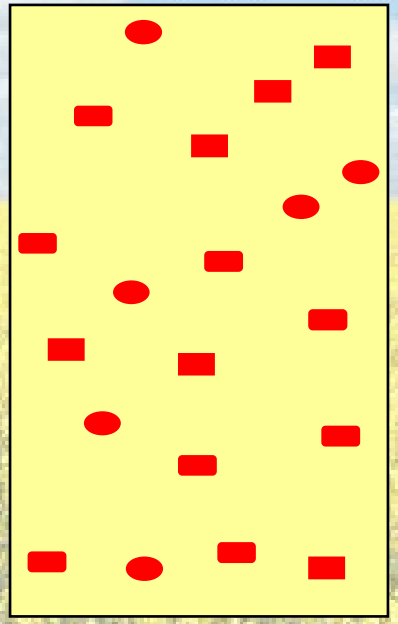
Canola oil quality

solvents residue

- hexane
- benzene
- toluene



oxidation products

- hexanal
- nonanal
- 2-t-nonenal

simplicity

rapidity

precision

procedure

LOD, LOQ

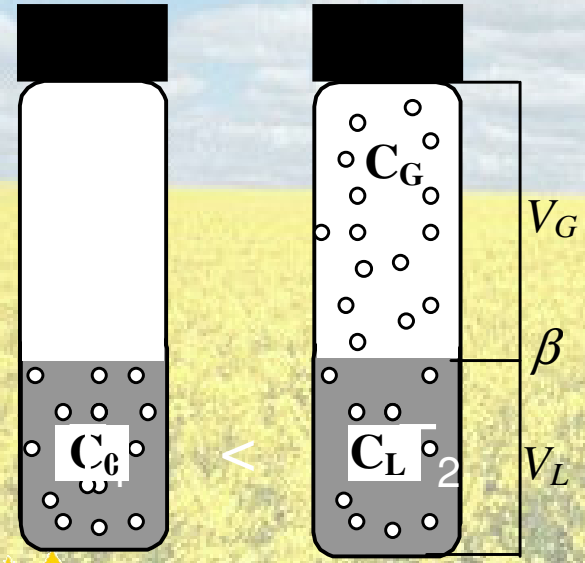
accuracy

low cost

Used techniques

HEADSPACE ANALYSIS

HSA

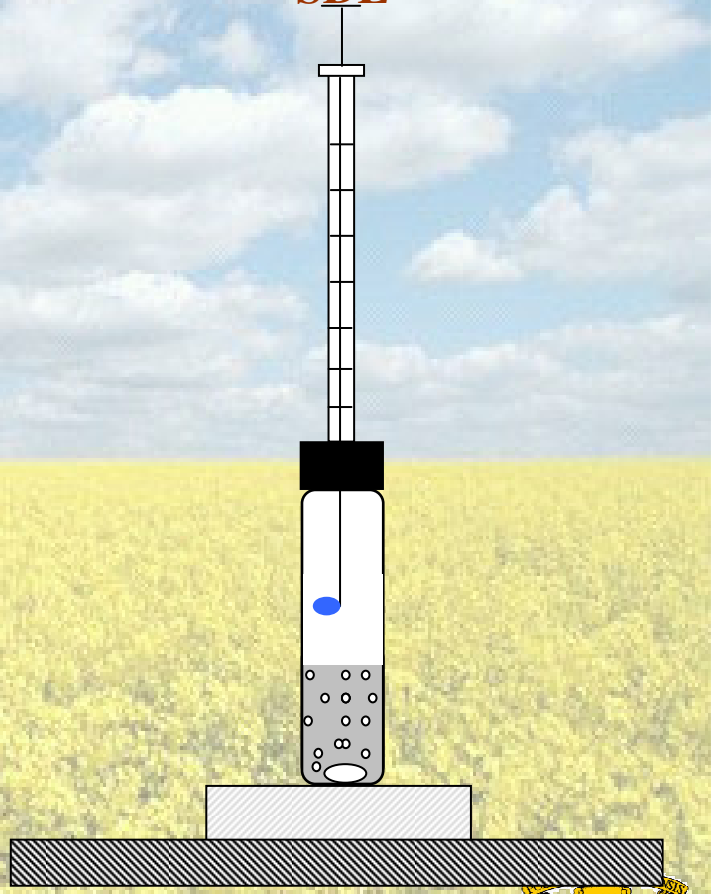


SOLID PHASE MICROEXTRACTION

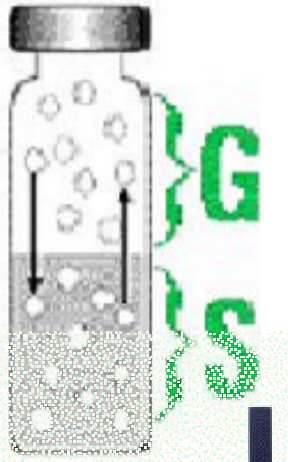
SPME

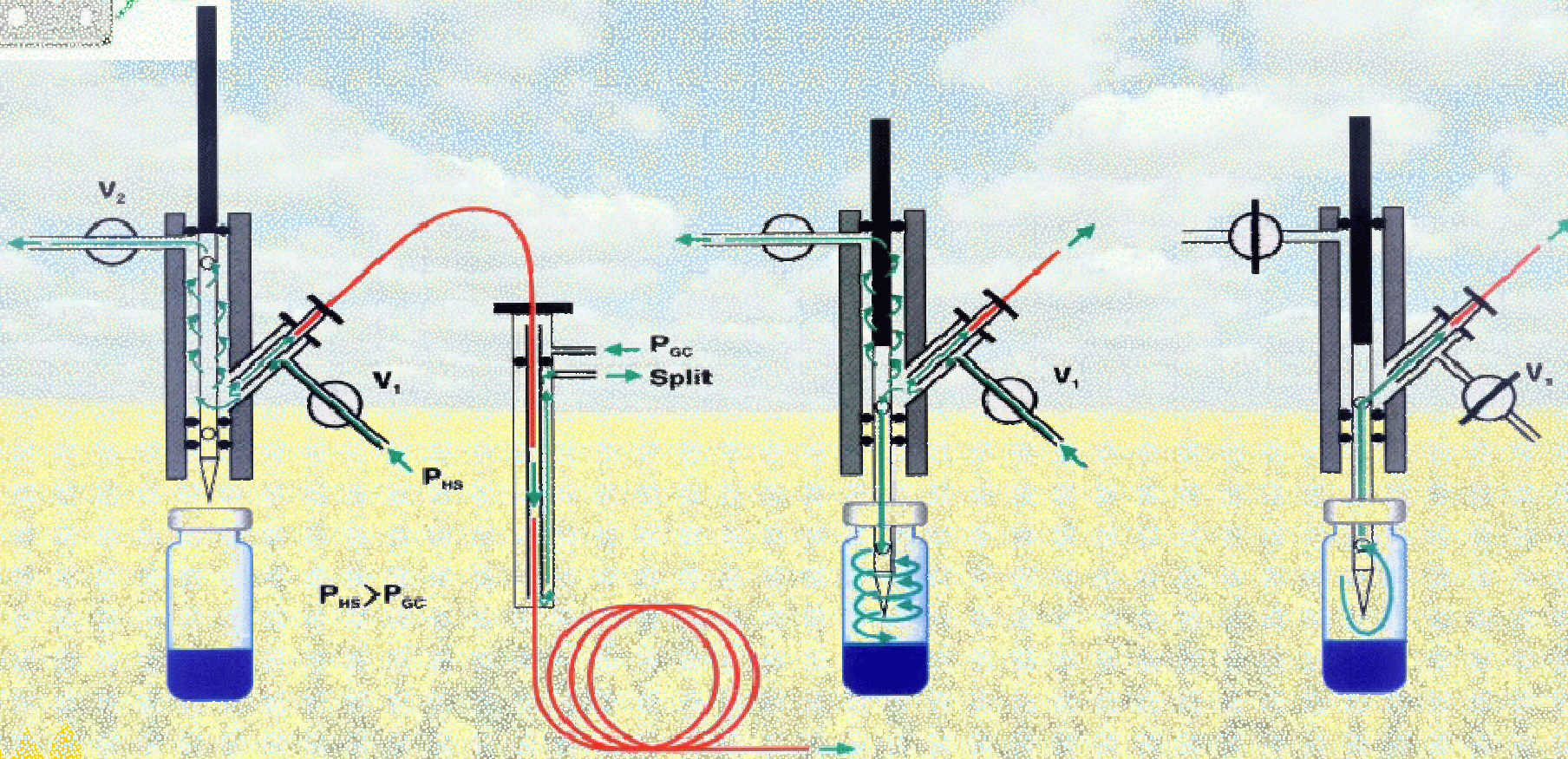
SINGLE DROP EXTRACTION

