LabWorks APPNOTE

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Analysis of Scented Crayons Using Direct Thermal Extraction with Gas Chromatography-Mass Spectrometry

John R. Stuff and Jaqueline A. Whitecavage

GERSTEL, Inc., 701 Digital Drive, Suite J, Linthicum, MD 21090, USA

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Abstract

Scented products, including car air fresheners, soaps and detergents, candles, and even garbage bags, are ubiquitous in our everyday lives. They are primarily intended to cover up malodors but can also enhance one's mood or be used in aromatherapy.

Thermal desorption is an introduction technique for gas chromatography that can be used for a wide variety of applications, including the analysis of fragrance compounds in consumer products. Options for thermal desorption include direct thermal extraction, Twister, Thin Film SPME, air sampling, and direct injection of liquids.

For scented products, the level of fragrance compounds in the product may need to be determined for quality control purposes or to see how long the compounds stay active (shelf life). Other components of scented products can also be determined using thermal desorption techniques.

This study used direct thermal extraction to determine fragrance compounds in scented crayons purchased at a local store.

Introduction

Direct thermal extraction (DTE) is a technique in which a solid or liquid sample (in a suitable holder) is heated with inert gas flow, and the evolved analytes are trapped. In an online system, the thermal desorber is used to heat and provide inert gas flow, and the analytes are trapped in the GERSTEL CIS 4 inlet liner. The analytes can be trapped cryogenically or on a sorbent. After analyte trapping is complete, the trap is rapidly heated to transfer the analytes onto the head of the GC column as a narrow band to provide optimum chromatographic performance. A sample size of 10-50 mg is typically used for this technique. The experimental variables that need to be optimized are extraction temperature, extraction time, and gas flow rate across the sample. Since there is very little dilution (split) of the analytes before entering the GC column, this technique can provide very low detection limits, even with the relatively small sample size.

This study uses the GERSTEL MPS LabWorks Platform with CIS and TDU to determine fragrance compounds in scented crayons from a local store.

Experimental

Instrumentation

GERSTEL LabWorks Platform, MPS with Peltier cooling option, Agilent 8890 GC/5977B Inert plus MSD.

Analysis Conditions LabWorks Platform

TDU	Splitless
	40 °C (0 min), 80 °C/min, 80 °C (5.0 min)
TDU Transfer	Ramped
CIS 4	Split 10:1
	Tenax® TA
	10 °C (0 min), 12 °C/s, 280 °C (3.0 min)

Analysis Conditions Agilent 8890 GC

Pneumatics	He, P_i = 7.1 psi (MSD)
	Constant flow = 1.0 ml/min
Column	30 m DB-5MS UI (Agilent)
	d_i = 0.25 mm, d_f = 0.25µm
Oven	40 °C (1.0 min), 15 °C/min, 280 °C (3 min)

Sample/Standard Preparation

Sixteen scented crayon samples were analyzed. The scents were banana, chocolate, mint, licorice, coconut, strawberry, melon, watermelon, orange, blueberry, cherry, raspberry, dragon fruit, apple, grape, and mango.

Approximately twenty milligrams of sample were weighed into a TDU microvial. A photo of a microvial is shown in Figure 1. The microvials were placed into empty TDU tubes, fitted with transport adapters, and placed into a 40-position TDU tray. No further sample preparation was needed.

Figure 1: TDU microvial.

Standards of diethyl phthalate were prepared in methanol. The standards were spiked onto the fritted end of a Tenax® TA-filled TDU tube. After spiking the tubes, dry nitrogen was passed through the tube at 50 mL/min for three minutes.

Sample/Standard Introduction

Samples were thermally extracted in splitless mode with 50 mL/min helium flow @ 80 °C for 5 minutes. Analytes were trapped in the CIS 4 inlet at 10 °C on a Tenax® TA liner. When extraction was complete, analytes were transferred to the column in split mode (10:1) by heating the inlet rapidly to 280 °C.

Diethyl phthalate (DEP) standards spiked onto Tenax® TA tubes were desorbed in splitless mode with 50 mL/min helium flow @ 280 °C for 3 minutes. DEP was trapped in the CIS 4 inlet at 10 °C on a Tenax® TA liner. When extraction was complete, analytes were transferred to the column in split mode (10:1) by heating the inlet rapidly to 280 °C.

