FOOD ANALYSIS

QUALITATIVE ANALYSIS OF E-CIGARETTE LIQUIDS USING GAS CHROMATOGRAPHY / MASS SPECTROMETRY

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ABSTRACT

This application brief demonstrates the use of the Agilent Technologies 5977E benchtop GC/MS system for the qualitative analysis of e-cigarette liquids. The GC/MS is used in full scan mode for the tentative identification of major and minor components by comparing mass spectra to the NIST14 EI mass spectral database.

INTRODUCTION

The use of electronic cigarettes (e-cigarettes) is becoming more and more popular. E-cigarettes do not burn tobacco, but produce an aerosol from a battery powered heating element and a liquid mixture contained in a small cartridge.

The liquid mixture varies in composition but the main constituents are usually Propylene glycol (CAS # 57-55-6) and Glycerin (CAS# 56-81-5) along with flavour mixtures and nicotine (CAS # 54-11-5). The concentration of nicotine formulated in e-cigarette liquids varies and can range from 3 mg/mL to levels in excess of 20 mg/mL. As things stand in 2015, e-cigarettes are regulated as general consumer products. However, the European Commission is planning to introduce new legislation in 2016 – the EU Tobacco Products Directive (TPD). E-cigarette liquids containing up to 20 mg/mL of nicotine will be subject to the TPD.

A benchtop GC/MS system is an ideal analytical tool for the analysis of e-cigarette liquids since it can be used to both quantify major components (such as nicotine) and screen for minor components whose presence may be considered a health risk. Components can be tentatively identified by library searching their electron impact (EI) mass spectra against large, commercially available, data bases such as NIST14.

GC/MS Configuration:

- 7650A Auto-Liquid Sampler
- 7820A Gas chromatograph with EPC split / splitlless inlet
- 5977E Single Quadrupole Mass Spectrometer with inert ion source

Agilent Technologies

SAMPLE ANALYSIS

Samples of e-cigarette liquids were analyzed using an Agilent Technologies 5977E benchtop GC/MS system equipped with a 50-position auto-liquid sampler and an electronically pneumatic controlled (EPC) capillary split / splitless inlet. Samples of e-cigarette liquids were prepared as 1% (10mg/mL) solutions in Dichloromethane and injected in either split mode or splitless mode, in order to analyze the major and minor components, respectively. Data was acquired in full scan mode. The GC and MS analysis conditions are given in Table 1 and all data processing was performed using MassHunter software.

GC Conditions

Auto-liquid sampler	Agilent 7850A
Gas Chromatograph	Agilent 7820A
Column	Agilent 30m x 0.32 mm ID, 1.8 µm DB-624 [123-1334]
Inlet	EPC capillary split / splitless
Injection	1µL split 50 : 1 and 1µL split 5:1 ; 1µL splitless
Injection port liner	Split mode : Straight, Ultra Inert liner with glass wool [5190-2294]
	Splitless mode : Single taper, Ultra inert liner with glass wool [5190-2293]
Inlet temperature	280 °C
Purge Flow to Split Vent	(Splitless mode) 50 mL/min at 0.5 min
Gas saver	20 ml/min at 2.0 min
Carrier Gas	Helium, constant pressure mode, 4.0 psig
Oven program	50 °C (2.0 min hold), 10 °C/min to 240 °C (10 min hold)

MS Conditions

Mass Spectrometer	Agilent 5977E single quadrupole
Ion source	Inert
MS Transfer line temp	280 °C
Tune	Electron impact ionization Autotune, gain normalized
Gain	10
Scan Range	30 – 300 amu
MS Temperatures	Ion source 280 °C, Quadrupole 150 °C
Data processing	Mass Hunter Qual B.07.00, MassHunter Unknowns Analysis B.07.00

Table 1. Gas chromatograph and mass spectrometer conditions for the qualitative analysis of E-cigarette liquids

RESULTS

A sample of a mint flavoured e-cigarette liquid was analyzed using a 1µL injection with a 50 : 1 split ratio. The full scan total ion chromatogram (TIC) is shown in Figure 1 and the main components are labelled, as tentatively identified by library searching against the NIST14 EI mass spectral database. Data processing and library searching of TICs was performed using Mass Hunter Qual software.

