Unattended Automated Standard Addition and Headspace Analysis for the Quantitative Determination of VOCs in Food Packaging

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Application Note 1010

Key Words
TRACE 1310 GC, ISQ GC-MS, TriPlus RSH, Volatile Organic Compounds in Food Packaging

Goal
To demonstrate fully automated quantitative determination of volatile components in food packaging

Introduction
Headspace analysis by means of a dedicated autosampler is a standard technique for the determination of volatile organic compounds (VOCs) possibly present in food packaging materials. The packaging sample is typically cut into square pieces and placed in headspace vials for incubation at a determined temperature before the headspace sampling. The main challenge with this kind of analysis is the quantification of volatile compounds that are present because these samples are typically layered solids that generate adsorption and migration effects. External calibration is not reliable because it does not consider the matrix effect, which is significant for these samples.

In contrast, the standard addition calibration is a reasonable quantification procedure for these difficult matrixes because it uses real sample for the calibration procedure. Until now, preparation of samples for the standard addition calibration has been performed off-line, typically executed manually by the operator before headspace analysis of the samples. This is a time-consuming and error-prone procedure, while performing sample preparation by means of the same robotic sampler used for headspace analysis enables the quantification sequence to be run automatically in an unattended way. Detection and quantification are performed by means of a gas chromatograph (GC) coupled with a single quadrupole mass spectrometer (MS).

Materials and Methods
Use the Thermo Scientific TRACE 1310 GC, coupled with the ISQ Single Quadrupole GC-MS, for analysis of the samples. Configure the GC with an instant connect split/splitless (SSL) module, operated in split mode.

The headspace incubation temperature is 80 °C and the incubation time is 15 min. The headspace injected volume is 1 mL. Use the Thermo Scientific TraceGOLD TG-624 GC Column (1.4 µm film thickness; 0.25mm ID; 60m length).

The VOCs standards solution is:

- Residual Solvents in Packaging Material Mixture 1, analytical standard, 7.14% (v/v) (Sigma-Aldrich®)
- Residual Solvents in Packaging Material Mixture 2, analytical standard, 9.09% (v/v) (Sigma-Aldrich)

Mix to obtain a single comprehensive stock solution.

Automatically perform subsequent sample preparation and injection steps using the Thermo Scientific TriPlus RSH Autosampler. The tool exchange capability and vortex mixing allow the dilution step, the standard addition step, and the headspace analysis step to be combined together in the same sequence.

Procedures
Automatic Standard Dilution Procedure
The stock solution is first automatically diluted 1/1000 with water by the TriPlus™ RSH autosampler. In this cycle, the autosampler takes the necessary aliquot of water and places it in an empty vial, adding the amount of stock solution to bring to final volume (in this case, 1 ml) using a different volume syringe.

The diluted solution obtained contains all the components in a concentration range of 0.035–0.045 µg/µL that is suitable for the determination of low levels of residual solvent in packaging material.

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Use the first calibration to check the linearity of the system and the accuracy of the overall sample preparation procedure. The autosampler automates this calibration by adding various volumes (from 1 to 5 µL) of diluted solution to a set of empty vials before the headspace analysis of the vials.

For quantification by means of the standard addition method, cut samples of foil packaging from a commercially produced croissant product into square pieces of 48 cm^2 each. Prepare five 20 mL sample vials by placing a foil piece in a headspace vial which is then crimped. For each sample, these five vials are then further prepared and analyzed by the TriPlus RSH autosampler.

The autosampler adds selected amounts of standard into the headspace vials, plus a volume of a solvent calculated to mantain constancy in the total volume of liquid in the vial. This ensures that the same conditions are kept constant across all vials.

For example, in this study the following volumes have been used:

- Vial 1 (sample + 7 µL water)
- Vial 2 (sample + 1 µL standard + 6 µL water)
- Vial 3 (sample + 3 µL standard + 4 µL water)
- Vial 4 (sample + 5 µL standard + 2 µL water)
- Vial 5 (sample + 7 µL standard)

Separations

Perform the sampling of the prepared vials by means of headspace injection on the TRACE™ 1310 GC coupled with the ISQ™ Single Quadrupole GC-MS system (Figure 1).

Perform analysis of the sample in full-scan mode for the identification of components. Run the quantification step in selected ion monitoring (SIM) mode of masses: 31, 43, 45, 55, 56, 59, and 91 *m/z*. Both modes alternating full-scan/SIM are performed simultaneously per each sample injection.

Use the TraceGOLD TG-624 column for separation of the VOCs.

Table 1 shows the GC and headspace parameters.

Figure 1. TriPlus RSH Autosampler and TRACE 1310 GC with the ISQ Single Quadrupole GC-MS system.