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Results and Discussion

Figure 2 shows the total ion chromatogram (TIC) for the direct thermal extraction of the banana-scented crayon. This crayon had a fruity, faint banana odor. The TIC shows isoamyl acetate and 2-methylbutyl acetate, which contribute directly to the banana odor. Other fragrance compounds present are isoamyl butyrate (fruity/apricot/banana), 2-methylbutyl butyrate (fruity/green apple), benzyl acetate (fruity/jasmin), cis-2-t-butylcyclohexyl acetate (fruity/bergamot), limonene (lemon/orange) and eucalyptol (camphor). Propylene glycol is seen in the chromatogram and is probably present as a solvent for the flavor mix. Surprisingly, diethyl phthalate, a plasticizer, is present.

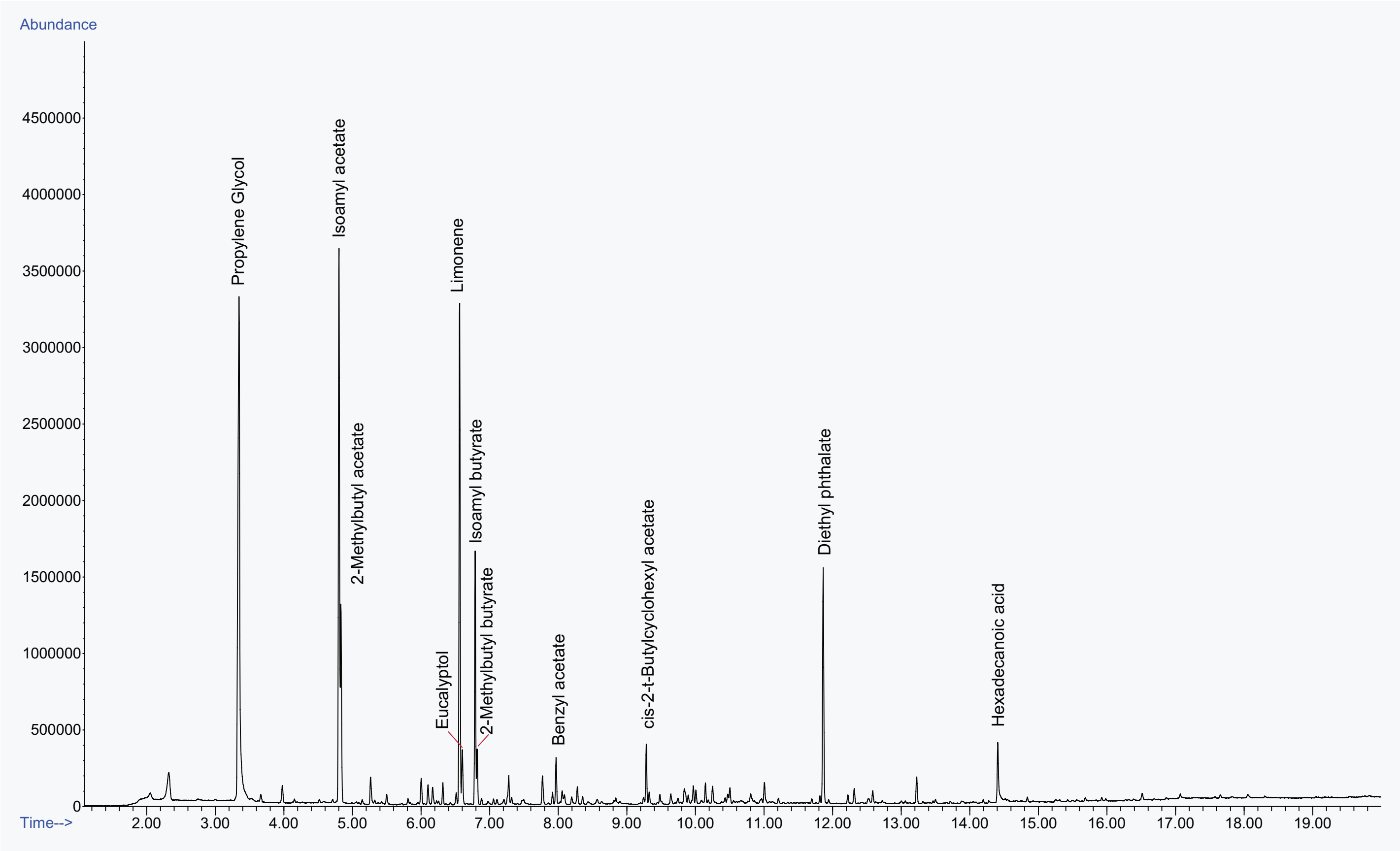

Figure 2: Chromatogram for DTE of banana crayon.

