



Analytical Comparison of Similar Perfumes Using the Polyarc® System

Application Note

Fragrances

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Abstract

Two complex perfumes advertised to have a similar scent were analyzed with the Polyarc/FID - mass spectrometer split system to allow for single injection identification and quantification. The two perfumes had many compounds in common, and the concentrations are compared in this application note.

Introduction

The global perfume market is worth in excess of 37 billion USD (Business Wire, 2017), and there is a growing interest in fragrance duplication, which allows companies to duplicate high-quality products. Most fragrance duplication methods currently rely on gas chromatography/mass spectrometry (GC/MS). This methodology is effective at identifying compounds, but accurately quantifying requires the analyst to calibrate for each individual compound. This is often difficult or unfeasible due to the unavailability of standards and the high number of individual standards required. Because of this, GC/MS is primarily used to identify the compounds and estimate amounts, and the duplication process becomes iterative and time consuming, employing the use of perfumers and GC/olfactometry.

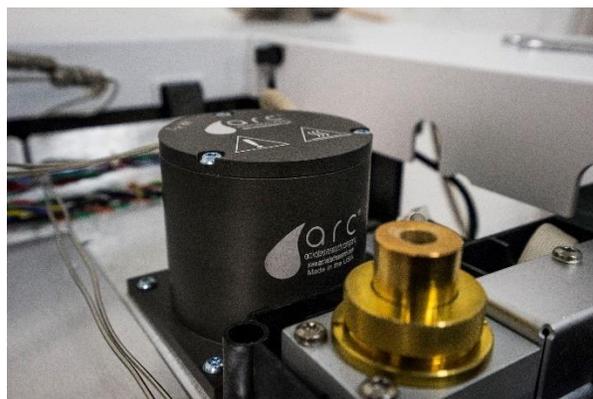
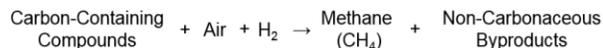


Figure 1. Polyarc System on an Agilent 7890 GC.

In this application note, it is shown how the Polyarc System (Figure 1) can be used to save time by characterizing perfumes both quantitatively and qualitatively in a single injection. The Polyarc is a catalytic microreactor that is an intermediate step after the column and before detection in the FID, in which all organic compounds are converted to methane through a two-step catalytic reaction:



The response-per-carbon in the FID is equivalent for all molecules because the FID only ionizes methane. Thus, the relative response of the FID to a single internal standard (or an external standard) can be used to quantify all other components in the mixture, without the need for calibration factors.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet (Agilent G3454-64000), capillary-optimized FID, mass spectrometer (Agilent 5973), and Polyarc[®] reactor (ARC PA-RRC-A02) were used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air purified with an ARC CO₂ trap (ARC PA-COT-R31) and H₂ from a VICI DBS hydrogen generator were supplied to the ARC electronic flow control module (PA-MFC-B09) and to the FID. The effluent of the GC column was connected to an Agilent 3-way CFT splitter (G3183-60500). The MS was connected to the splitter via a retention gap column (Agilent, 160-2635-5, 0.61 m, 0.1 mm ID). The inlet capillary to the Polyarc[®] was connected directly to the splitter. The splitter was controlled by an EPC (with restrictor frit removed) set to 4 psig.

GC conditions

Front inlet	Split/splitless
Inlet temperature	300 °C
Inlet liner	Agilent 5190-3165
Carrier gas	He; 40 cm/sec constant flow
Septum purge flow	3 sccm
Oven	40 °C (hold 4 min) to 250 °C at 15 °C/min (hold 25 min)
Column	HP-5MS (30 m × 0.25 mm × 0.25 µm film)
Syringe	10 µL
Injection volume	0.5 µL

FID conditions

Temperature	315 °C
H ₂	1.5 sccm
Air	350 sccm
Makeup	5 sccm (He)