Table 1. GC and headspace parameters

Oven Method	
Initial Temperature (°C)	35
Initial Time (min)	4
Heating Rate (°C/min)	4
Final Temperature (°C)	200
Hold Time (min)	0
SSL Method	
Temperature (°C)	200
Mode	split
Split Flow (mL/min)	80
Carrier Method	
Mode	Helium, Constant Flow
Value (mL/min)	1
TriPlus RSH Method	
Sample Volume (µL)	1000
Incubation Time (min)	15
Incubation Temperature (°C)	80
Syringe Temperature (°C)	120

Results and Discussion

The results show good correlation factors and limits of quantification <0.01 mg/m² for the majority of the components analyzed.

Linearity of Standard Addition

Figure 2 reports the list of components and the overlay of chromatograms obtained for each volume of standard (from 1 to 5 µL) added into empty vials.

The linearity of the system and the limits of quantification for all components are derived by converting the data of addition volumes into an absolute amount expressed in mg/m² (assuming that the sample surface in the vial is 48 cm²). The graphs in Figure 3 show good linearity of the system. Quantification limits below 0.01 mg/m² have been calculated for all compounds except THF, ethanol, and ethoxy ethanol.

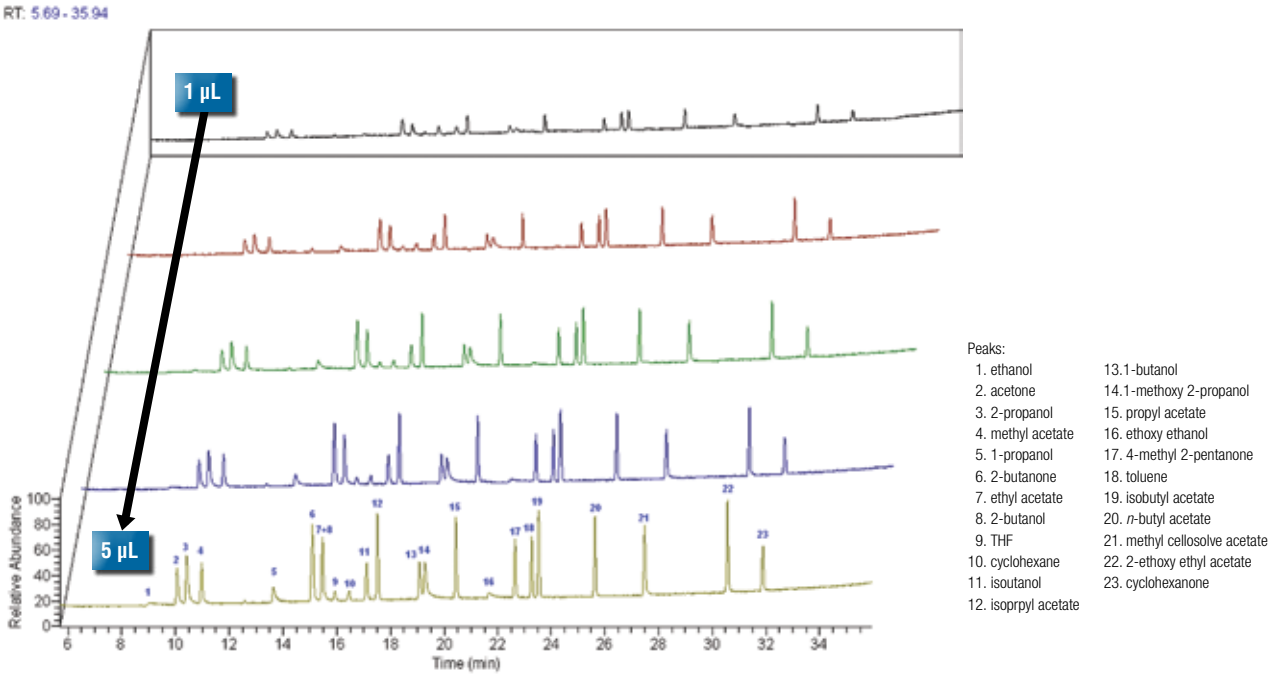

Figure 2. Component list and overlay of chromatograms in the elution order.

