thermo scientific

APPLICATION NOTE 10689

Rapid qualitative and quantitative analysis of residual solvents in food packaging by static headspace coupled to GC-FID/MS

Authors

Giulia Riccardino and Cristian Cojocariu

Thermo Fisher Scientific, Runcorn, UK

Keywords

Residual solvents, flexible food packaging, food safety, valve and loop, headspace-gas chromatography, HS-GC, multiple headspace extraction, MHE, flame ionization detector, FID, mass spectrometer detector, MS, single quadrupole GC-MS, ISQ 7000, TriPlus 500 HS

Goal

The aim of this application note is to demonstrate the qualitative and quantitative performance of the Thermo Scientific™ TriPlus™ 500 Gas Chromatography Headspace Autosampler coupled to a dual-detector GC-FID/MS for the determination of residual solvents in food packaging according to the European Standard EN 13628-1 method[1] and to highlight a highly efficient workflow through extended automation from sampling to data reporting.

Introduction

Packaging materials are essential for maintaining food integrity and to ensure safe handling, transportation, and storage. 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 that could affect human health, change the composition, or modify the organoleptic

ThermoFisher SCIENTIFIC

properties of the product.[2] In the United States a migration limit of 50 ppm is applicable for residual solvents and non-volatile food additives.[3] In addition, precise quantification of residual solvents in flexible packaging is also regulated through set methods such as EN 13628-1:2002.

Analysis of volatile impurities in solid polymers is challenging, especially with regard to sampling and extraction techniques. Liquid injections of such samples require dissolution of packaging polymers into a suitable solvent prior to gas chromatography (GC) injection. This can result in high viscosity solutions containing non-volatile, long chain polymers that can potentially contaminate the GC injector ports. This, in turn, will require frequent inlet liner replacement and system maintenance that will increase the cost of analysis.

An alternative to liquid injections is headspace sampling: 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)[4] can be used for absolute quantitative analysis of volatiles in solid matrices. This technique is particularly useful when matrix-matched calibration reference materials are not available.

In this study, the quantitative results for residual solvent analysis in food packaging materials, obtained with the TriPlus 500 Headspace (HS) autosampler, are reported. A dual detector FID/MS configuration allowed for the detection, identification (flame ionization detection), and confirmation (mass spectrometry detection) of unknown impurities. The experiments also focused on assessing method linearity[1] according to EN 13628:1:2002 and precision, as well as the overall quantitative performance of the analytical setup for routine analysis of residual solvents in food packaging.

Experimental

In all experiments, a TriPlus 500 HS autosampler was coupled to a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph equipped with a Thermo Scientific™ Instant Connect Split/Splitless SSL Injector. A Thermo Scientific™ Dual Detector Microfluidics device (P/N 19071030) was used to split 1:1 the carrier gas flow from the analytical column between a Thermo Scientific™ Instant Connect Flame Ionization Detector (FID) and a Thermo Scientific™ ISQ™ 7000 Single Quadrupole GC-MS system.

Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-1MS GC capillary column, 30 m × 0.32 mm × 3.0 µm (P/N 26099-4840). Additional HS-GC-FID/MS conditions are given in Table 1. The GC oven temperature program was optimized to decrease the analysis time and improve sample throughput; all peaks of interest are eluting in <7 minutes with adequate peak chromatographic resolution (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.

Table 1 (part 1). HS-GC-FID and ISQ 7000 mass spectrometer operating conditions for residual solvent determination

TRACE 1310 GC	
Inlet Module and Mode:	SSL, split
Split Ratio:	20:1
Septum Purge Mode, Flow (mL/min):	Constant, 5
Carrier Gas, Carrier Mode, Pressure (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 2 (°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 GC-MS system	
Ion Source:	ExtractaBrite
Transfer Line Temp. (°C):	250
Source Temperature (°C):	250
Ionization Mode:	EI
Electron Energy (eV):	70
Acquisition Mode:	Full-scan (*m/z* 25-350)

Table 1 (part 2). HS-GC-FID and ISQ 7000 mass spectrometer operating conditions used for residual solvent determination

TriPlus 500 HS Autosampler Parameters (MHE)	
Incubation Temp. (°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 Temp. (°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

