Accurate Fragrance Duplication with a Single Injection using the Polyarc® System

Application Note

Flavors and Fragrances

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Abstract

A complex test mixture containing 21 fragrance components was analyzed with the Polyarc system. In a blind study, the Polyarc was shown to provide accurate fragrance component concentrations with a single injection and without the need for calibration of the system. The method using the Polyarc was more accurate than an uncalibrated GC/MS method for 20 out of 21 of the components.

Introduction

Fragrance duplication requires knowledge of the exact concentration of molecules in complex fragrance mixtures. To obtain this, gas chromatography/mass spectrometry (GC/MS) is typically used. While GC/MS is highly useful for determining the identity of molecules in a mixture, it not as efficient at quantifying molecules, especially when standards are not available or cumbersome. Fragrances will contain several components chosen from more than 1,000 different species, therefore it is impractical to create calibration curves for each independent component. GC/MS is used to identify and *estimate* the amount of each component rather than provide exact quantitative concentrations.

In this application note, we describe the use of the Polyarc® system (Figure 1) coupled with a flame ionization detector (FID) to accurately quantify complex fragrance mixtures using a single injection without using calibration standards. The Polyarc converts all carbon-containing molecules to methane with the two-step reaction:

$$\text{Carbon-Containing Compounds} + \text{Air} + H_2 \rightarrow \text{Methane } (CH_4) + \text{Non-Carbonaceous Byproducts}$$

where every mole of carbon is converted to one mole of methane. Then, the FID response-per-carbon atom is equivalent for all organic molecules. This allows quantitative information to be obtained as long as the molecular weight and number of carbon atoms can be determined by a MS. Here, we used a split system to simultaneously identify with the MS and quantify with the Polyarc.

Figure 1. Polyarc System installed in the back detector position next to an FID on an Agilent 7890 GC.

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-SYC-403) were used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air (zero grade, Praxair) and H_2 (99.999%, Praxair) were supplied to the ARC electronic flow control module (PA-MFC-A09) and to the FID. The effluent of the GC column was connected to an Agilent 3-way CFT splitter (ARC p/n/ PA-SPL-KIT). 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.

Samples were injected directly into the GC without the use of an internal or external standard.

GC conditions

Front inlet	Split/splitless 50:1 split
Inlet temperature	250 °C
Inlet linter	Agilent 18740-80190
Carrier gas	He; 1 sccm constant flow
Septum purge flow	3 sccm
Oven	80 °C (hold 2 min) to 275 °C at 5 °C/min (hold 30 min)
Column	DB-5 UI (30 m × 0.25 mm × 1 µm film)
Syringe	10 µL
Injection volume	0.5 µL

FID conditions

Temperature	300 °C
H_2	1.5 sccm
Air	350 sccm
Makeup	20 sccm (He)

Polyarc® System conditions

Setpoint	293 °C
H_2	35 sccm
Air	2.5 sccm

Results and Discussion

A fragrance mixture with 21 components (see Table 1) was injected into the system described above and the Polyarc/FID chromatogram is shown in Figure 2. The test mixture was a neat mixture of fragrance components that did not contain any solvents. In a blind study, the concentration of each component was determined with the Polyarc (Table 1, column labeled 'Polyarc'). Then, the actual concentrations of the molecules were revealed, and the difference between the actual concentrations and those determined with the Polyarc were calculated. On average, the Polyarc-determined concentrations were less than 5% (relative) different than the actual gravimetric concentrations. Furthermore, the Polyarc method was more accurate than the MS-only method for 20 out of 21 components.

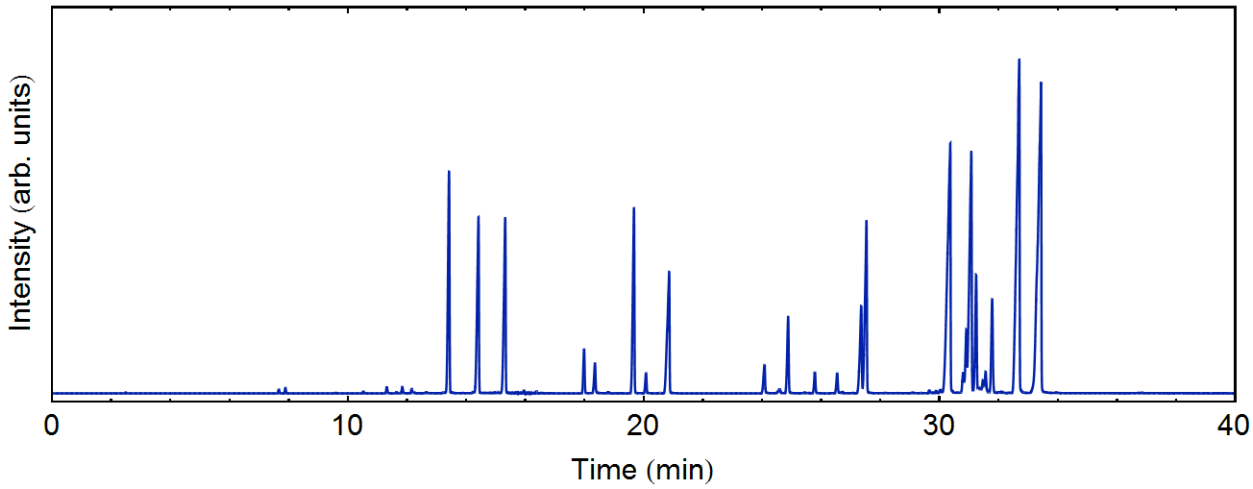

Figure 2. Polyarc/FID chromatogram for the analysis of a fragrance mixture (neat).