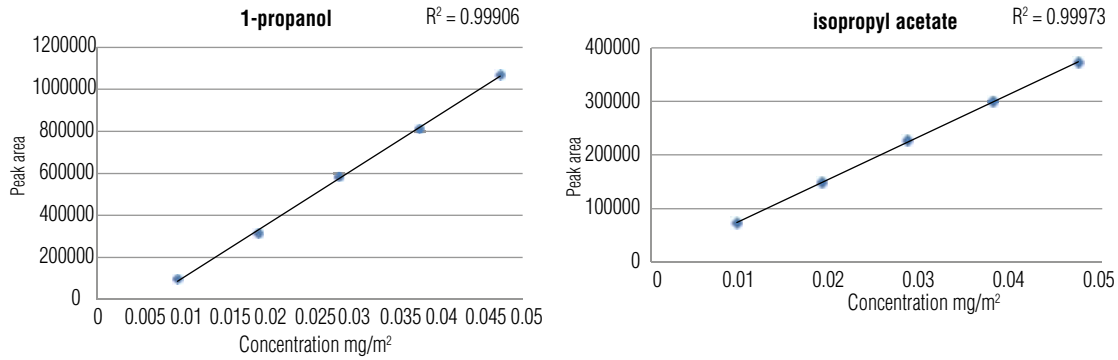

Figure 3. System linearity for 1-propanol and isopropyl acetate.

Sample Analysis (Components Identification)

A full-scan chromatogram of the packaging sample was performed in order to identify the components possibly present.

Figure 4 shows the presence of numerous residual solvents. The larger ethanol peak comes from the croissant itself where ethanol is used as a preservative.

Sample Analysis (Components Quantification)

Quantification performed by means of the standard addition method was carried out for the peaks identified in the chromatogram in Figure 4. Figure 5 shows the standard addition calibration curve for *n*-butyl acetate together with the results of quantification in the sample.

Table 2 presents the results of the quantification.

In Figure 6, the graphical representation of the quantification analysis shows that the two main residual solvents identified in the sample are 1-methoxy 2-propanol and 2-propanol. Their amounts do not exceed the level of 0.1 mg/m² each, while the other detected residual solvents have been quantified in the level of 0.01 mg/m² or lower.

Conclusion

A completely automated method for analyzing and quantifying VOCs in food packaging materials is presented. The combination of sample preparation steps and an analytical step in the same sequence allows high accuracy in quantification, high sample throughput, and minimizes error-prone manual manipulations. For the majority of residual solvents analyzed in this method, their individual limit of quantitation was below 0.01 mg/m².

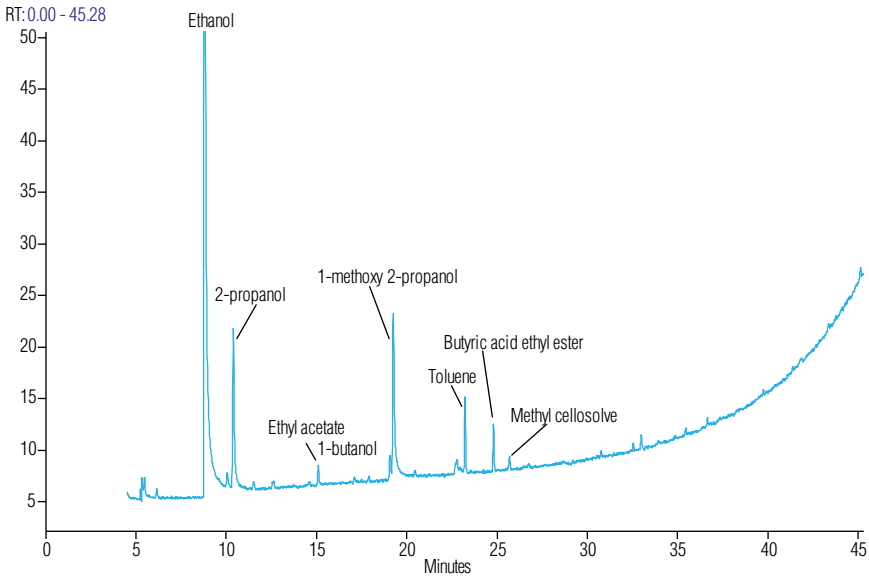

Figure 4. Full-scan sample analysis by headspace.