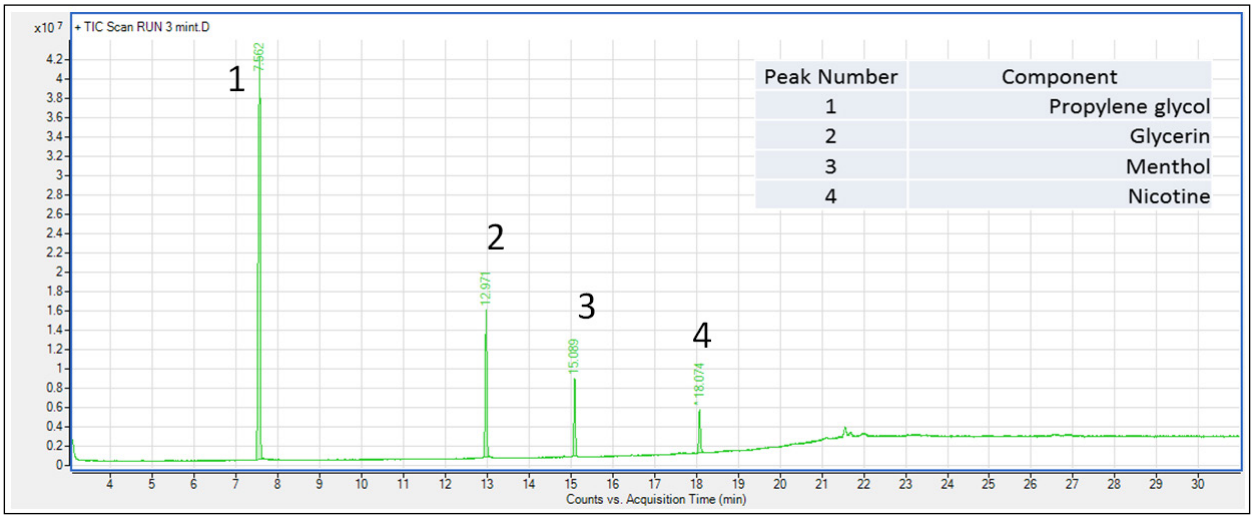

Figure 1. Full scan TIC of a mint flavoured e-cigarette liquid, 1 µL injected of a 1% solution in Dichloromethane, injected with a 50 : 1 split ratio.

A sample of a 'Tutti Frutti' flavoured e-cigarette liquid was analyzed using a 1µL injection with a 50 : 1 split ratio and a 1 µL injection in splitless mode. The full scan TICs are shown in Figures 2 and 3, respectively. The higher sample amount transferred to the column in splitless mode enabled the tentative identification of some of the minor flavouring components of the e-cigarette liquid by library searching against the NIST14 EI mass spectral database.