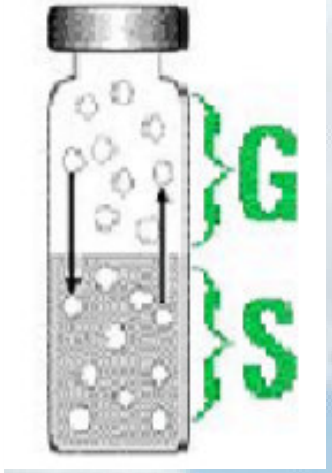
SDE



Headspace analysis (HSA)







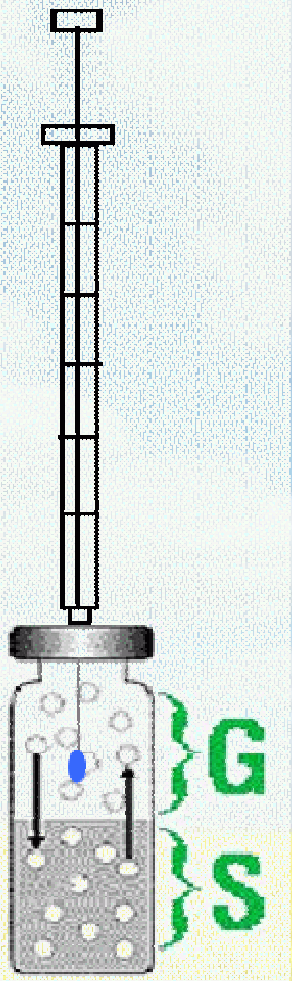
Headspace analysis (HSA)

- selective - NO
- sensitive - NO
- expensive - YES/NO
- automated - YES
- simple - YES
- fast - YES/NO
- labour-consuming - NO
- proecological - YES

Headspace solid phase microextraction (SPME)

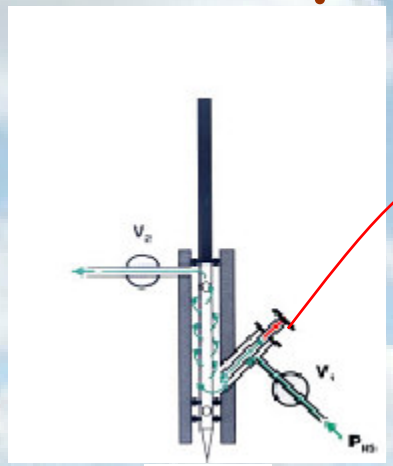
- selective – YES
- sensitive – YES
- expensive – YES/NO
- automated – YES
- simple – YES
- fast – YES/NO
- labour-consuming – NO
- proecological - YES