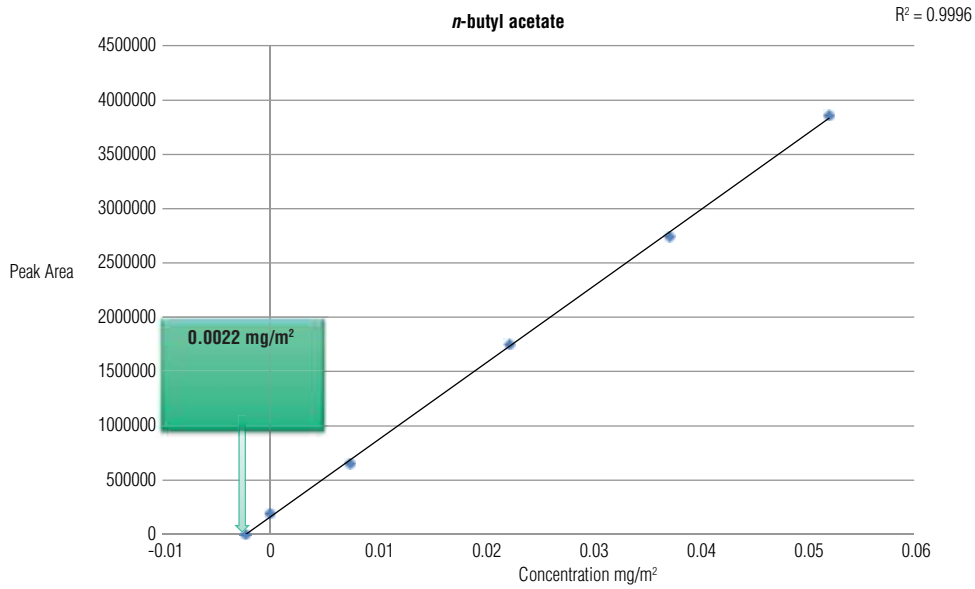

Figure 5. Quantitation via standard addition calibration for *n*-butyl acetate.

Table 2. Quantification results from a real croissant packaging foil sample of 48 cm^2 area

	µL added					
Component	**0**	**1**	**3**	**5**	**7**	
2-propanol	3337694	4162371	6363394	7060114	8101360	area
	0	0.009469	0.028406	0.047344	0.066281	concentration mg/m^2
	5.02E-02					calculated amount mg/m^2
ethyl acetate	302671	973347	2755297	4304253	6115361	area
	0	0.007438	0.022313	0.037188	0.052063	concentration mg/m^2
	2.00E-03					calculated amount mg/m^2
1-butanol	385906	761497	1708139	2203362	3191062	area
	0	0.007438	0.022313	0.037188	0.052063	concentration mg/m^2
	7.55E-03					calculated amount mg/m^2
1-methoxy 2-propanol	3873000	4854145	5683277	6258900	7857878	area
	0	0.009469	0.028406	0.047344	0.066281	concentration mg/m^2
	7.44E-02					calculated amount mg/m^2
4-methyl 2-pentanone	374131	837187	1642593	2555176	3209676	area
	0	0.009469	0.028406	0.047344	0.066281	concentration mg/m^2
	9.57E-03					calculated amount mg/m^2
toluene	1077304	1512873	2382486	2972530	3683690	area
	0	0.007438	0.022313	0.037188	0.052063	concentration mg/m^2
	2.31E-02					calculated amount mg/m^2
n-butyl acetate	190875	649615	1751135	2741910	3859582	area
	0	0.007438	0.022313	0.037188	0.052063	concentration mg/m^2
	2.26E-03					calculated amount mg/m^2

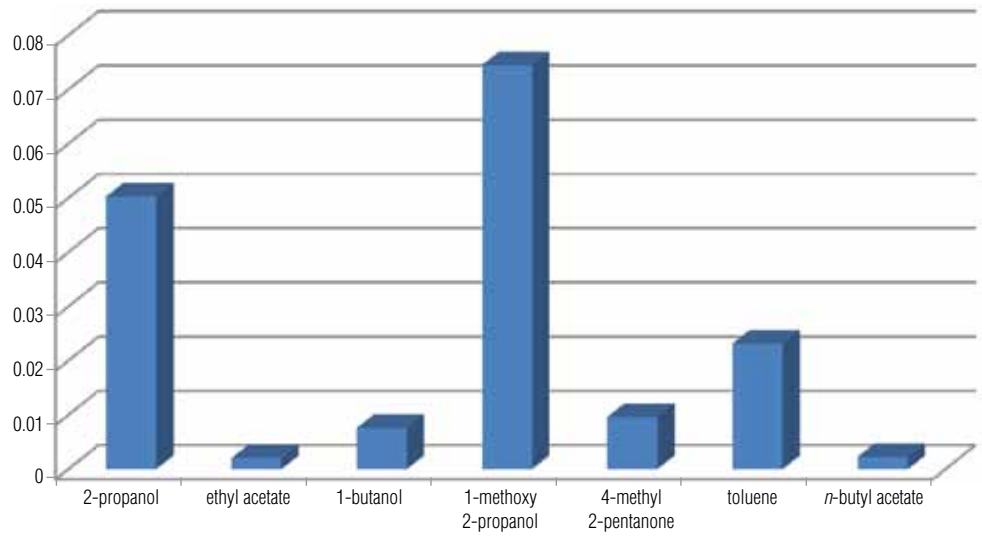

Figure 6. VOCs detected in croissant packaging and their relative distribution.

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