Table 1 (part 3). HS-GC-FID and ISQ 7000 mass spectrometer operating conditions for residual solvent determination

TriPlus 500 HS Autosampler Parameters (total vaporization)	
Incubation Temp. (°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 Temp. (°C):	120
Loop Filling Pressure (kPa):	34
Loop Equilibration Time (min):	1
Needle Purge Flow Level:	4
Injection Mode:	Standard
Injection Time (min):	1

Data acquisition, processing and reporting

The data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2. Integrated instrument control ensures full automation from instrument set-up to raw data processing, reporting, and storage. Simplified e-workflows deliver effective data management ensuring ease of use, sample integrity, and traceability. Chromeleon CDS also offers the option to scale up the data handling process in the laboratory from a single workstation to an enterprise environment to further improve productivity.[5]

Standard and sample preparation

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. A complete list of analyzed compounds is reported in Table 2.

Samples of packaged foods (pizza, cookies, bread, salad, and salami) were purchased locally and the packaging (cling film, wraps, and trays) was separated from the food and analyzed following the EN 13628-1:2002 method. A sample surface of 40 cm^2 (2 × 20 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.

Table 2. Correlation coefficients (R^2) calculated using the full-scan EI traces. For all compounds in the reference standard $R^2 \geq 0.997$. Correlation coefficients for FID data were 1.000 for all components, hence data are not shown.

MHE Linearity		
Component Name	RT (min)	Correlation Coefficient (R^2)
Methanol	1.72	0.997
Ethanol	2.11	0.997
Acetone	2.37	0.998
2-Propanol	2.44	0.999
Methyl acetate	2.73	0.999
1-Propanol	2.98	0.998
2-Butanone	3.33	0.999
2-Butanol	3.42	1.000
Ethyl acetate	3.53	0.999
2-Methyl-1-propanol	3.68	0.999
2-Methoxyethanol	3.74	0.997
Tetrahydrofuran	3.80	0.999
Isopropyl acetate	4.04	0.998
1-Methoxy-2-propanol	4.20	0.997
Cyclohexane	4.34	0.998
Propylacetate	4.57	0.999
4-Methyl-2-pentanone	4.89	0.998
Isobutyl acetate	5.22	0.999
Toluene	5.38	0.997
Butyl acetate	5.63	0.999
2-Methoxyethyl acetate	5.74	0.997
2-Etoxyethyl acetate	6.47	0.998
Cyclohexanone	6.66	0.999

Results and discussion

MHE linearity assessment according to EN 13628-1:2002 method

A reference solvent standard mix was prepared as described in the standard and sample preparation section and analyzed using the total vaporization technique[4] applying the MHE conditions reported in Table 1. MHE allows the extrapolation of the total content of analytes in a liquid or solid matrix through multiple headspace cycles. The amount of analyte 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.

MHE linearity was assessed by plotting the natural logarithm of the peak areas in the standard solution versus the number of headspace cycles (n = 4). Chromeleon CDS interactive charts and reprocessing features allowed for fast MHE calibration plots and correlation coefficient calculations without the need of external calculation tools, as shown in Figure 1. For all the investigated compounds, the calculated correlation coefficients (R^2) were 1.000 for FID data and ≥0.997 for EI full-scan MS traces (Table 2). In both cases calculated correlation coefficients met the method requirement ($R^2 \geq 0.98$) confirming an excellent linearity.

Quantification of residual solvent in food packaging materials using MHE

The packaging materials were prepared as described and analyzed using the MHE conditions reported in Table 1. The microfluidic device allowed for splitting the gas flow 1:1 to the FID and the ISQ single quadrupole mass spectrometer, ensuring a minimal effect on the retention times (max RT shifts 0.04 min) by choosing either the FID or MS chromatogram as reference. The sample and the standard solution FID chromatograms were compared to verify the presence of known residual solvents. Several residual solvents such methanol (RT = 1.72 min) and ethylacetate (RT = 3.53 min) were detected in the sliced salami lid (D) and plastic tray (E), whereas ethanol (RT = 2.11 min) and acetone (RT = 2.37 min) were present in salad wrap (C) (Figure 3).

