Addressing the Challenges of Residual VOCs in Food Packaging by an Advanced HS-GCMS System

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ABSTRACT

Packaging materials and food containers are essential to ensure product quality, safety during shipping and storage and shelf-life. Organic solvents used in printing inks, varnishes, dyes and adhesive applied to the final package can leach from the surface and contaminate the food product determining significant health risks and negatively impacting on the taste, aroma and appearance of the product. Besides the good manufacturing practices, United States and the European Union have implemented regulations to address the use and to quantitate residual solvents in packaging material. To overcome the challenges of liquid injections and to reduce the sample preparation to the minimum, residual organic solvents in packaging materials have traditionally been analyzed by multiple extraction headspace gas-chromatography (MHE-GC). In this study the new Thermo Scientific™ TriPlus™ 500 HS Autosampler was coupled to a Thermo Scientific™ TRACE™ 1310 GC and the sample injection was split between a Thermo Scientific™ Instant Connect Electron Flame Ionization Detector (FID) and Thermo Scientific™ ISQ™ 7000 Single Quadrupole MS using a Thermo Scientific™ Dual Detector Microfluidics device. The data demonstrates outstanding MHE linearity and excellent quantitative performance in addition to automated data processing and reporting capabilities.

Figure 1. TriPlus 500 HS Autosampler coupled to a TRACE 1310 GC and ISQ 7000 Single Quadrupole MS.

INTRODUCTION

Common food packaging materials are polymer-based thin films or paper-based coatings often layered or imprinted on the outside with inks, dyes and paints intended to address the consumer appeal and convenience. The chemical components of such food packaging (especially from polymers, dyes and inks) can migrate into the food products modifying the organoleptic properties and the composition of the food and posing health risks to the consumer. As a consequence, regulatory measures are in place to make sure that food contact materials do not transfer any components to the packed foodstuff in quantities which could affect human health, or change the composition, or the organoleptic properties of the product.[1] Precise quantification of residual solvents in flexible packaging is regulated through set methods such as EN 13628-1:2002.[2] Liquid injections of solid polymers requires complex sample preparations moreover non-volatile, long chain polymers can potentially contaminate the GC injector ports requiring frequent inlet liner replacement and system maintenance that will increase the cost of analysis. Headspace sampling is a fast and simple technique that enables the extraction of volatile and semi-volatile compounds from food packaging samples without the need for time-consuming sample preparation. In particular static headspace with multiple headspace extraction (MHE) can be used for absolute quantitative analysis of volatiles in solid matrices as it allows to extrapolate the total content of analytes in the matrix through multiple headspace cycles. The amount of analytes present in the sample is calculated by direct comparison of the peak area responses to external standards previously analyzed in a similar way but without matrix. This technique is particularly useful when matrix-matched calibration reference materials are not available.

MATERIALS AND METHODS

Two standard mixtures, each containing different residual solvents that can be found in packaging materials (mixture 1 and mixture 2 at 7.14% v/v and 9.09% v/v respectively) were purchased from Sigma Aldrich® (P/N 48994-U and 48995-U). A volume (1 µl) of each standard solution (corresponding to 71.4 µg and 90.9 µg of mixture 1 and 2 respectively) was spiked into the same 10 mL empty sealed headspace glass vial and used as retention time reference for compound identification as well as for MHE linearity assessment with total vaporization. Samples of packaged foods (pizza, cookies, bread, salad and salami) were purchased locally and the packaging (cling film, wraps and trays) were separated from the food and analyzed following to the EN 13628-1:2002 method. A sample surface of 40 cm^2 (2X20 cm) was cut, coiled and sealed into a 10 mL crimp cap headspace vial (vials P/N 10CV, caps P/N 20-MCBC-ST3). As specified in the EN 13628-1:2002 method, the ratio between the sample area (in cm^2) and the vial volume (in mL) was maintained between 3 and 5.

Standards and samples were then analyzed to assess MHE method linearity, fundamental to achieve an accurate quantitation of residual solvents in food packaging. MHE-GC-FID/MS operating parameters are reported in Table 1.

The data was acquired, processed and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2. Chromeleon advanced reprocessing features allowed for fast MHE calibration plots and correlation coefficient calculations without the need of external calculation tools.