Single drop extraction (SDE)



- selective – YES
- sensitive – YES/NO
- expensive – NO
- automated – YES
- simple – YES
- fast – YES/NO
- labour-consuming – NO
- proecological - YES

Scheme of HSA-GC procedure



sample

thermostat

GC

RESULTS

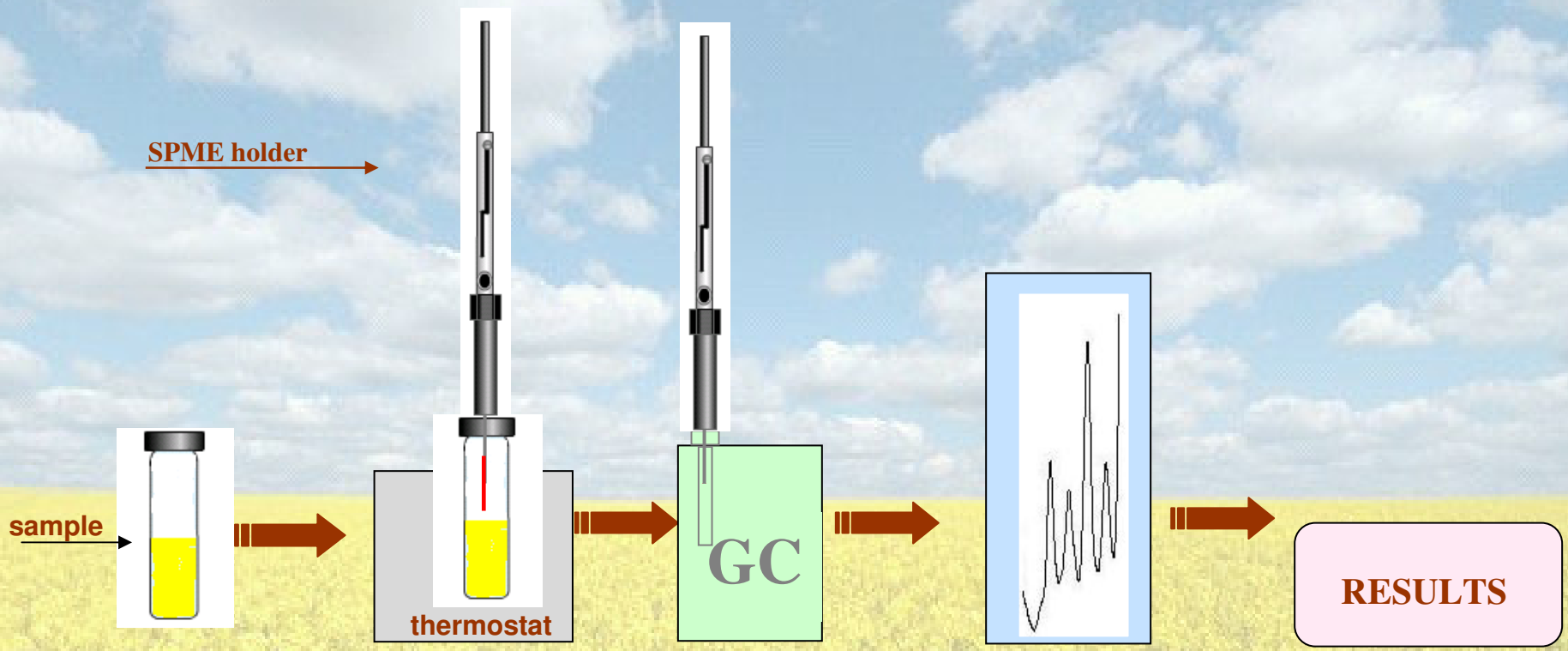
sample preparation

extraction

injection
separation
detection

data interpretation

Scheme of HS-SPME-GC procedure



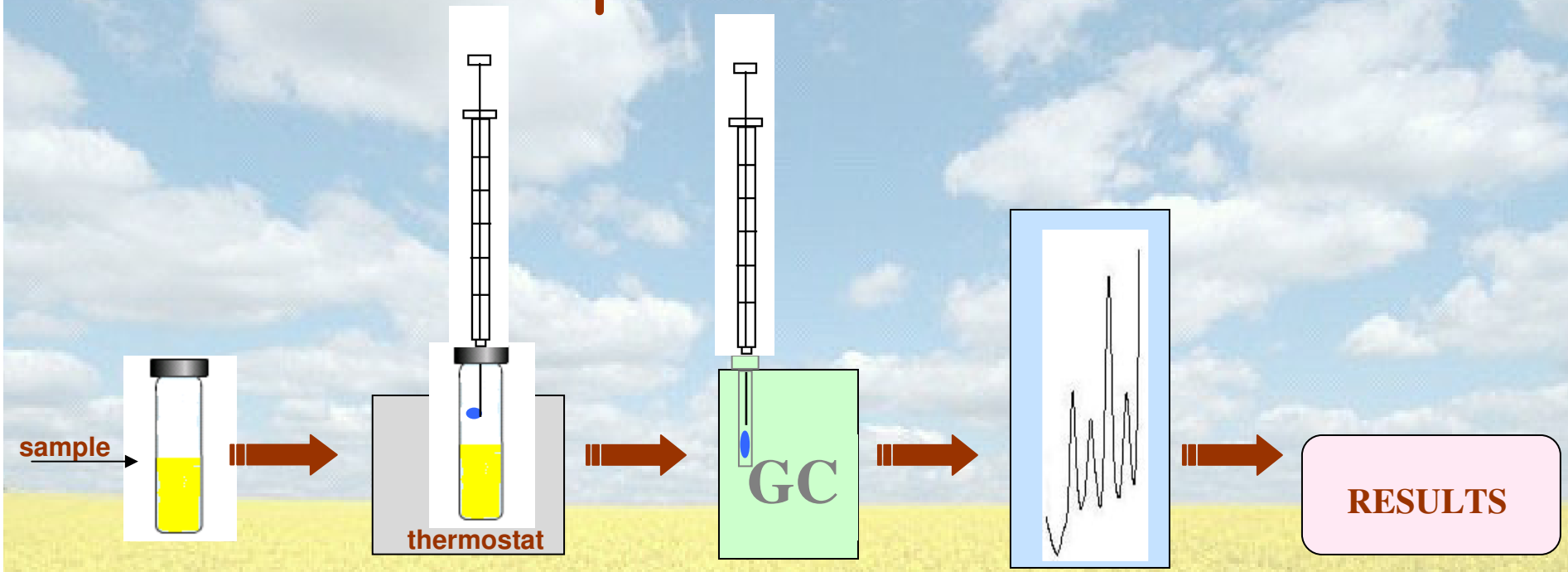
sample preparation

extraction

thermal desorption separation, detection

data interpretation