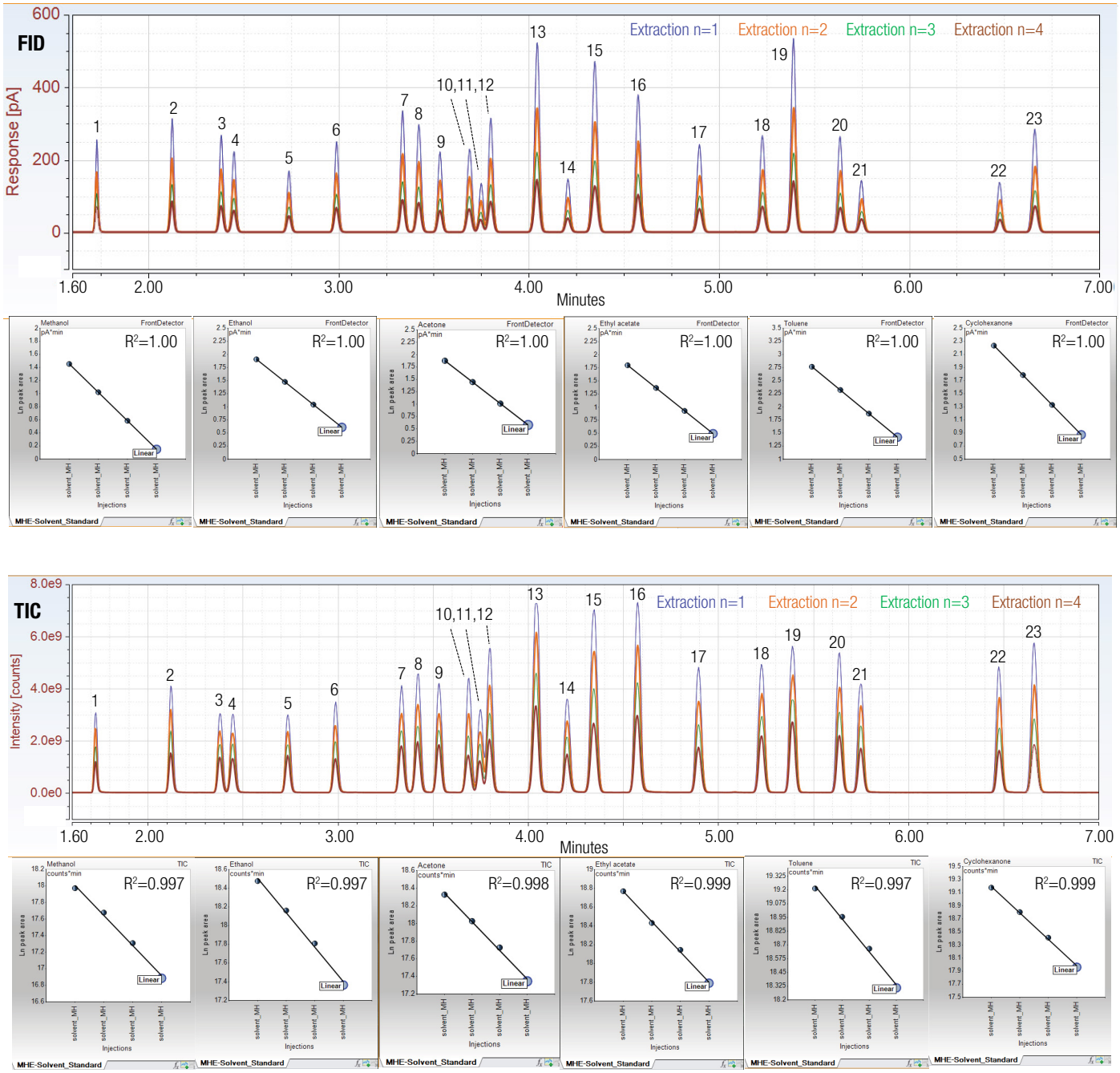

Figure 1. FID and TIC (full-scan, EI at 70 eV) traces for reference standard and corresponding MHE calibration curves for selected compounds (left to right: methanol, ethanol, acetone, ethyl acetate, toluene, and cyclohexanone) as examples. Calibration curves were obtained by plotting the natural logarithm of peak area responses (total vaporization MHE) versus the corresponding MHE extraction step.