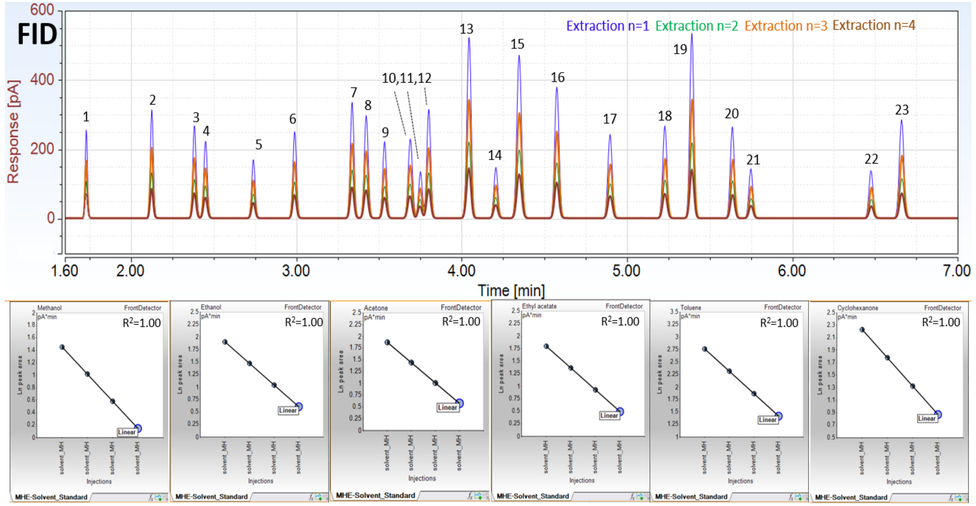
Table 1. Gas Chromatograph and Mass Spectrometer Instrument Parameters

TRACE 1310 GC Parameters	
Inlet Module and Mode:	SSL, split
Split Ratio:	20:1
Septum Purge Mode, Flow (mL/min):	Constant, 5
Carrier Gas, Carrier Mode, Flow (kPa):	He, constant pressure, 110
Oven Temperature Program:	
Temperature 1 (°C):	50
Hold Time (min):	1
Temperature 2 (°C):	110
Rate (°C/min):	30
Temperature 2 (°C):	250
Rate (°C/min):	20
FID:	
Temperature (°C):	250
Air Flow (mL/min):	350
H_2 Flow (mL/min):	35
N_2 Flow (mL/min):	40
Acquisition Rate (Hz):	25
ISQ 7000 Single Quadrupole MS :	
Ion Source:	ExtractaBrite
Transfer Line Temperature(°C):	250
Source Temperature (°C):	250
Ionization Mode:	EI
Electron Energy (eV):	70
Acquisition Mode:	Full Scan (m/z 25-350)
Chromatographic Column:	
Trace GOLD TG-1 MS (P/N 26099-4840)	30 m x 0.32 mm x 3.0 µm

TriPlus 500 HS Autosampler Parameters (MHE)	
Incubation Temperature (°C):	120
Incubation Time (min):	40
Vial Shaking:	Medium
Vial Pressurization Mode:	Pressure
Vial Pressure (kPa) (Auxiliary Gas Nitrogen):	55
Vial Pressure Equilibration Time (min):	1
Loop size (mL):	1
Loop/Sample Path Temperature (°C):	120
Loop Filling Pressure (kPa):	34
Loop Equilibration Time (min):	1
Extraction Cycles:	4
Needle Purge Flow Level:	4
Injection Mode:	MHE
Injection Time (min)	1

TriPlus 500 HS Autosampler Parameters (total vaporization)	
Incubation Temperature (°C):	120
Incubation Time (min):	40
Vial Shaking:	Medium
Vial Pressurization Mode:	Pressure
Vial Pressure (kPa) (Auxiliary Gas Nitrogen):	55
Vial Pressure Equilibration Time (min):	1
Loop size (mL):	1
Loop/Sample Path Temperature (°C):	120
Loop Filling Pressure (kPa):	34
Loop Equilibration Time (min):	1
Needle Purge Flow Level:	4
Injection Mode:	standard
Injection Time (min)	1

Figure 2. FID traces for reference standard and corresponding MHE calibration curves for selected compounds (methanol, ethanol, acetone, ethyl acetate, toluene and cyclohexanone) as examples. Calibration curves were obtained by plotting the natural logarithm of peak area responses (total vaporization MHE) versus the corresponding MHE extraction step.



1=Methanol, 2=Ethanol, 3=Acetone, 4=2-Propanol, 5=Methyl acetate, 6=1-Propanol, 7=2-Butanone, 8=2-Butanol, 9=Ethyl acetate, 10=2-Methyl-1-propanol, 11=2-Methoxyethanol, 12=Tetrahydrofuran, 13=Isopropyl acetate, 14=1-Methoxy-2-propanol, 15=Cyclohexane, 16=Propyl acetate, 17= 4-Methyl-2-pentanone, 18= Isobutyl acetate, 19=Toluene, 20=Butyl acetate, 21= 2-Methoxyethyl acetate, 22= 2-Ethoxyethyl acetate, 23= Cyclohexanone

RESULTS

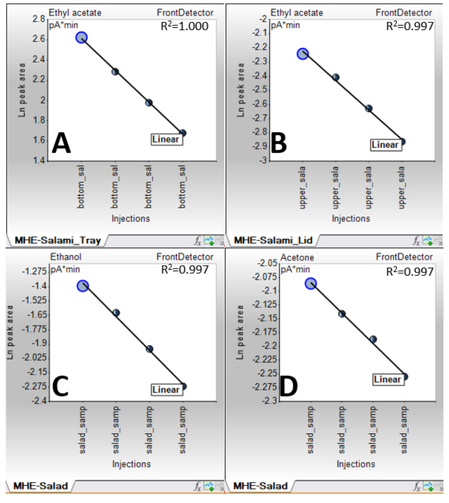
MHE linearity assessment in the standard solution according to EN 13628-1:2002 method