Polyarc[®] System conditions

Setpoint	293 (450 °C actual temp.)
H ₂	35 sccm
Air	2.5 sccm

Analysis Procedure

Methane produced from combustion-reduction reactions in the Polyarc is measured with the FID resulting in an equimolar carbon response. The concentration of each analyte can therefore be calculated from the concentration/Area ratio of an arbitrary standard using the following equation:

$$C_A = C_s \left(\frac{Area_A}{Area_S} \right) \left(\frac{\#C_S}{\#C_A} \right) \left(\frac{MW_A}{MW_S} \right)$$

where:

C_A = Mass concentration of analyte
 $Area_A$ = Integrated peak area of the analyte
 MW_A = Molecular weight of the analyte
 MW_S = Molecular weight of the standard
 $\#C_S$ = Number of carbon atoms for standard
 $\#C_A$ = Number of carbon atoms for analyte

More Details can be found within the "Quantification with the Polyarc.pdf" on the web at <https://www.activatedresearch.com/documents/>

Results and Discussion

Two perfume samples were analyzed with the GC/MS-Polyarc-FID described. Perfume 2 was formulated as a generic to mimic the aroma of Perfume 1 at a lower price point. They were directly injected into the system without dilution resulting in the chromatograms in Figures 2 and 3. Peaks were identified using simultaneous data collection from a mass spectrometer and NIST library matches to fragmentation patterns (see Table 1 for identifications and quantification results).

Analyte	Perfume 1		Perfume 2	
	Area	Concentration (µg/mL)	Area	Concentration (µg/mL)
Ethanol	2.07E+10	471442	2.23E+10	508347
D-Limonene	2.32E+08	3130	8.40E+07	1133
1-Propanol, 2-(2-hydroxypropoxy)-	1.36E+08	3021	5.12E+08*	11337*
Linalool	3.45E+08	5263	2.79E+08	4263
Phenylethyl Alcohol	2.40E+08	3631	7.77E+07	1175
2-Hexene, 6,6-dimethoxy-2,5,5-trimethyl-	7.20E+07	1207	4.07E+07	683
Citronellol	7.02E+07	1085	2.58E+07	400
Geraniol	2.43E+08	3718	4.88E+07	746
Octanal, 7-hydroxy-3,7-dimethyl-	7.89E+07	1346	5.64E+07	961
2-Buten-1-one, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-, (E)-	2.69E+06	39	1.64E+06	24
2-Cyclopenten-1-one, 3-methyl-2-(2-pentenyl)-, (Z)-	3.05E+06	45	5.75E+06	85
2(3H)-Furanone, 5-hexyldihydro-	1.03E+07	174	2.46E+06	41
Butanoic acid, 1,1-dimethyl-2-phenylethyl ester	3.66E+07*	569*	2.54E+07	396
Butylated Hydroxytoluene	4.62E+06	67	4.77E+06	69
Lilial	1.25E+08	1805	1.51E+08	2175
1-(2-Methyl-4-propoxy-phenyl)-ethanone	1.33E+08*	1938*	5.98E+07*	873*
Cyclopentaneacetic acid, 3-oxo-2-pentyl-, methyl ester	9.36E+08*	16136*	1.88E+08	3248
Octanal, 2-(phenylmethylene)-	2.03E+08	2901	2.85E+08	4074
Isopropyl myristate	3.53E+08	5562	9.15E+07	1441
Oxacycloheptadec-8-en-2-one, (8Z)-	2.30E+07	359	8.39E+06	131

* Peaks tentatively quantified

Table 1: Concentration comparison for common compounds between Perfume 1 and Perfume 2

Table 1 shows the mass concentrations of compounds that are common in Perfume 1 and Perfume 2. In total, Perfume 1 showed 106 detectable compounds, and Perfume 2 showed 45 detectable compounds; 23 compounds were common on both mixtures. It is apparent from the data in Table 1 and the chromatograms in Figures 2 and 3 that there are higher concentrations measured in Perfume 1 for nearly all compounds. The area for ethanol, which comprised approximately 75% of each sample, was similar for both samples (8% difference), indicating similar amounts of ethanol used to dilute aroma molecules.