Full-scan data were used to putatively confirm the identity of detected solvent impurities, increasing the confidence in compound indentification. When searching the mass spectrum of the peak eluting at RT = 1.72 min against NIST17 library, the best library match was acetaldehyde (not included in the standard mixtures) with a SI score of 953 (sliced salami tray:E) and 729 (sliced salami lid:D) (Figure 3). Acetaldehyde is usually present in meat and meat products.[6] Using the same approach, ethanol and acetone in salad wrap (C) and ethyl acetate in sliced salami (lid:D and tray:E) were also putatively confirmed with a SI score of 929, 913, 874, and 950, respectively. These chemicals are actually released by the packaging since they are typically used in solvent-based inks imprinted on the external layer of flexible packages.[7] Additional unknown compounds (*) detected in the samples were confirmed using spectral library comparison against NIST17 library (Figure 2).

Peaks (A):

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

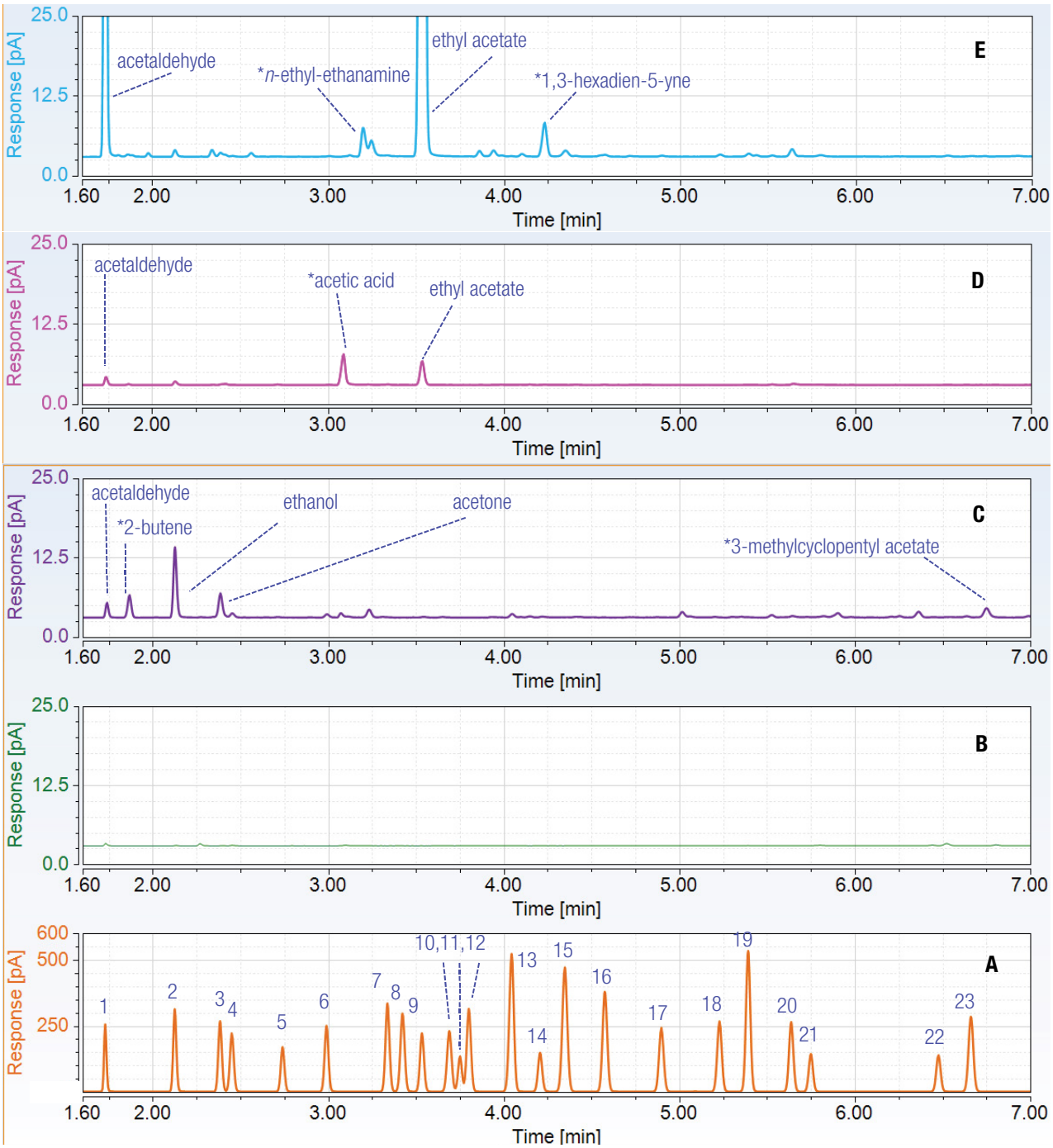

Figure 2. FID chromatograms showing a comparison between the residual solvents in the reference standard solution (A), empty blank vial (B), salad wrap (C), sliced salami wrap: lid (D) and tray (E). Based solely on retention time comparison, methanol and ethyl acetate were detected in both sliced salami samples (lid:D, tray:E). Ethanol and acetone were found in salad wraps (C). FID signal responses (y-axis) are normalized for the empty vial (B) and samples (C,D,E). Unknown peaks (*) in the samples were confirmed comparing their mass spectra (full-scan, EI traces) against the NIST17 library and are reported as an example. Peaks not annotated were below the integration threshold of 0.04 pA * min.