Scheme of HS-SDE-GC procedure



sample preparation

extraction

injection, separation, detection

data interpretation

Optimization

HSA	SPME	SDE
• temperature • time • sample volume • injection volume	• temperature • time • sample volume • type of fibre • temperature of desorption	• temperature • time • sample volume • solvent • drop volume

Validation

Definition:

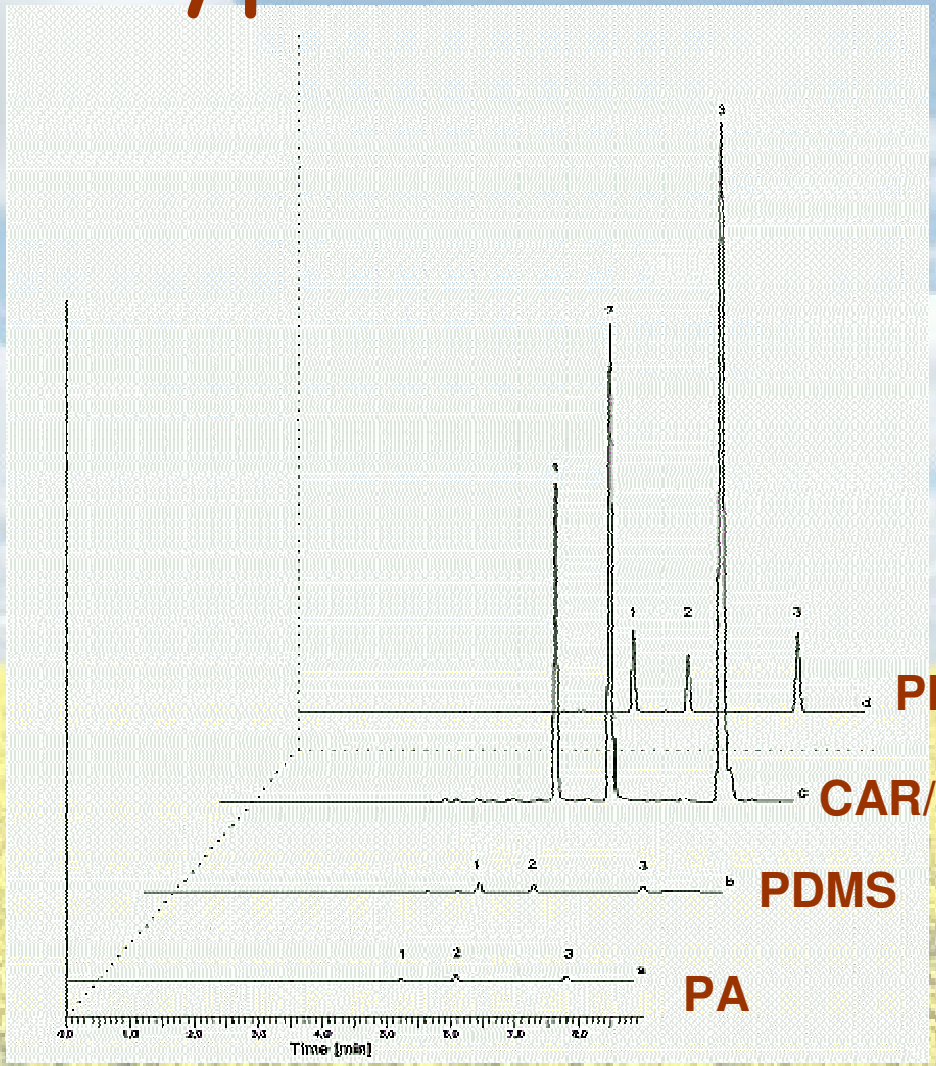
Validation is the confirmation by examination and provision of objective evidence that the particular requirements for specific intended use are fulfilled.