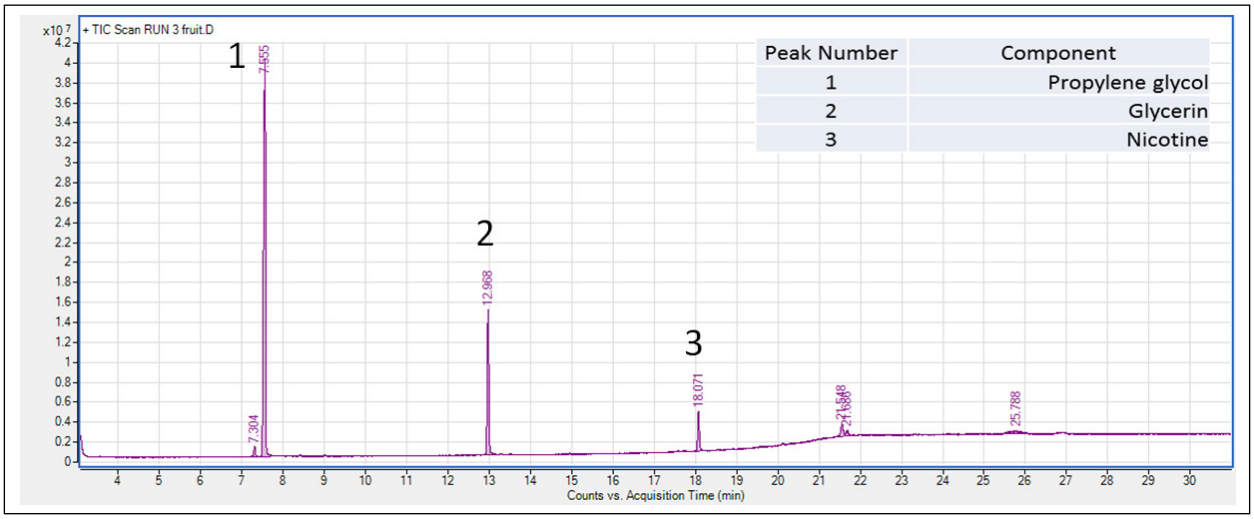

Figure 2. Full scan TIC of a 'Tutti Frutti' flavoured e-cigarette liquid, 1 µL injected of a 1% solution in Dichloromethane with a 50 : 1 split ratio.

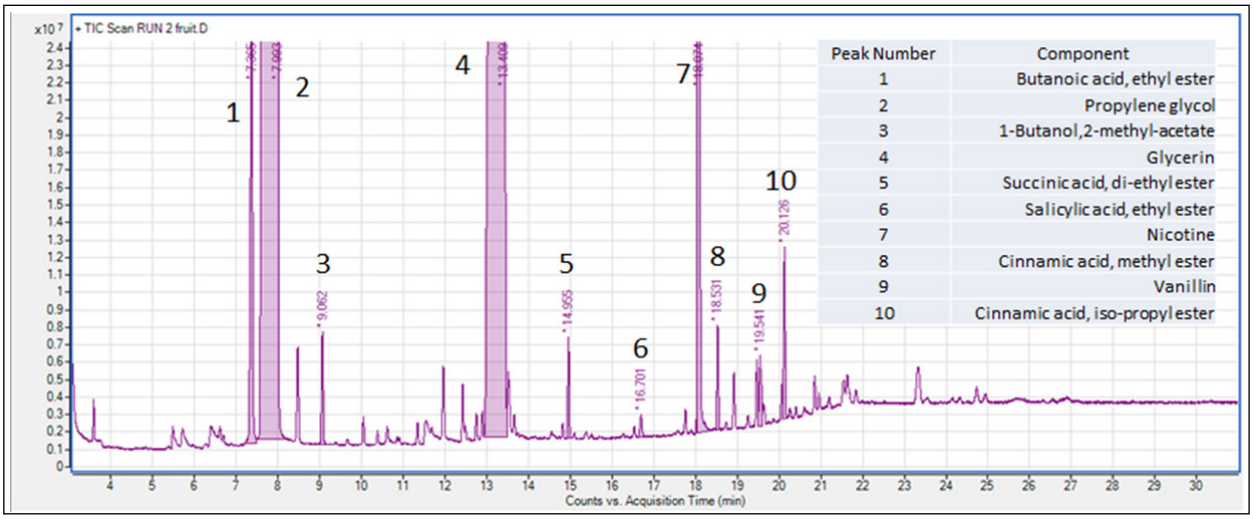

Figure 3. Full scan TIC of a 'Tutti Frutti' flavoured e-cigarette liquid, 1 µL splitless injection of a 1% solution in Dichloromethane

In order to demonstrate the sensitivity of the 5977E MSD and to demonstrate the tentative identification of trace components, a sample of 'Tutti Frutti' flavoured e-cigarette liquid was spiked with 5 components considered to be potentially harmful by inhalation : Diacetyl [CAS# 431-03-8], Acetylpropionyl [CAS# 600-14-6], Acetoin [CAS# 513-86-0] and Diethylene glycol [CAS# 111-46-6] at 0.01% v/v and Ethylene glycol [CAS# 107-21-1] at 0.1 % v/v.