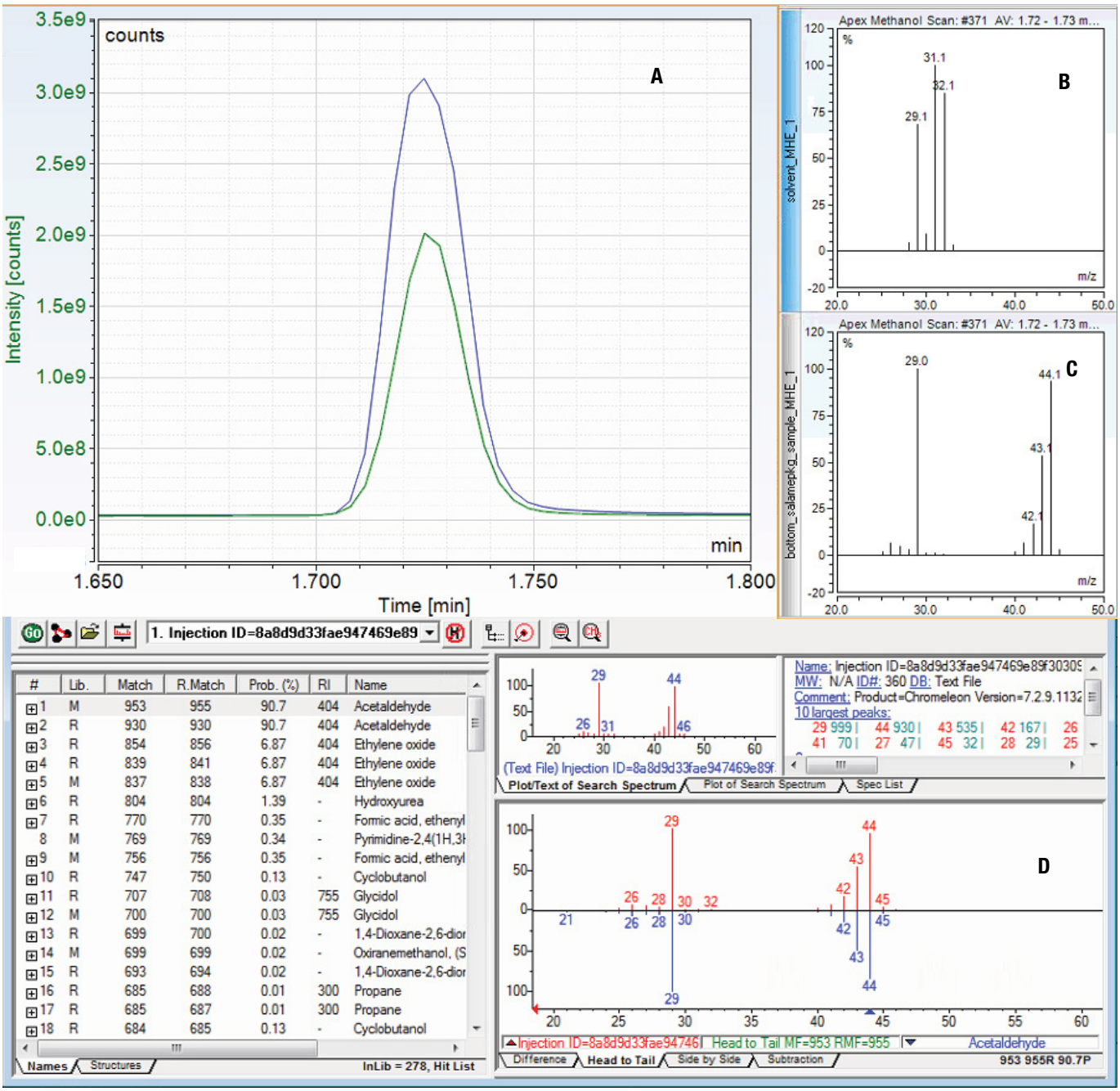

Figure 3. Identification of residual solvent peak eluting at RT=1.72 min in salami tray sample. Comparison of TIC chromatograms (full-scan, EI at 70 eV) showing retention time comparison of peak eluting at RT=1.72 min in solvent standard (blue) and salami tray (green) (A). Background subtracted EI mass spectra for this peak in solvent standard (B) and in the sliced salami tray (C) did not confirm methanol. NIST library result (D) putatively identified this compound as acetaldehyde with a SI score of 953 and a probability of 91%.

Obtaining good ($R^2 \geq 0.98$) MHE linearity is fundamental to achieve accurate quantitation of residual