Description	Measured [1]	Polyarc Neat [2]	Polyarc Extract	Uncalibrated Neat	Polyarc Neat Δ	Uncalibrated Neat Δ
	%	%	%	%	Δ	Δ
CIS-3-HEXENOL (LEAF ALCOHOL)	0.10	0.10	0.11	0.03	0.00	0.07
ETHYL-2-METHYLBUTYRATE	0.10	0.08	0.13	0.03	0.02	0.07
BENZALDEHYDE	0.10	0.12	0.24	0.09	0.02	0.01
CIS-3-HEXENYL ACETATE	0.10	0.09	0.15	0.04	0.01	0.06
DELTA DECALACTONE	0.55	0.53	0.49	0.39	0.02	0.16
GAMMA OCTALACTONE	0.50	0.50	0.51	0.32	0.00	0.18
GAMMA DECALACTONE	0.53	0.52	0.46	0.43	0.01	0.10
STYRALLYL ACETATE (GARDENOL)	1.01	1.02	1.32	0.88	0.01	0.13
VELTOL PLUS (ETHYL MALTOL)	0.98	0.95	0.20	0.61	0.03	0.38
VANILLIN	1.00	0.96	0.25	0.83	0.04	0.17
ORANGE TERPENES (NATURAL)	5.04	4.78	6.06	4.26	0.26	0.78
DIHYDRO MYRCENOL	5.01	5.01	5.59	3.65	0.00	1.36
LINALOOL	4.99	4.89	5.67	3.41	0.10	1.58
LINALYL ACETATE	5.02	4.95	5.11	4.01	0.07	1.01
HYDROXYCITRONELLAL PURE	5.00	4.87	2.38	3.31	0.13	1.69
ALDEHYDE C-16 PURE	5.01	5.01	5.97	4.29	0.00	0.72
LYSMERAL (LILIAL)	5.00	4.90	4.72	6.12	0.10	1.13
BENZYL BENZOATE	15.01	16.15	16.56	18.17	1.14	3.16
HEDIONE (METHYL DIHYDROJASMONATE)	14.97	15.48	18.00	23.62	0.51	8.64
ISO E SUPER (MCM 50)	14.99	14.89	13.66	8.72	0.10	6.28
HEXYL CINNAMIC ALDEHYDE	14.99	14.20	12.40	16.81	0.79	1.82
Total	100	100	100	100		

[1] Mixture components are not 100% pure.

[2] Polyarc reported results have been slightly modified from the original report to remove analytes that were not of interest for the purpose of this discussion. The Alpha-pinene and beta-myrcene are impurities present in other components, and were not directly measured.

Table 1. Comparison of actual concentrations (measured) with those determined with the Polyarc® system and also an uncalibrated MS method. The Polyarc is more accurate than the MS for 20 out of 21 components.

Analysis Procedure

The area-per-mol of carbon is equivalent for all carbon-containing analytes because every molecule is completely converted to methane. This property allows for the determination of the concentration of any analyte without the need for standards. Analyte concentrations were calculated using the following formula:

$$C_A = \frac{(Area_A \cdot RMRF_A)}{\sum_{i=1}^{n}(Area_i \cdot RMRF_i)} * 100 \quad (8)^*$$

$$RMRF_A = \left(\frac{Mw_A}{Mw_S}\right)\left(\frac{\#C_S}{\#C_A}\right) \quad (2)^*$$

where:

C_A = Wt. % of analyte
$Area_A$ = Integrated peak area of the analyte
Mw_A = Molecular weight of the analyte
Mw_S = Molecular weight of the reference molecule (any component can be chosen)
$\#C_S$ = Number of carbon atoms for reference molecule
$\#C_A$ = Number of carbon atoms for analyte
RMRF = Relative mass response factor

*See "Quantification with the Polyarc.pdf" at https://www.activatedresearch.com/documents/ for more information.

Conclusions

The Polyarc system is useful for the analysis of fragrances because it can provide more accurate results than using a GC/MS alone. This may lead to quicker fragrance duplication as more accurate results reduce the time required for fragrance finalization. The Polyarc is the only known technique that is able to quantify accurately without standards. Future work should explore the wide range of fragrance analyses that the Polyarc is applicable to.

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.

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