

Unattended Quantitative Determination of VOCs in Food Packaging Samples Using a Robotic Sampler for Standard Addition and Analysis

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Overview

Purpose: Exploring the possibility to perform a quantitative determination of volatiles components in food packaging in a completely automatic way.

Methods: The quantification of Volatile Organic Components (VOC) is performed by means of unattended automated standard addition method followed by headspace sampling and GC/MS analysis.

Results: The results show good correlation factors and limit of quantification lower than 0.01 mg/m² for the majority of components analyzed.

Introduction

The headspace analysis by means of a dedicated autosampler is a standard technique for the determination of volatile organic compounds possibly present in the food packaging materials. The packaging sample is generally cut into square pieces and placed in headspace vials for the incubation at determined temperature before the headspace sampling. The main problem for this kind of analysis is the quantification of volatile compounds present, as these samples are normally layered solids, generating adsorption and migration effects. The external calibration is not reliable as it doesn't consider the matrix effect, which is significant for these samples. The standard addition calibration is instead a reasonable quantification procedure for these difficult matrices, as it uses the real sample for the calibration procedure. Until now, preparation of the samples for the standard addition calibration has been performed offline, normally manually by the operator, before the headspace analysis of the samples. This was a time-consuming and error-prone procedure. The possibility of performing the sample preparation, by means of the same robotic sampler used for the headspace analysis, allows the automatic running of the quantification sequence in an unattended way. The detection and quantification is performed by means of a gas chromatograph coupled with a single quadrupole mass spectrometer.

Methods

Sample Preparation

The VOCs standards solutions that were used follow:

Residual Solvents in Packaging Material Mixture-1 7.14 % (v/v) (Sigma-Aldrich®).

Residual Solvents in Packaging Material Mixture-2 9.09 % (v/v) (Sigma-Aldrich).

The two solutions have been mixed together in order to have a single comprehensive stock solution vial.

The sequent sample preparation steps have been automatically performed by the Thermo Scientific TriPlus RSH autosampler. The tool exchange capability and the vortex mixing allowed for the dilution step, the standard addition step and the headspace analysis step to be combined together in the same sequence.

FIGURE 1. TriPlus™ RSH autosampler and Thermo Scientific TRACE 1310 GC with the Thermo Scientific ISQ mass spectrometer



Automatic standard dilution procedure :

The stock solution has been water diluted 1/1000. In this cycle, the autosampler takes an aliquot of stock solution and places it into an empty vial, adding the water up to final volume, in this case 1 mL, with a different volume syringe.

FIGURE 2. SW Parameters for the Dilution Step

Parameter Name	Value	Unit	Range	Default
Dilution 1 to 1000	Prepare			Prepare
Solvent with internal standard	Skip			Prepare
Solvent without internal standard	Skip			Prepare
Total Volume	1000	µL		1000
Internal standard	Omit			Include
Bottom sense internal stan...	On			Off
Height from bottom internal stan...	0.500	mm	0.000 - 30.000	0.500
Repetitions	1		1 - 3	1
Tool 10µL	LS2			
Tool 1000µL	LS1			
Dilution row tray	Tray 3			
Standard wash station	Standard Wash 1			
Large volume wash station	Large Wash 1			
Rinse cycles	2		1 - 15	2
Wash cycles	2		1 - 15	2
Aspirate pickup delay	3.000	s	0.000 - 15.000	3.000
Overflow rate	5.000	%	0.000 - 10.000	5.000
Delay After Filling Strokes	1.000	s	0.000 - 10.000	1.000
Solvent vial penetration depth	30.000	mm	15.000 - 44.000	44.000
Internal standard penetration de...	28.000	mm	15.000 - 30.000	28.000
Wash vial penetration depth	44.000	mm	15.000 - 44.000	44.000
Sample vial dispense depth	10.000	mm	5.000 - 10.000	8.000
Waste penetration depth	12.000	mm	10.000 - 30.000	12.000
Vortex mixer	Vortexer 1			
Vortex frequency	20.000	Hz	1.667 - 50.000	20.000

Automatic standard addition procedure:

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.

A first calibration, used to check the linearity of the system and the accuracy of the overall sample preparation procedure, has been performed adding automatically various (from 1 µL up to 5 µL) volumes of diluted solution to a set of empty vials. This step has been performed automatically by the autosampler before the headspace analysis of the vials.