GC oven ramp was optimized to improve sample throughput (total run time<7 min) but ensuring an adequate chromatographic resolution for all peaks (Rs>1). An incubation time of 40 minutes per MHE step was optimized to cover the majority of food packaging material types. According to the EN 13628-1:2002 method, linearity was assessed on n=4 headspace extraction cycles. Correlation coefficient (R^2) were calculated by plotting the natural logarithm of the peak areas versus the number of headspace cycles (n=4). FID data were used for compound identification and quantitation, TIC traces (full scan, EI at 70eV) were used to compare peak mass spectra with NIST17 library and putatively confirm their identity. The calculated correlation coefficients (R^2) of the standard solutions met the method requirement (R^2≥0.98) confirming an excellent linearity being 1.000 for the investigated compounds (Figure 2).

Quantification of residual solvent in food packaging materials using MHE

No residual solvents were found in the majority of samples, some traces of ethyl acetate were found in the sliced salami wrap (lid and tray), ethanol and acetone were present in salad wrap. MHE linearity in these samples was assessed as previously described. Correlation coefficient (R^2) resulted 0.997 and 1,000 for sliced salami (lid and tray respectively), 0.997 for ethanol and acetone in salad wrap (Figure 3).
The concentration (in mg/m^2) of residual solvents detected in the samples was calculated applying the equations 1, 2, and 3 as reported in the EN method. Ethyl acetate in the sliced salami wrap resulted to be 0.76 mg/m^2 (lid) and 29 mg/m^2 (tray). In salad wrap, ethanol and acetone resulted to be 0.97 mg/m^2 and 1.9 mg/m^2 respectively. All levels were well within the safety limits reported for residual solvent and non-volatile food additives.[3]

Figure 3. MHE linearity (FID data) for ethyl acetate in sliced salami lid (A) and tray (B), ethanol (C) and acetone (D) in salad wrap. Correlation coefficient (R^2) resulted 0.997 and 1.000 for sliced salami (lid and tray respectively), 0.997 for ethanol and acetone in salad wrap.



Calculation of the total peak area e_n for one residual solvent in the standard mix

(equation 1) $$e_n = \frac{(e_1)^2}{(e_1 - e_2)}$$

e1= peak area for the residual solvent in n=1 extraction cycle

e2= peak area for the residual solvent in n=2 extraction cycle

Calculation of the total peak area a_n for one residual solvent in the sample

(equation 2) $$a_n = \frac{(a_1)^2}{(a_1 - a_2)}$$

a1= peak area for the residual solvent in n=1 extraction cycle

a2= peak area for the residual solvent in n=2 extraction cycle

Amount *Q* of residual solvent in the packaging material (in mg/m^2)

(equation 3) $$Q = \frac{a_n * p}{e_n * S}$$

p= mass of the solvent in the standard mix (in mg)

S= area of the specimen (in m^2)

CONCLUSIONS

- The results obtained with TriPlus 500 HS Autosampler are compliant with the EN 13628-1:2002 standard method requirements providing excellent performance and outstanding reliability for MHE quantitative analysis in routine laboratory use.
- The MHE capability allows for absolute quantitative analysis of residual solvent impurities in solid samples, overcoming the matrix effect and eliminating the need of sample preparation. Using the MHE mode, excellent linearity with correlation coefficient R^2≥0.997 was obtained for all analytes in both solvent standard and samples, meeting the minimum required value of R^2≥0.98 thus confirming excellent instrument performance for MHE quantitative analysis.
- Traces of residual solvents were found in three of the five analyzed food packaging. Acetone and ethanol were found at 1.9 and 0.97 mg/m^2 in salad wrap samples respectively and ethyl acetate was found in sliced salami lid at 0.76 mg/m^2 and tray at 29.0 mg/m^2. No residual solvents were detected in pizza cling film, cookies and bread wraps.
- The low bleed and superior inertness of the Thermo Scientific™ TraceGOLD™ column allowed for highly reliable results. The high column efficiency allowed for a faster GC oven ramp maintaining adequate chromatographic separation (Rs≥1.0) for all the analyzed compounds, supporting shorter analysis time and high sample throughput to easily meet the needs of routine laboratories. Moreover up to 240 sample vials can be accommodated into the trays for unattended 24 hour operations.

REFERENCES (if necessary)

1. Food Contact Materials - Regulation (EC) No 1935/2004 – European Implementation Assessment Study, May 2016
2. EN 13628-1:2002 Packaging- Flexible Packaging Material – Determination of residual solvents by static headspace gas chromatography – Part 1.;Absolute methods
3. Title 21, Code of Federal Regulation, Direct Additive Part, 170.3, Indirect Additive, Part 174-179
4. Thermo Fisher Scientific (2019) Food Packaging Application Note

TRADEMARKS/LICENSING

PO10695-EN 0219S

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