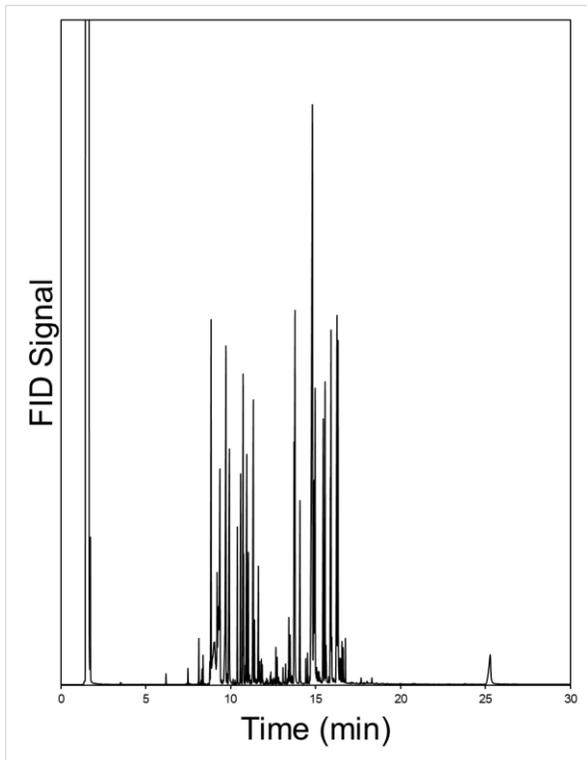


Figure 2. FID Chromatogram of Perfume 1 using the Polyarc System.

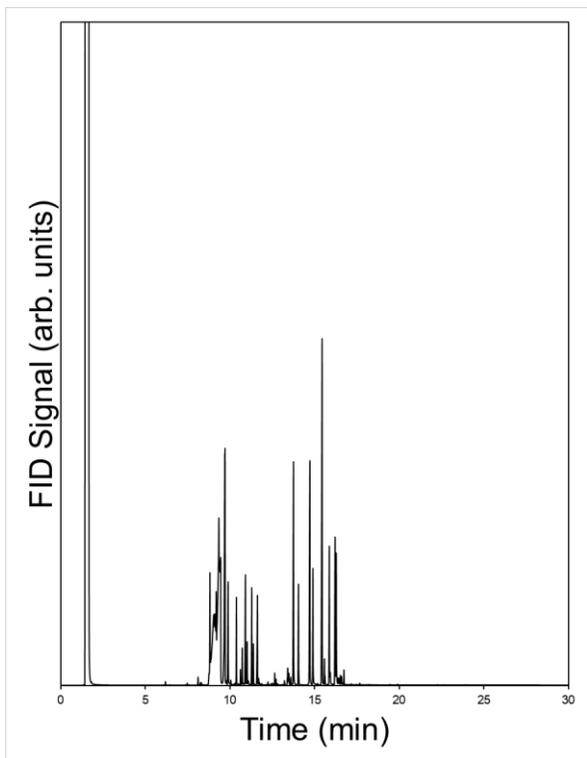


Figure 3. FID Chromatogram of Perfume 2 using the Polyarc System.

Conclusions

The Polyarc System is a useful tool for the analysis of fragrances because of the complexity associated with these samples and difficulties of obtaining calibration standards. Traditional methods for fragrance duplication include time-consuming calibrations of each individual component. With the Polyarc System, this process is greatly simplified because every molecule gives a uniform (equimolar) response in the FID. This can increase the accuracy of fragrance duplication and save time and money.

Contact Us

For more information or to purchase a Polyarc® system, please contact us at 612-787-2721 or contact@activatedresearch.com.

Please visit our website for details and additional technical literature, www.activatedresearch.com.

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