For the quantification, by means of the standard addition method, a sample of packaging from commercial croissant has been cut in squared pieces of 48 cm² each. Five 20-mL sample vials have been prepared manually placing the foils in each vial.

The automatic standard addition has been performed by the sampler with the following scheme: vial 1 (sample); vial 2 (sample + 1 µL standard); vial 3 (sample + 3 µL standard); vial 4 (sample + 5 µL standard); vial 5 (sample + 7 µL standard). In order to keep the same conditions for all the vials, the autosampler injected the same compensation volume of water for each vial keeping the total added volume constant to 7 µL.

Separations

The sampling of the vials prepared has been done by means of headspace injection on the TRACE™ 1310 Gas Chromatograph, coupled with the ISQ™ mass spectrometer. The analysis data have been acquired using Thermo Scientific Xcalibur software (2.1. release).

The analysis of the sample has been performed in Total Ion Current for the identification of components. The quantification step has been run in SIM mode using the following masses: 31 m/z, 43 m/z, 45 m/z, 55 m/z, 56 m/z, 59 m/z, 91 m/z,

The column used for the separation of the VOCs is: TraceGOLD TG-624 column (60 m; 0.25 mm; 1.4 µm)

FIGURE 3. GC and HS Parameters

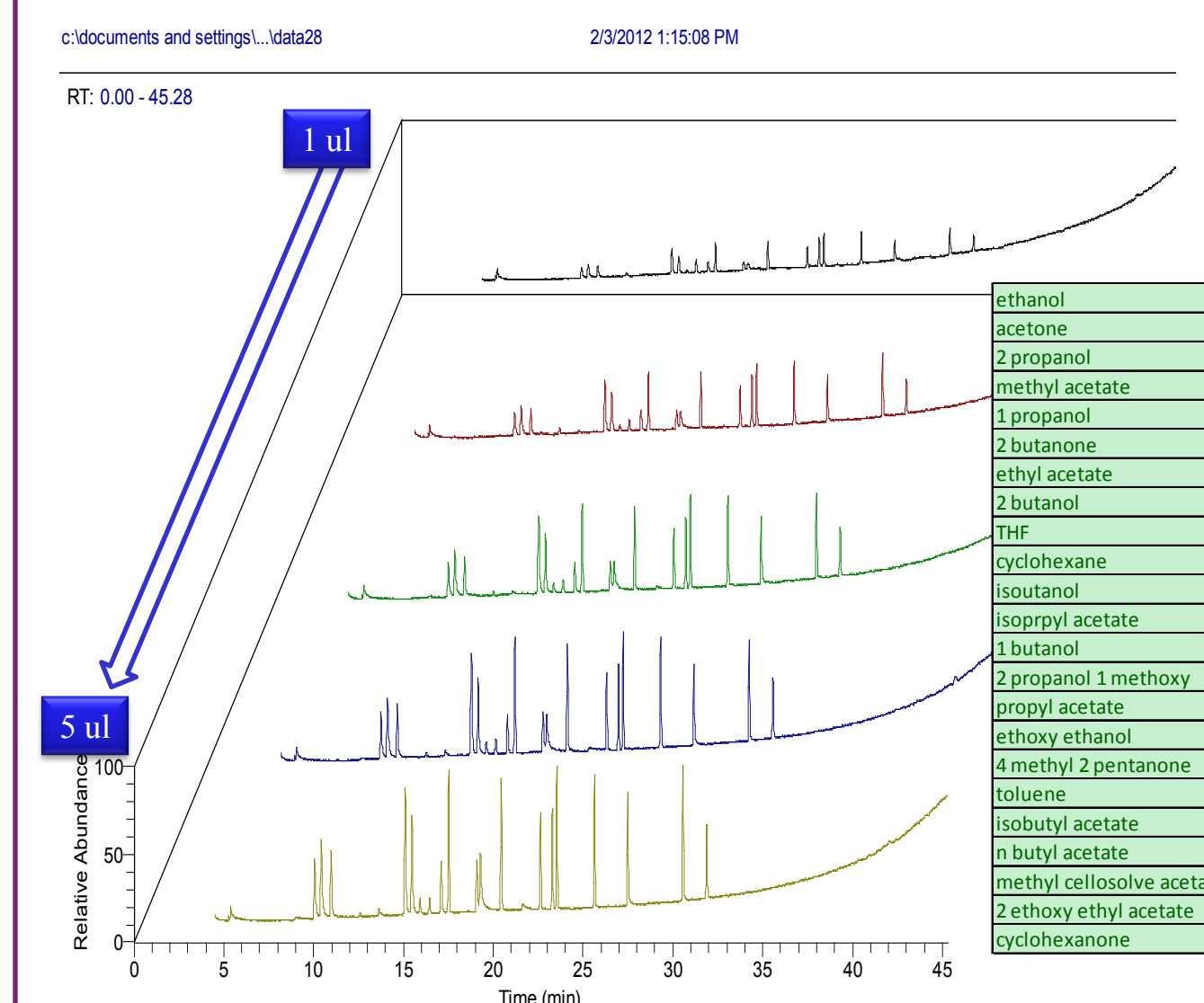
Oven Method	
Initial Temperature (°C):	35
Initial Time (min):	4
Number of Ramps:	1
Rate #1 (deg/min):	4
Final Temperature #1 (°C):	200
Hold Time #1 (min):	0
SSL Method	
Base Temperature (°C):	200
Mode:	split
Split Flow Flow (ml/min):	80
Carrier Method:	
Mode:	Constant Flow
Value (ml/min):	1
TriPlus RSH Method:	
Sample volume (µl):	1000
Incubation time (min):	15
Incubation temperature (°C):	80
Syringe temperature (°C):	120