solvents in solid food packaging materials. MHE linearity in the samples was assessed as previously described. The correlation coefficients (R^2) were 0.998 and 0.995 for ethyl acetate in sliced salami (lid and tray, respectively). R^2 for ethanol and acetone in salad wrap were 0.996 and 0.998, respectively (Figure 4).

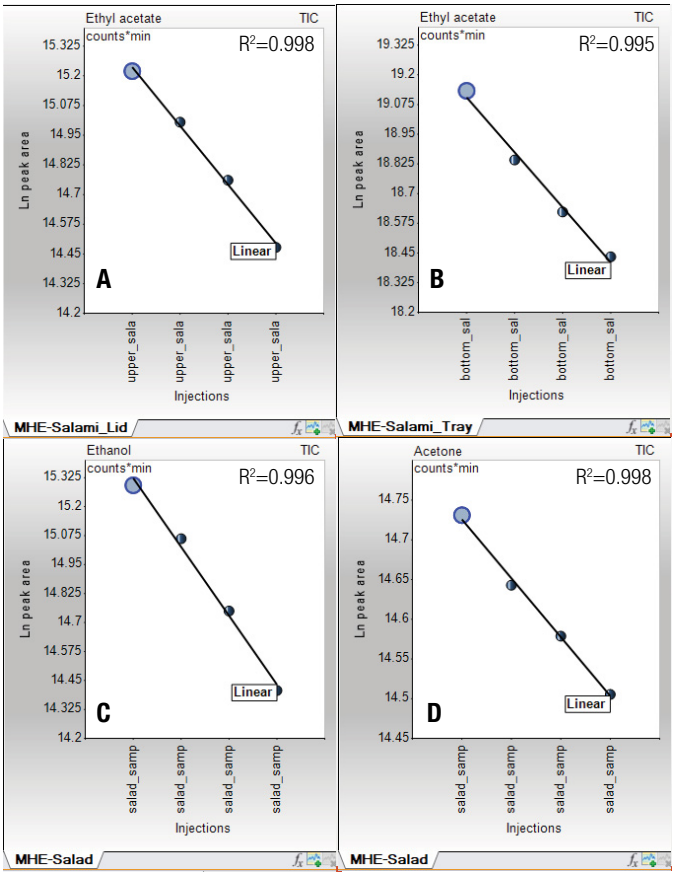

Figure 4. MHE linearity for ethyl acetate in sliced salami lid (A) and sliced salami tray (B), ethanol (C), and acetone (D) in salad wrap. The resulting correlation coefficients (R^2) were 0.998 and 0.995 for sliced salami (lid and tray, respectively) and 0.996 and 0.998 for ethanol and acetone, respectively, in salad wrap.