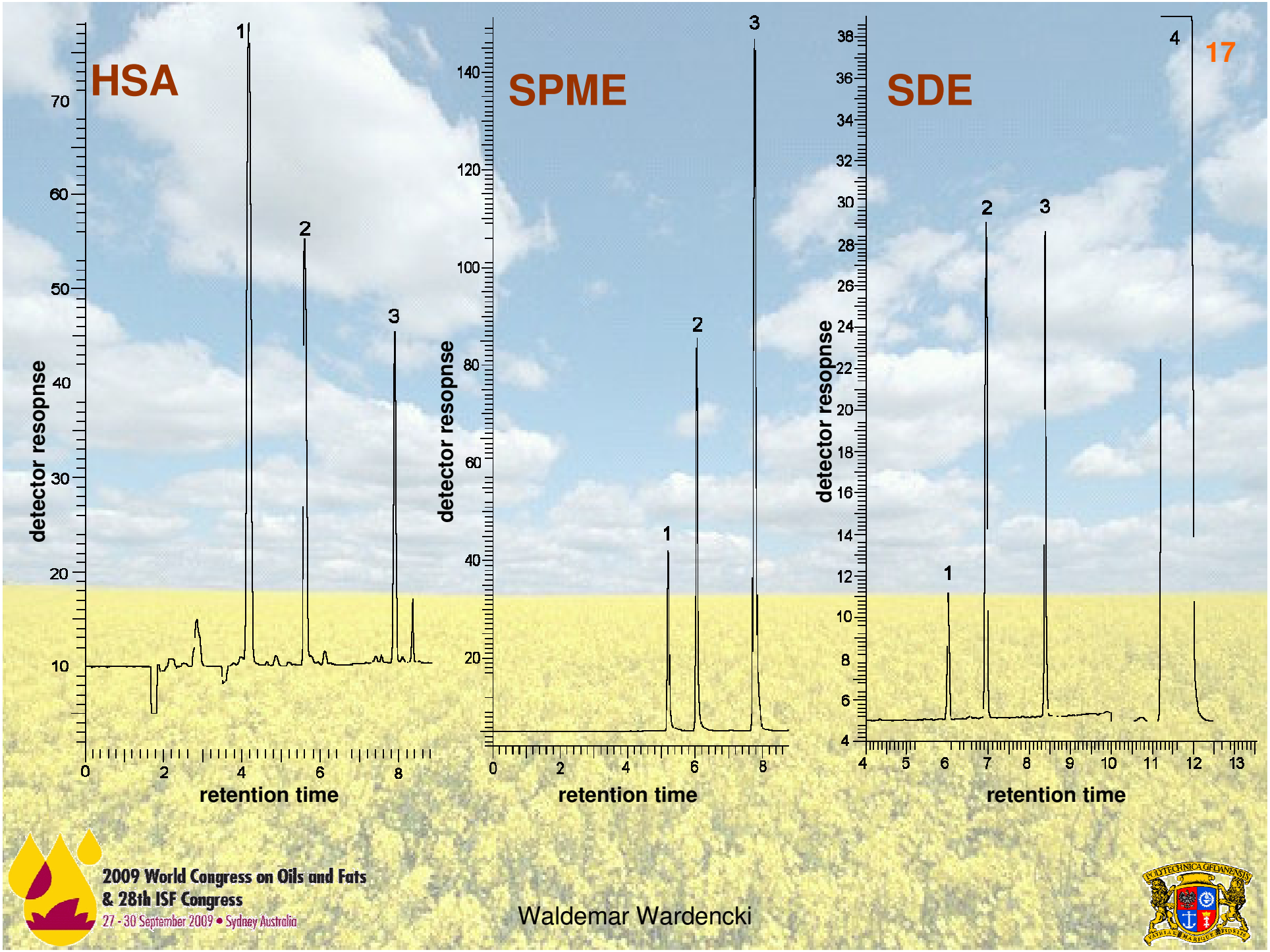
Validation procedure

- **LOD** – the limit of detection is the lowest amount of an analyte in a sample which can be detected but not necessarily quantified as an exact value.
- **LOQ** – limit of quantification is the lowest amount of an analyte in a sample which can be determined as an exact value.
- **RANGE** – the interval between the upper and lower concentration of analyte in the sample for which it has been demonstrated that the analytical procedure has a suitable level of precision, accuracy and linearity.
- **LINEARITY** – linearity refers to the fidelity of an output signal with respect to its input signal. In a linear relationship, output is directly proportional to input.
- **PRECISION** – the closeness of agreement between independent test results obtained under stimulated conditions. Can be measured in terms of the standard deviation of the measurement system.

Solvents residues

Type of fibre



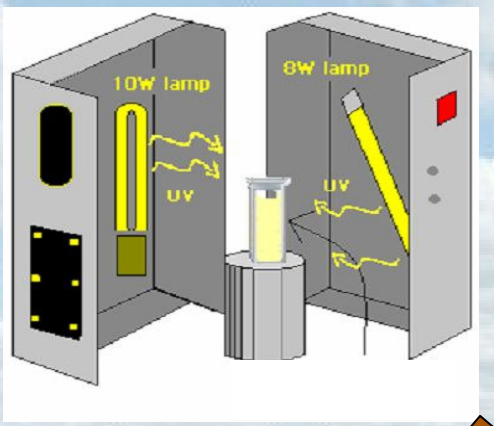

HSA
SPME
SDE
detector resopnse
retention time
1
2
3
4

Comparisone of validation parameters

Validation parame-ters	HSA			SPME			SDE		
	LOD [µg /kg]	LOQ [µg /kg]	Repeat ability [%]	LOD [µg /kg]	LOQ [µg/ kg]	Repeat ability [%]	LOD [µg/ kg]	LOQ [µg/ kg]	Repeat ability [%]
hexane	3.4	10	2.5	0.64	1.9	4.7	300	900	2.5
benzene	4.3	13	3.6	0.41	1.2	3.6	370	1100	2.0
toluene	30	90	5.2	0.10	0.30	5.1	110	330	1.2