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Figure 3 shows the total ion chromatogram for the dragon fruit crayon. This crayon had a floral/fruity scent. The chromatogram shows limonene (lemon/orange), terpineol (floral), cis-2-t-butyl-cyclohexyl acetate (fruity), gamma-nonalactone (coconut), gamma-undecalactone (fruity), alpha-ionone (floral), and beta-ionone (floral). Diethyl phthalate is also present in this crayon. Three dipropylene glycol isomers are present. It is commonly used as a solvent or plasticizer. 1,1-oxybis-2-propanol, used as a plasticizer, is also present.

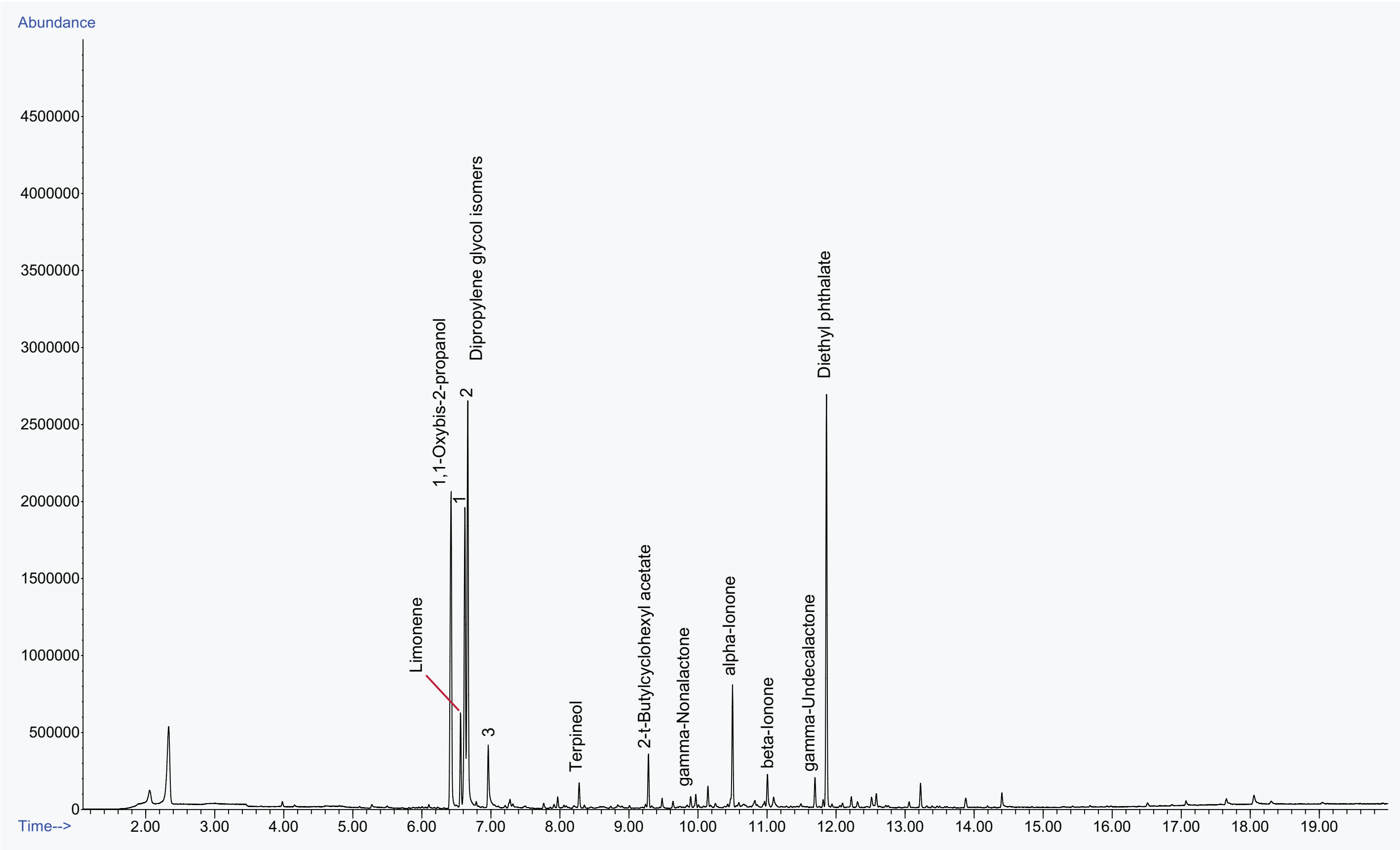

Figure 3: Chromatogram for DTE of dragon fruit crayon.