The concentration (in mg/m^2) of residual solvents detected in the samples was calculated using the FID data applying the formula reported in paragraph 9.2.10.1 of the EN method. No residual solvents were found in the majority of samples. Traces of ethyl acetate were found in the sliced salami wrap (lid: 0.76 mg/m^2, tray: 29 mg/m^2). Ethanol (0.97 mg/m^2) and acetone (1.9 mg/m^2) were also present in salad wrap. All levels were within the safety limits reported for residual solvent and non-volatile food additives.[3]

Conclusions

The results obtained with the TriPlus 500 HS autosampler are compliant with the EN 13628-1:2002 standard method requirements.

- 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 $R^2 \geq 0.995$ was obtained for all analytes in both solvent standard and samples, meeting the minimum required value of $R^2 \geq 0.98$, thus confirming excellent instrument performance for MHE quantitative analysis.
- Traces of residual solvents were found in three of the six analyzed food packaging samples. Acetone and ethanol were detected at 1.9 and 0.97 mg/m^2 in salad wrap samples, respectively, and ethyl acetate was found in sliced salami tray at 29 mg/m^2 and lid at 0.76 mg/m^2. No residual solvents were present in pizza cling film, cookies, and bread wraps.
- The dual detector configuration FID/MS increases the confidence in compound identification, allowing for the detection of possible analyte co-elution, otherwise difficult to assess in the absence of MS data. Moreover several unknown peaks in the samples have been putatively confirmed (using spectral library match score thresholds of >950 SI) through comparison with NIST17 spectral library.
- The low bleed and superior inertness of the TraceGOLD column allowed for highly reliable results. The high analytical column efficiency allowed for fast GC oven ramp with adequate chromatographic separation (Rs ≥ 1.0) for all the analyzed compounds, reducing analysis time. Moreover, up to 240 sample vials can be accommodated into the trays for unattended 24-hour operation.

thermo scientific

- The automated cycle time optimization allows for continuous sample processing ensuring the overlapping between the MHE cycles of the same sample. The overlapping capability is maintained between the final injection of one sample and the incubation of the next one increasing the sample throughput.
- Chromeleon CDS software ensures data integrity, traceability, and effective data management from instrument control to the final report. The integrated charts and the advanced report capability allowed for easy and integrated MHE data reprocessing, thus eliminating the need for external calculation tools.

Overall the results obtained show that the TriPlus 500 HS autosampler coupled to the TRACE 1310 GC and the ISQ 7000 single quadrupole GC-MS system represents a robust analytical configuration for routine laboratories delivering outstanding reliability for MHE quantitative analysis of residual solvents in food packaging.

References

1. EN 13628-1:2002 Packaging- Flexible Packaging Material – Determination of residual solvents by static headspace gas chromatography – Part 1.; Absolute methods.
2. Food Contact Materials - Regulation (EC) No 1935/2004 – European Implementation Assessment Study, May 2016.
3. Title 21, Code of Federal Regulation, Direct Additive Part, 170.3, Indirect Additive, Part 174–179.
4. Kolb, B., Ettre, I., Static headspace-gas chromatography Theory and Practice, Second Edition Wiley, 2006.
5. Thermo Fisher Scientific, Chromeleon CDS Enterprise – Compliance, Connectivity, Confidence, BR72617-EN0718S.
6. Kosowska, M., Majcher, M.A., Fortuna, T., Volatile compounds in meat and meat products, Food Science and Technology, Campinas, vol. 37 issue 1, Jan-March 2017, 1–7.
7. Packaging Materials - Printing inks for food packaging composition and properties of printing inks, International Life Science Institute ILSI Europe, December 2011.

Find out more at **thermofisher.com/TriPlus500**

AN10689-EN 0319S

ThermoFisher SCIENTIFIC