The full scan TIC of the un-spiked (blank) e-cigarette liquid is shown in the upper chromatogram and the TIC of the spiked e-cigarette liquid is shown in the lower chromatogram in Figure 4, respectively.

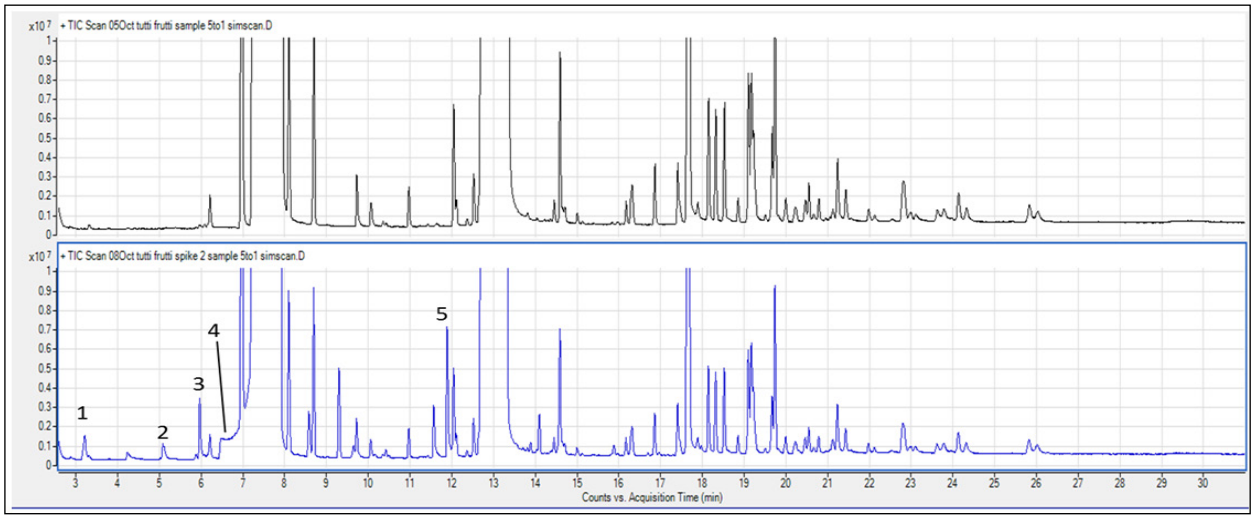

Figure 4. Full scan TICs of a 'Tutti Frutti' flavoured e-cigarette liquid, 1 µL injections of a 1% solution in Dichloromethane with a 5 : 1 split ratio. Upper chromatogram: Un-spiked, Lower Chromatogram : Spiked with 0.01% v/v of Diacetyl [1], Acetylpropionyl [2], Acetoin [3] and Diethylene glycol [5] ; 0.1% v/v Ethylene glycol [4]

The peak averaged, background subtracted EI mass spectra of the 5 components are shown in Figure 5. These spectra were searched against the NIST14 EI mass spectral database. The EI mass spectra in Figure 5 are annotated with the library match scores, out of 1000. All hits were #1 in the NIST14 library search results list.