Results

Linearity of Standard Addition

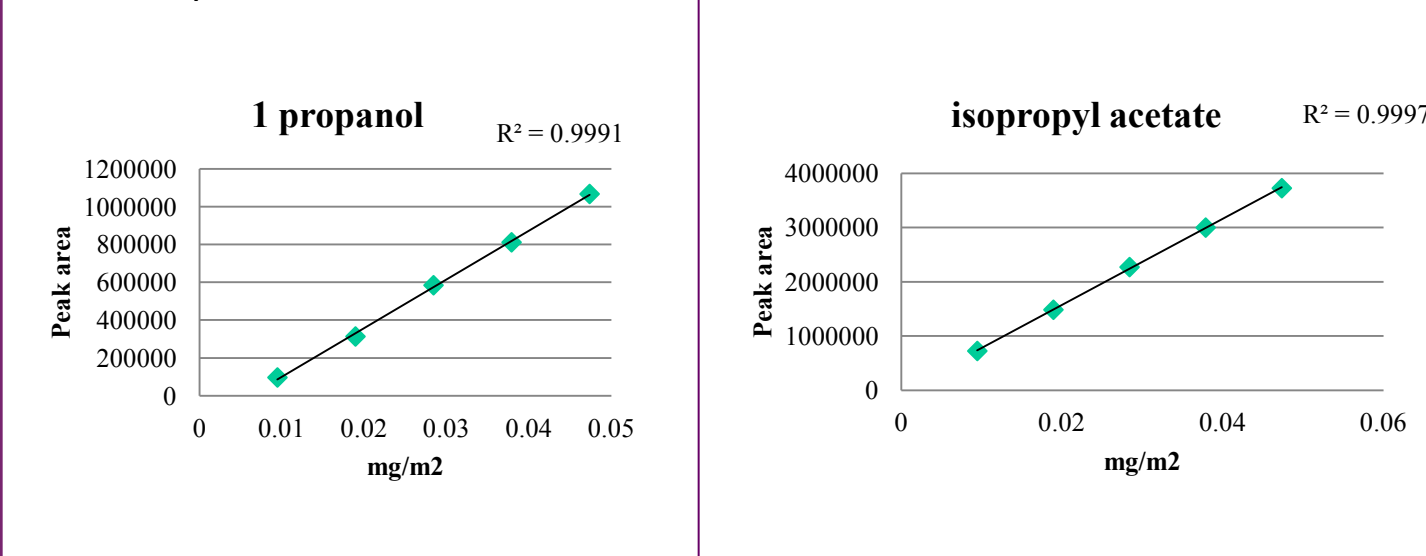
Figure 3 reports the list of components and the overlay of chromatograms obtained for each amount of standard addition volume (from 1 µL up to 5 µL) into empty vials.

FIGURE 3. Component List and Chromatogram Overlay



Converting the data of addition volumes into absolute amount, expressed in mg/m², assuming that the sample surface into the vial is 48 cm², the linearity of the system and the limits of quantification for all the components can be derived. The graphics in Figure 4 show a good linearity of system. Quantification limits below 0.01 mg/m² have been calculated for the majority of components (except the THF, the Ethanol, the Ethoxy Ethanol).