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Figure 4 shows the total ion chromatogram for the DTE of the grape crayon. This crayon had a faint grape/fruity odor. Methyl anthranilate is the main component responsible for the grape odor. The same plasticizers/solvent peaks seen in the dragon fruit, dipropylene glycol, 1,1'-oxybis-2-propanol, and diethyl phthalate are present in the chromatogram. Other fragrance compounds include limonene (lemon/orange), linalool (floral/citrus), cis-2-t-butylcyclohexyl acetate (fruity), trans-2-t-butylcyclohexyl acetate (fruity),4-t-butylcyclohexyl acetate (woody), alpha-ionone (floral), and beta-ionone (floral), nopyl acetate (herbal), propyl propionate (fruity) and benzophenone (balsamic). Benzyl benzoate is present. It is used as a solvent for fragrance compounds.

The other crayons showed similar peaks for plasticizers and solvents. Table 1 shows the key fragrance compounds for the other crayons.

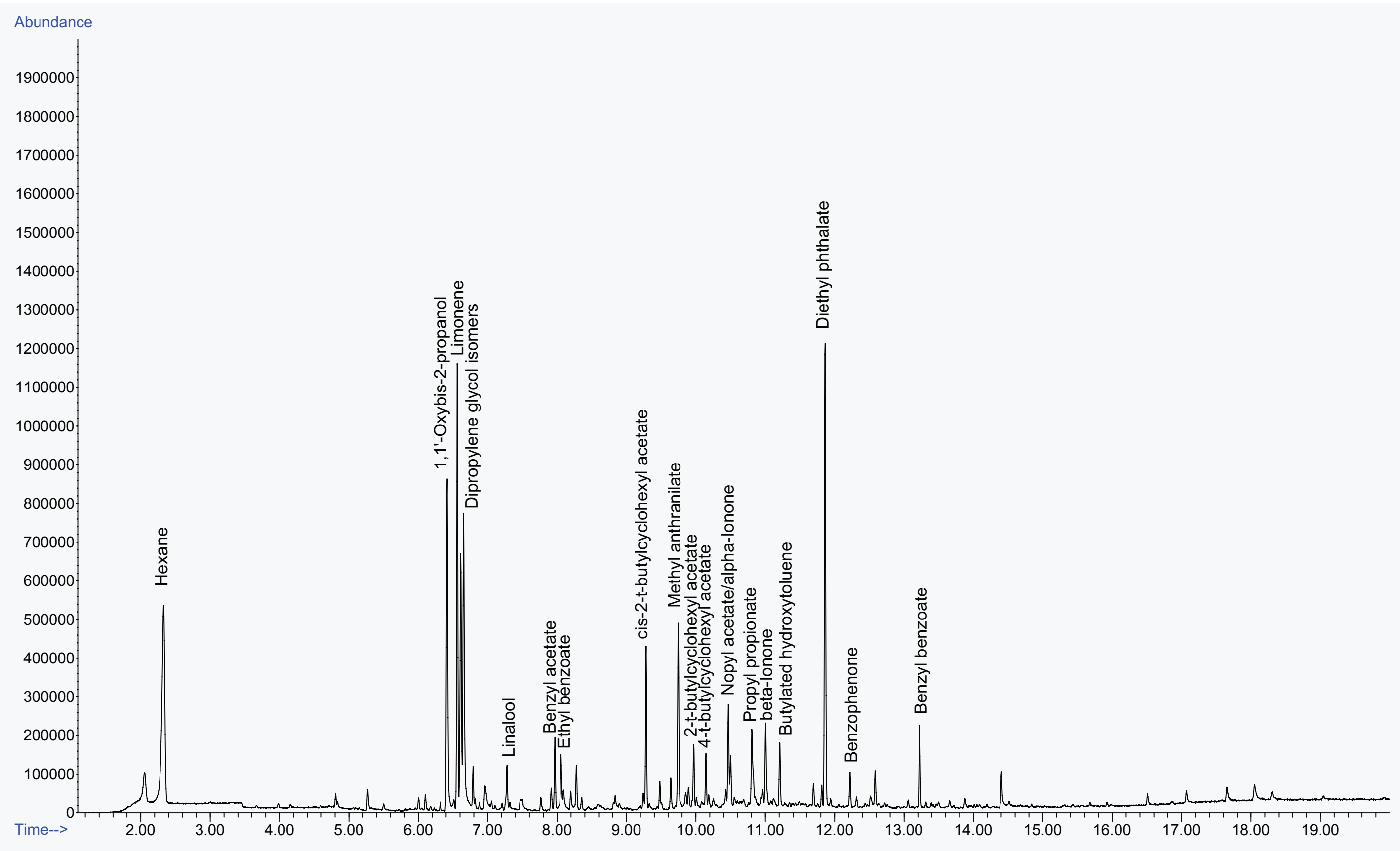

Figure 4: Chromatogram for DTE of grape crayon.