Oxidation markers

Methods

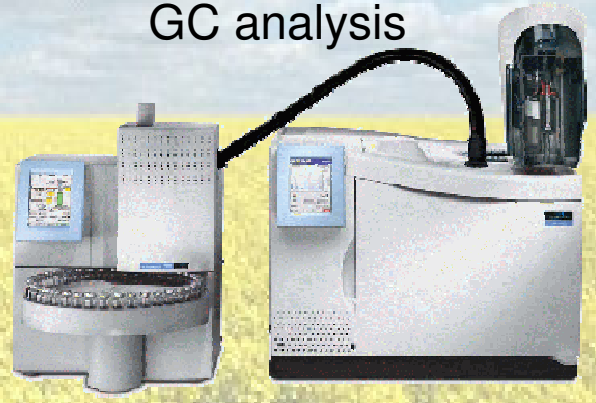


Oxidation acceleration

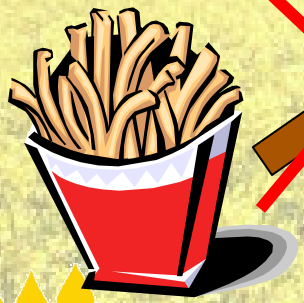
Sample preparation

SPME

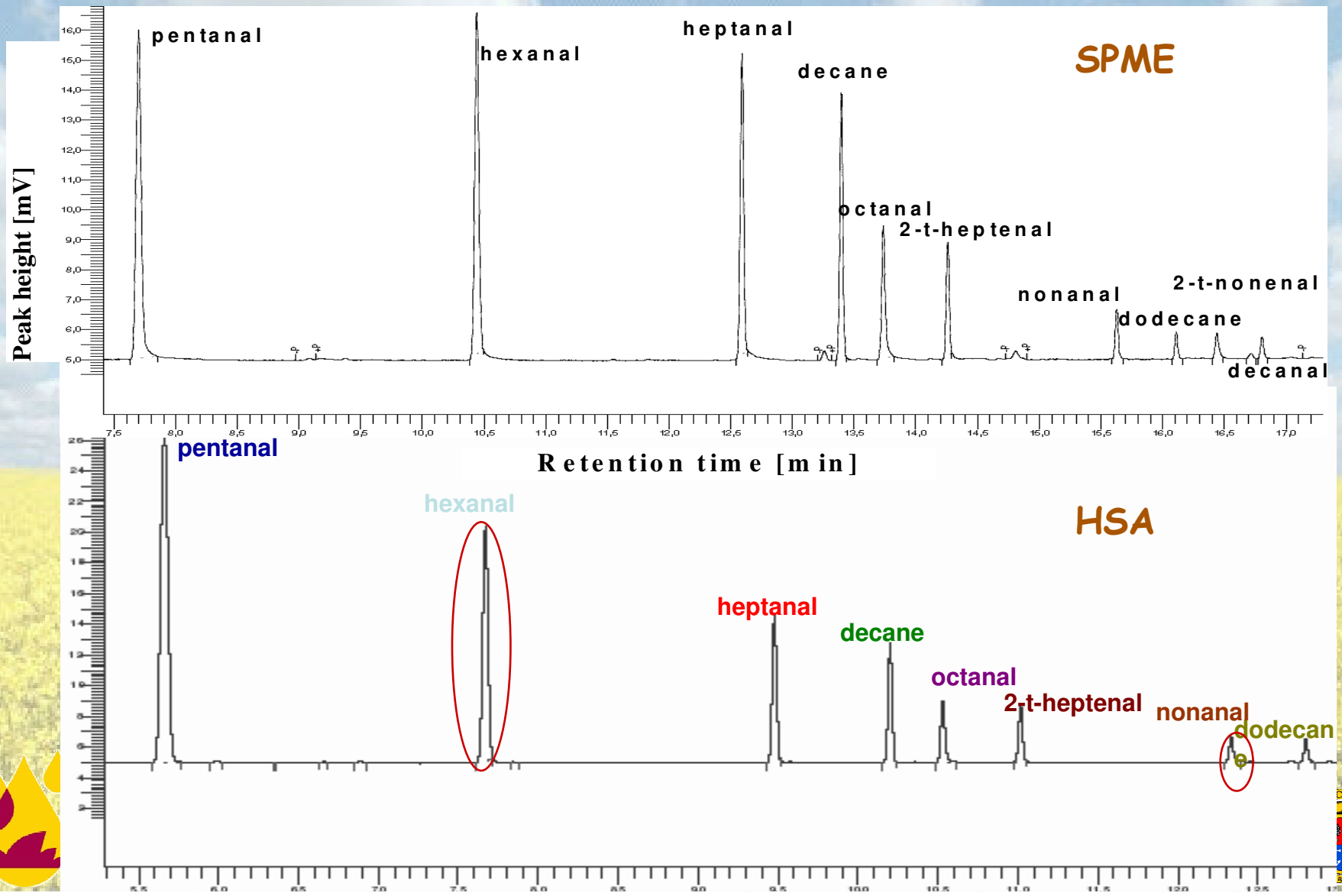
GC analysis



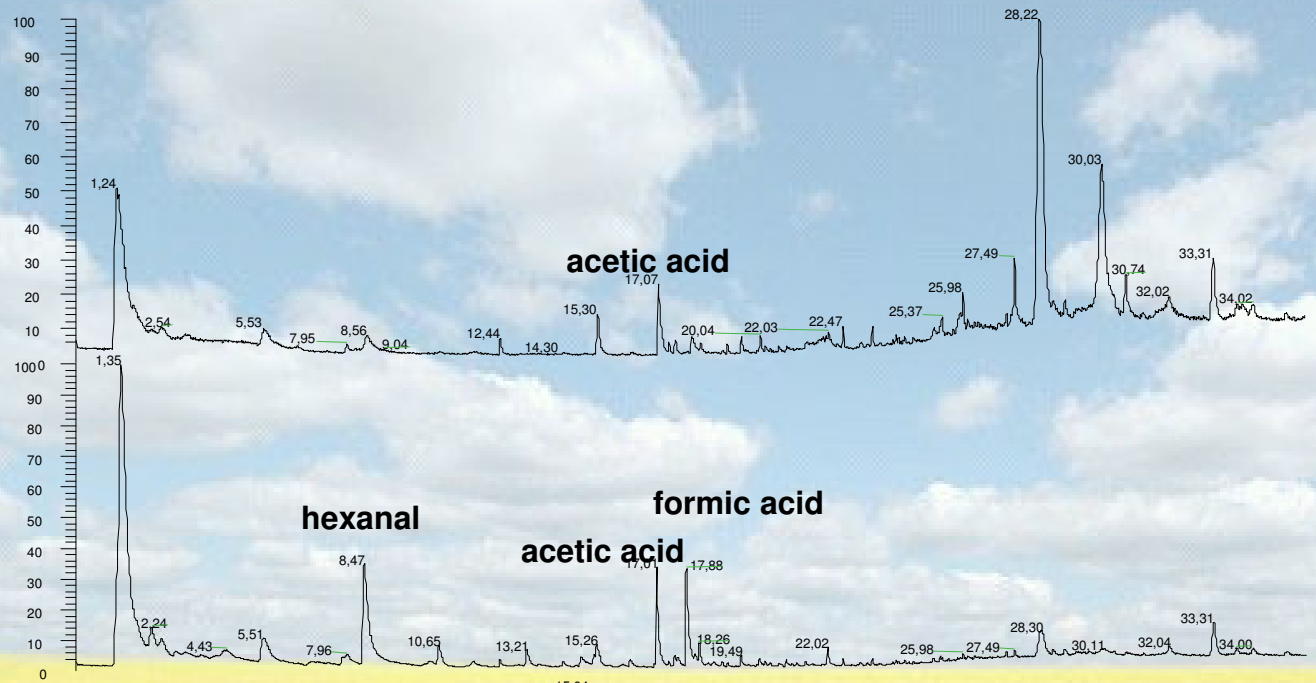
HSA

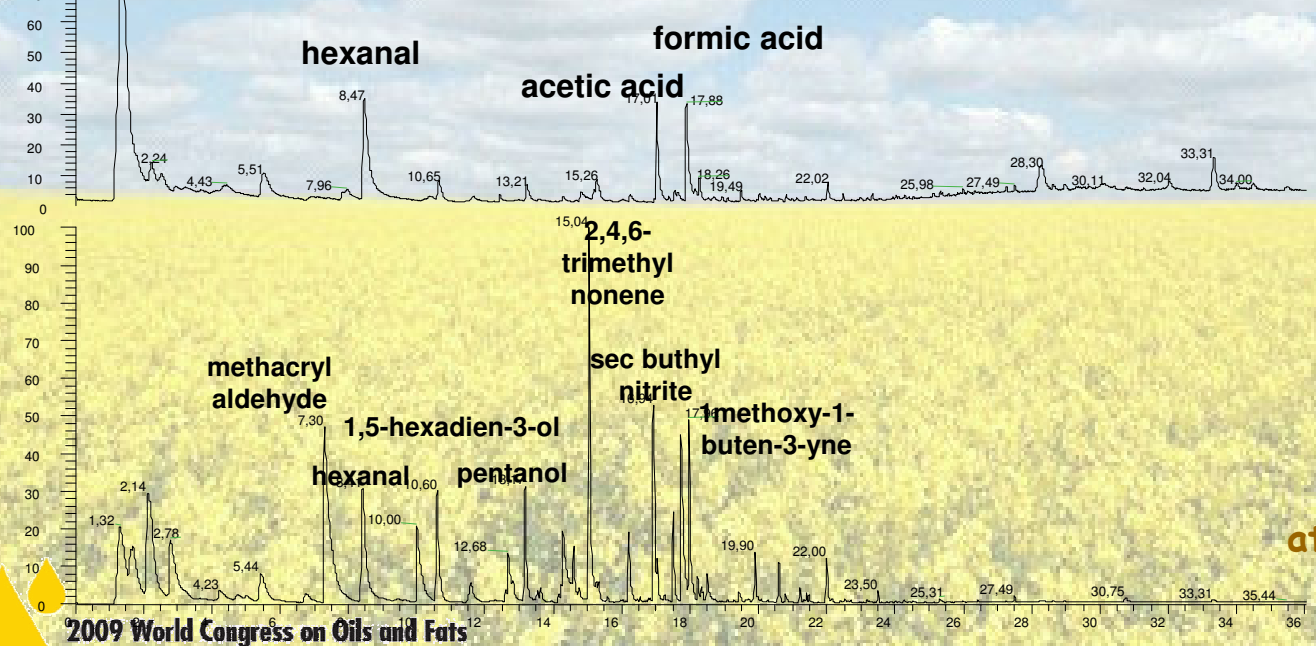


Chromatogram of standards

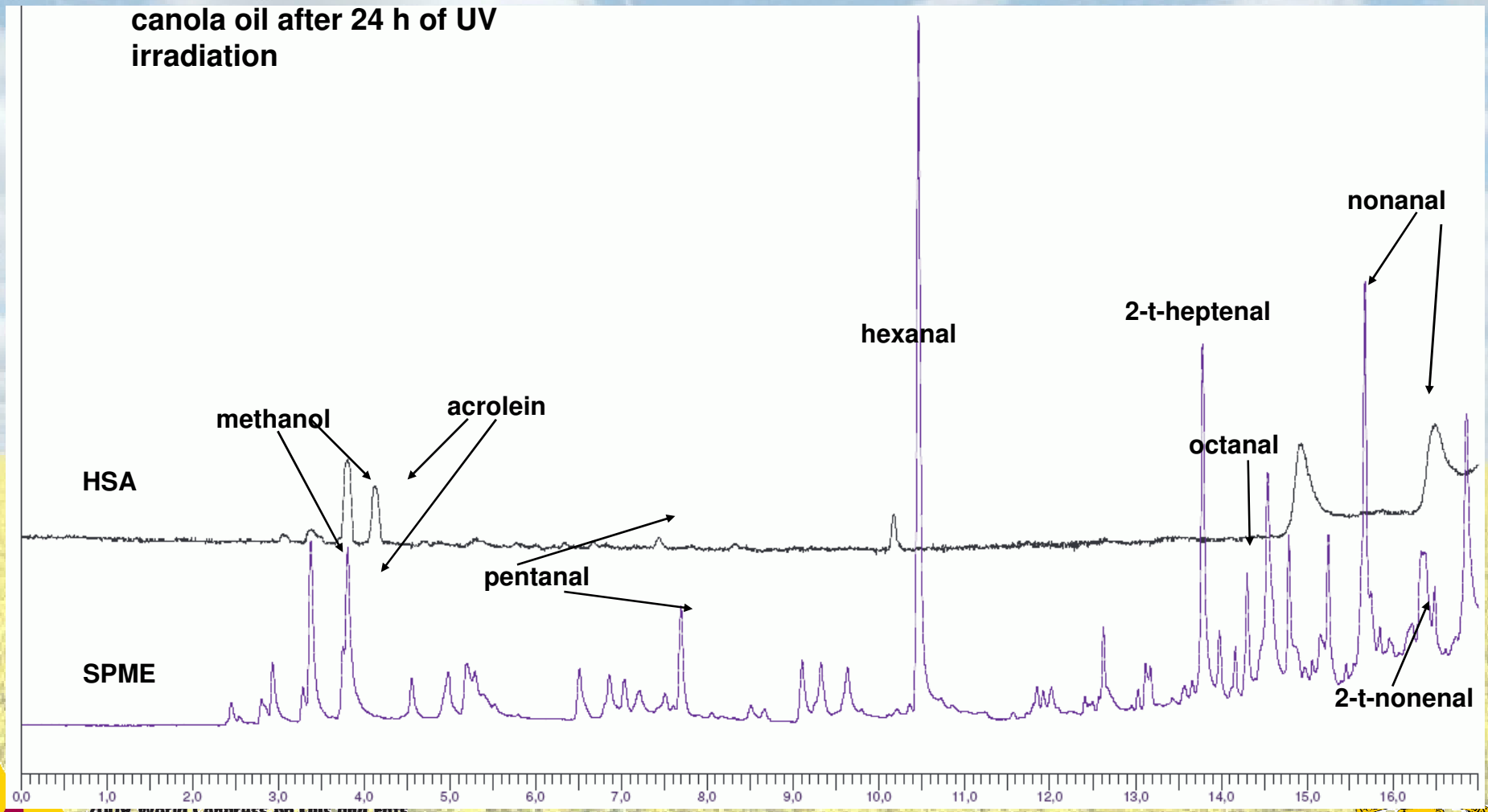


SPME/GC-MS of canola oil





Chromatograms after HSA and SPME



Comparison of the optimal parameters

extraction parameters	HSA	SPME
injector/detector temperature	170 ^{0}C / 230 ^{0}C	250 ^{0}C / 230 ^{0}C
sample volume	8 ml in the 15 ml vial	
equilibrium time	20 min	10 min