FIGURE 4. System Linearity for Some Components (1-propanol and isopropyl Acetate)

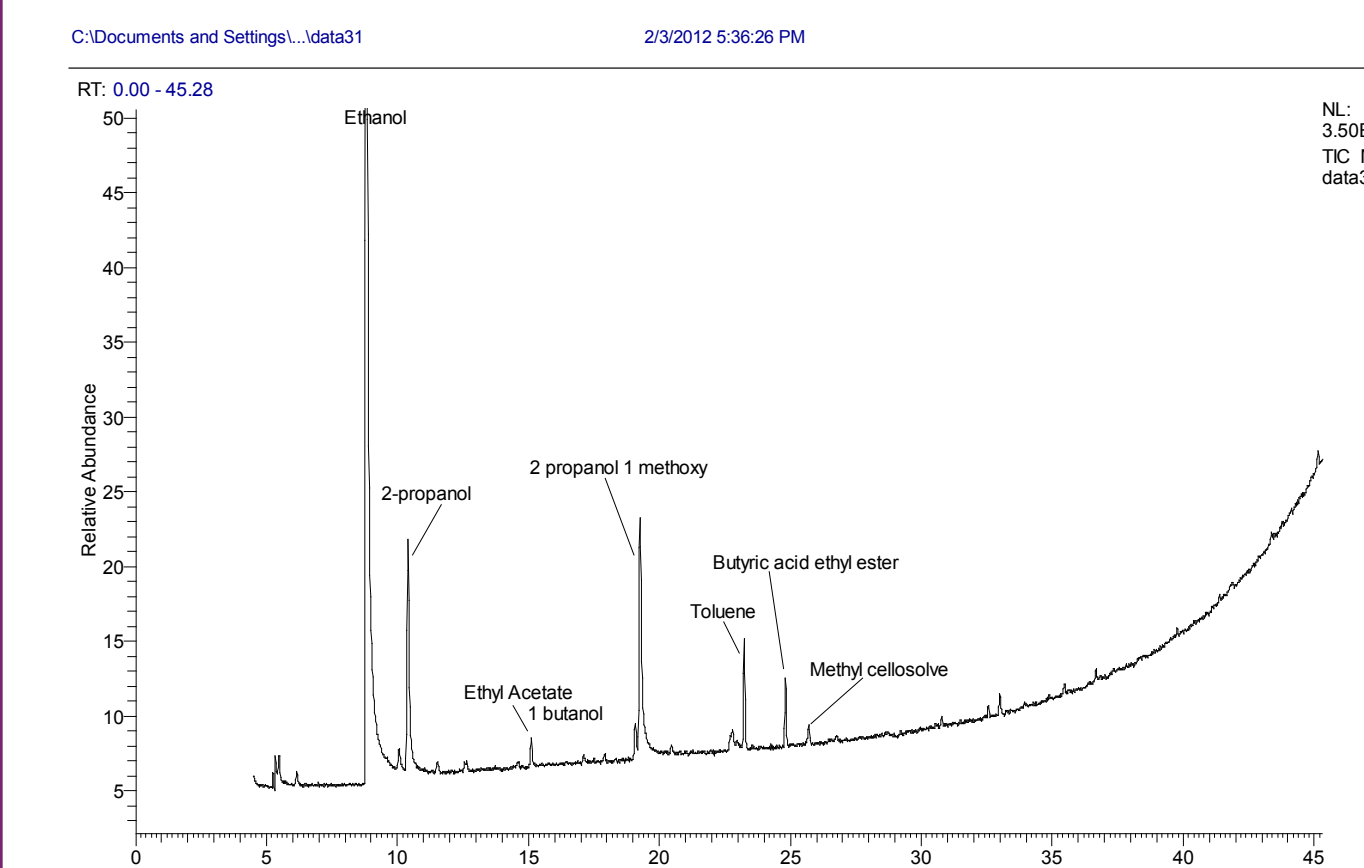


Sample Analysis (Components Identification)

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

In Figure 5, the presence of few residual solvents is observed. The larger Ethanol peak is realistically coming from the croissant itself as it is used as preservative.