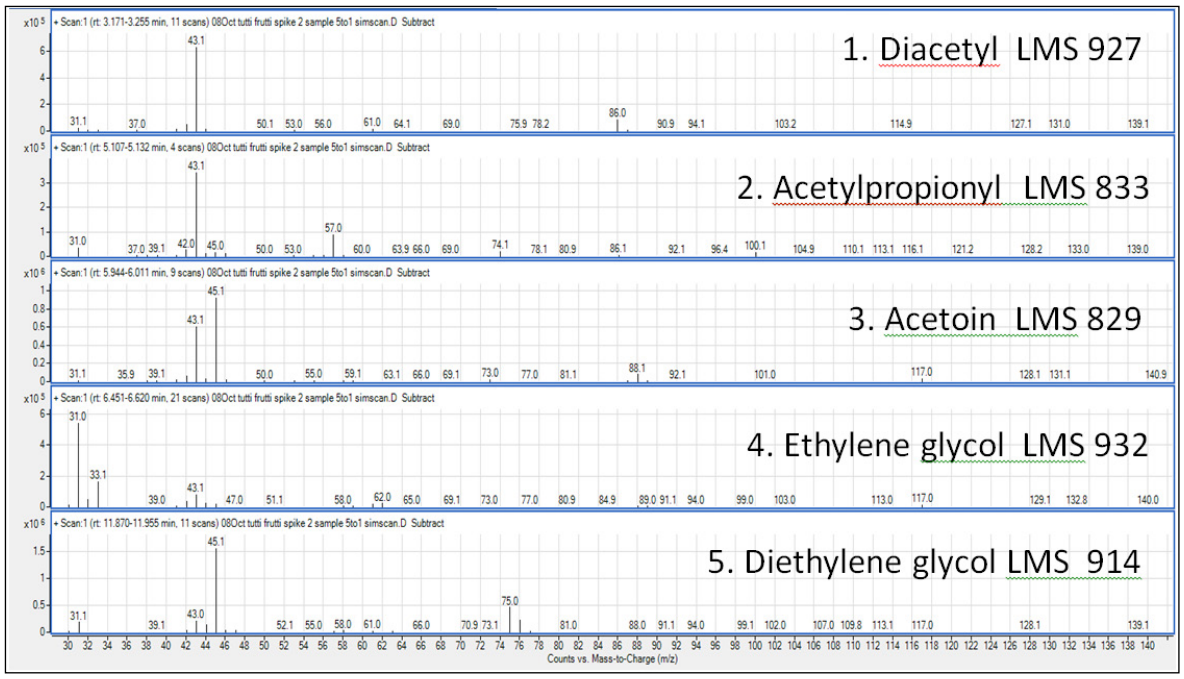

Figure 5. Peak averaged, background subtracted spectra of the 5 components labelled in Figure 4. The numbers are the library match scores vs the NIST14 EI database, scores out of 1000. All hits were #1 in the NIST14 library search results list.

Analysing flavoured e-cigarette liquids can give rise to complex chromatograms and it is quite likely that many components will overlap or co-elute. Co-eluting components will not be visible in the total ion chromatogram and therefore may be missed if a library search is made based on the TIC. MassHunter software includes, as standard, a powerful deconvolution and library search program which can tentatively identify co-eluting components by library searching their deconvoluted mass spectra. This program is MassHunter 'Unknowns Analysis'.

An example of using Unknowns Analysis to perform deconvolution and library searching is shown in Figure 6 which displays the TIC for the spiked Tutti Frutti e-cigarette liquid (black trace), enlarged between 18 and 20 minutes. The TIC shows a cluster of 3 peaks eluting between 19.10 and 19.30 minutes, yet the results of the deconvolution process clearly show the presence of 5 components (red peaks). The 5 components were tentatively identified by library searching their deconvoluted mass spectra against the NIST14 MS database. The results are shown in Table 2, the match factors are scores out of 100.

