ABSTRACT
Purpose: This work is focused to highlight performance and benefits of a new valve-and-loop static headspace sampler coupled to a GC-MS-FID detector configuration, for the determination of residual solvents in food packaging according to the regulatory requirements (EN 13628-1:2002).

Methods: The dual detector GC-MS/FID allows for simultaneous identification and confirmation of known and unknown compounds, increasing the confidence in compound identification and allowing possible impurities to be confirmed. Reliable quantification is achieved through automated Multiple Headspace Extraction (MHE) calibration and reporting easily through the Thermo Fisher Scientific's Chromatography Data System, for a fully automated workflow.

Results: MHE calibration showed excellent linearity with correlation coefficient R² ≥ 0.995 for all analytes in both solvent standard and samples, exceeding the minimum required value. Table of residuals of solvents were found in three of the six analyzed food packaging samples, in the range of 0.76 – 29 mg/m².

INTRODUCTION
Packaging materials and food containers are essential to ensure safety, quality, and product shelf-life. Volatile organic compounds (VOCs) used in printing inks, varnishes, dyes and adhesive applied to the final package can leach from the surface and contaminate the food production machinery, shipping, and storage determining significant health risks and negatively impacting on the taste, aroma and appearance of the product.

Bests the good manufacturing practices, United States and the European Union have implemented regulations to address the use and to quantify residual solvents in packaging material. Residual VOCs in food packaging are traditionally analyzed by headspace gas chromatography (HS-GC), representing a fast and simple technique without the need for time-consuming sample preparation. Innovative design features now available in modern valve and loop headspace autosamplers provide high analytical performance when it comes to routine solvent analysis.

MATERIALS AND METHODS
A Thermo Scientific™ TriPak™ 500 Headspace (HS) autosampler was coupled to a Thermo Scientific™ TRACE 1310 Gas Chromatograph. A dual detector Microsampler device (P/N 1907103) was used to split 1:1 the same gas flow from the analytical column between a Thermo Scientific™ Instant Connect Flame Ionization Detector (FID) and a Thermo Scientific™ 5977 Single Quadrupole GC-MS system, as shown in Figure 1. Chromatographic separation was achieved on a Thermo Scientific™ TraceGold™ TG-1MS GC capillary column, 30 m × 0.32 mm × 0.50 μm (P/N 259099-4440). Additional HS-GC-MS/FID conditions are given in Table 1.

Sample Preparation
Two standard mixtures, each containing different residual solvents that can be found in packaging materials (mixture 1 containing 1.74% v/v and 3.99% v/v) of ethyl acetate and ethoxyethyl acetate, respectively, were purchased from Sigma Aldrich® (P/N 489941 and 2224895-U). A volume (1 μL) of each standard solution (corresponding to 7.14 mg and 9.92 μL 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. When searching the mass spectrum of the peak eluting at RT = 1.72 min against NIST17 library, these chemicals are actually released by the packaging since they are typically used in solvent wrap (lid and tray), reference.

These chemicals are actually released by the packaging since they are typically used in solvent wrap (lid and tray), reference. The packaging materials were prepared as described and analyzed using the MHE conditions reported in Table 1. The chromatographic device allowed for splitting the gas flow 1:1 to the FID and the ISO 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 chromatograms as reference.

The sample and the standard FID chromatograms were compared to verify the presence of known residual solvents. 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 acetic acid were present in sliced wrap (Figure 4). MHE linearity in these samples was assessed as previously described. Correlation coefficient (R²) resulted 0.997 and 1.000 for sliced salami (lid and tray) and 0.997 for ethanol and acetic acid in sliced wrap. The content (in mg/m²) of residual solvents detected in the samples was calculated applying the equation 2 and 3 reported in Table 1. Ethyl acetate in the sliced salami wrap resulted to be 0.76 mg/m² and 29 mg/m² (tray and lid) respectively. Full-scan data were used to confidently confirm the identity of detected solvent impurities, increasing the confidence in compound identification. When searching the mass spectrum of the peak eluting at RT = 1.72 min against NIST11 library, the best library match was acetatealdehyde (not included in the standard mixture) with a SI score of 953 (sliced salami tray and lid and sliced salami (lid D) and tray E). These chemicals are actually released by the packaging since they are typically used in solvent-wrap (tray). In conclusion, different chemicals were released by the packaging, they are actually released by the packaging since they are typically used in solvent-wrap (tray).

RESULTS
MHE Linearity Assessment according to EN 13628-1:2002 Method
A solvent standard mix was analyzed using the total vaporization technique, as the MHE conditions reported in Table 1. MHE allows the extrapolation of the total content of analytes in a liquid or solid material through multiple headspace cycles. For each extraction, the number of counts of target analytes decreases exponentially, allowing for a linear extrapolaion of a total area count on a semilogarithmic plot (Figure 2). The amount of analyte present in the sample is calculated by direct application of the equation 1, using the calibration parameters (R² > 0.98) confirming an excellent linearity.

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

REFERENCES

TRADEMARKS/LICENSES
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