FIGURE 5. Sample Full Scan Analysis by Headspace



Sample Analysis (Components Quantification)

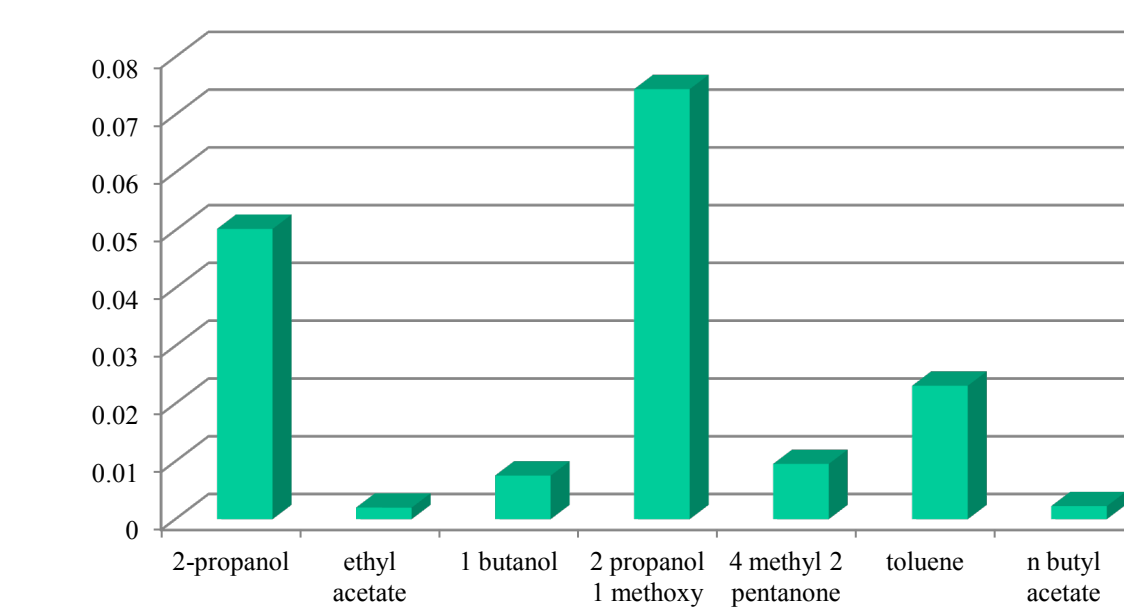
The quantification performed by means of the standard addition method has been carried out for the peaks identified in the chromatogram. In Figure 6, the results of the quantification is presented.

In Figure 7, the graphical representation of the quantification analysis shows that the two main residual solvents identified in the sample are 2-propanol 1-methoxy and 1-propanol. Their amount doesn't exceed the level of 0.1 mg/m², while the other detected residual solvents have been quantified in the level of 0.01 mg/m² or lower.

FIGURE 6. Quantification Results on Real Sample

component	ul added					area
	0	1	3	5	7	
2-propanol	3337694	4162371	6363394	7060114	8101360	
	0	0.009469	0.028406	0.047344	0.066281	calculated amount mg/m ²
ethyl acetate	302671	973347	2755297	4304253	6115361	
	0	0.007438	0.022313	0.037188	0.052063	calculated amount mg/m ²
1-butanol	385906	761497	1708139	2203362	3191062	
	0	0.007438	0.022313	0.037188	0.052063	calculated amount mg/m ²
2-propanol 1-methoxy	3873000	4854145	5683227	6258900	7857878	
	0	0.009469	0.028406	0.047344	0.066281	calculated amount mg/m ²
4-methyl 2-pentanone	374131	837187	1642593	2555176	3209676	
	0	0.009469	0.028406	0.047344	0.066281	calculated amount mg/m ²
toluene	1077304	1512873	2382486	2972530	3683690	
	0	0.007438	0.022313	0.037188	0.052063	calculated amount mg/m ²
n butyl acetate	190875	649615	1751135	2741910	3859582	
	0	0.007438	0.022313	0.037188	0.052063	calculated amount mg/m ²

FIGURE 7. VOCs Detected in Croissant Packaging and their Relative Distribution



Conclusion

The possibility to analyze and quantify VOCs in food packaging materials in a completely automated way has been presented. The combination of the sample preparation steps along with the analytical step in the same sequence allows high accuracy in quantification, minimizing the error prone manual manipulations, and high sample throughput. The overall sensitivity was below the 0.01 mg/m² for the majority of residual solvents analyzed.

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