extraction temperature	80 ^{o}C	30 ^{o}C
extraction time	-	15 min
pressure time	1 min	-
total time	21 min	25 min
headspace volume	0,16 ml	-
sample agitation	no	yes

Comparison of the validation parameters

Validation parameter	HSA			SPME		
	LOD [mg/kg]	LOQ [mg/kg]	Repeatability [%]	LOD [mg/kg]	LOQ [mg/kg]	Repeatability [%]
pentanal	4,41	13,23	2,3	0,216	0,648	4,02
hexanal	3,21	9,62	6,9	0,222	0,666	4,35
heptanal	20,37	61,11	9,3	0,250	0,750	7,65
decane	16,21	48,62	9,4	0,215	0,645	6,32
2-t-heptenal	26,91	80,73	7,1	0,208	0,624	8,38
octanal	21,41	64,23	13,3	0,219	0,657	8,53
nonanal	50,66	151,97	19,7	0,238	0,714	8,17
dodecane	27,02	81,07	8,2	0,346	1,038	7,30
2-t-nonenal	-	-	-	0,162	0,486	8,51
decanal	-	-	-	0,293	0,879	8,24

Conclusions

- The time of each analysis is relatively short.
- Developed procedures are comparable in term of precision (Coefficient of variation – CV: 2 - 8 %).
- The linearity for all developed procedures is satisfactionary.
- For procedures using SPME for extraction of analytes LOD is 3 orders of magnitude lower then for SDE procedures and 2 orders of magnitude for HSA procedures.
- SDE technique represents a cheap and attractive, alternative to SPME requiring only a standard GC syringe.

Acknowledgements

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