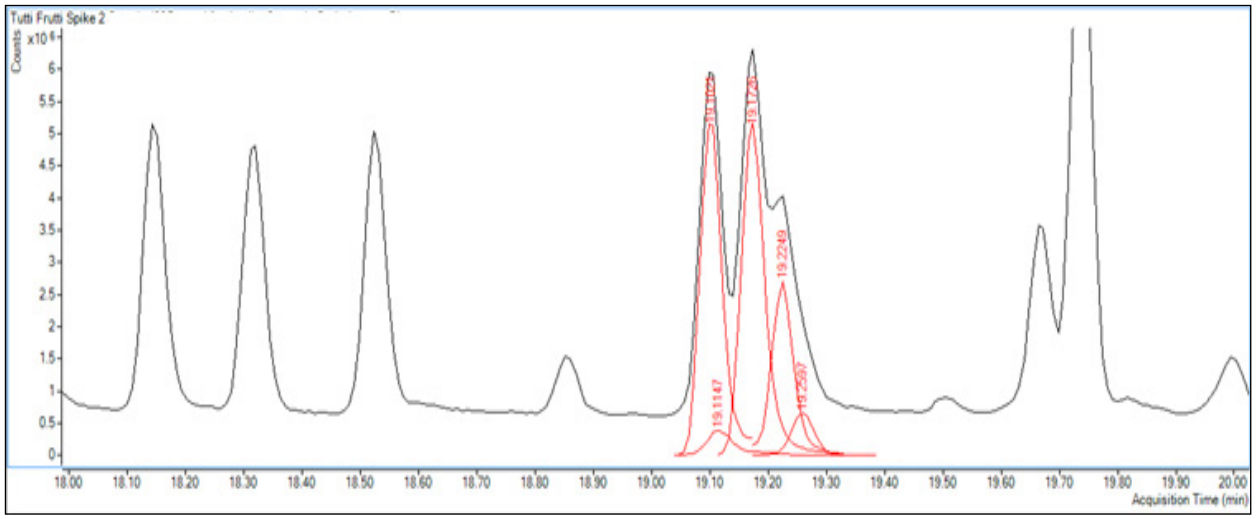

Figure 6. Spiked Tutti Frutti e-cigarette liquid chromatogram enlarged between 18 – 20 minutes. TIC (black) and deconvoluted components (red) shown for peaks eluting between 19.1 - 19.3 minutes, using the MassHunter Quant 'Unknowns Analysis' program.

Components

Component RT	Compound Name	Formula	CAS#	Match Factor	Library File
19.1021	Butanedioic acid, diethyl ester	C8H14O4	123-25-1	80	NIST14.L
19.1147	Pyridine, 3-(3,4-dihydro-2H-pyrrol-5-yl)-	C9H10N2	532-12-7	83	NIST14.L
19.1726	Vanillin	C8H8O3	121-33-5	98	NIST14.L
19.2249	Butanedioic acid, diethyl ester	C8H14O4	123-25-1	90	NIST14.L
19.2597	2-Propenoic acid, 3-phenyl-, ethyl ester	C11H12O2	103-36-6	92	NIST14.L

Table 2. MassHunter Quant 'Unknowns Analysis' library search results for the deconvoluted component mass spectra eluting between 19.1 - 19.3 minutes. NIST14 scores are out of 100.

CONCLUSIONS

The increasing popularity of e-cigarettes and the very large number of different types of e-cigarette liquids currently available creates a requirement for a robust, reliable and sensitive instrument for the analysis of GC-amenable components. The Agilent 5977E benchtop GC/MS system provides high-efficiency separations of complex mixtures by capillary gas chromatography coupled with the high sensitivity of the 5977 mass spectrometer. E-cigarette liquid mixtures which predominately contain Propylene Glycol and Glycerin – with or without Nicotine - may also contain small amounts of different flavour mixtures. The EI mass spectra of the major and minor components of e-cigarette liquids can be automatically searched against large, commercially available, mass spectral databases such as NIST14. MassHunter Qual software provides fast and flexible data processing that can be customized to meet the needs of individual users.

Additionally, MassHunter Unknowns Analysis provides the ability to automatically deconvolute and library search components in complex mixtures revealing additional components which may be unobserved when reviewing the total ion chromatogram.

Printed in EU, 27 October, 2015
5991-6412EN

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