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Table 1: Fragrance compounds for each crayon.

Crayon	Fragrance Compounds
Chocolate	Vanillin, ethyl vanillin, isobutyl phenyl acetate, isoamyl acetate, limonene, eucalyptol, benzyl acetate, α-ionone, β-ionone
Mint	Menthol, menthone, linalool, eucalyptol, limonene, fenchol, cis-green acetate
Licorice	Limonene, benzyl acetate, ethyl maltol, vanillin, ethyl vanillin, α-ionone, isobornyl acetate, ethyl methylphenylglycidate
Coconut	Limonene, γ-nonalactone, coumarin, hexylcinnamaldehyde
Strawberry	Benzyl acetate, 3-methoxy-3-methylbutanol, limonene
Melon	3-methoxy-3-methylbutanol, limonene, α-ionone, cis-green acetate
Watermelon	Limonene, linalool, phenethyl alcohol, cis-green acetate
Blueberry	β-Ionone, isomethyl ionone, raspberry ketone, γ-undecalactone, limonene, vertenex
Cherry	Limonene, benzyl acetate, α-terpineol, verdox, γ-nonalactone, α-ionone, γ-decalactone, β-ionone, γ-undecalactone
Raspberry	Limonene, verdox, γ-nonalactone, α-ionone, β-ionone, α-isomethyl ionone, γ-undecalactone
Apple	Limonene, verdox, γ-nonalactone, vertenex, α-ionone, β-ionone, γ-undecalactone
Mango	Limonene, benzyl acetate, verdox, β-ionone
Orange	α-Pinene, β-pinene, limonene, γ-terpinene, α-terpineol

It was surprising to see diethyl phthalate in all sixteen chromatograms from the scented crayons. Phthalates are a class of endocrine-disrupting chemicals that can have adverse health effects. Many phthalates have been phased out as plasticizers and replaced with less toxic compounds.

The amount of diethyl phthalate (DEP) in each crayon was quantitated using an external calibration method. A known amount of DEP was spiked onto three separate Tenax®-TA filled TDU tubes to generate a calibration curve. The curve is shown in Figure 5. The results are shown in Table 2. DEP amounts range from 0.30-2.7 µg/g (ppm). The amount of the orange, 1.1 ug/g, was an average of n=5 replicates with an RSD of 34%.

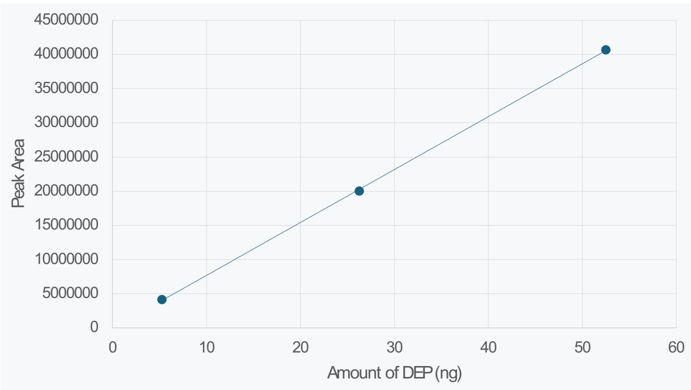

Figure 5: Calibration curve for diethyl phthalate.

Table 2: Quantitative results for diethyl phthalate.

Crayon	DEP (µg/g)
Banana	0.44
Chocolate	0.54
Mint	0.41
Licorice	0.54
Coconut	2.7
Strawberry	0.45
Melon	2.6
Watermelon	0.21
Blueberry	0.71
Cherry	1.86
Raspberry	2.1
Dragon fruit	0.92
Apple	1.4
Grape	0.30
Mango	2.3
Orange	1.1

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Conclusion

Direct thermal extraction of scented crayons was used to examine the fragrance compounds responsible for the various scents in the crayons. Plasticizers and fragrance "solvents" were also found in the chromatograms. Diethyl phthalate, a plasticizer, was quantified using external standards.

Direct thermal extraction is one of many techniques that can be performed using the GERSTEL Labworks Platform. Sample preparation is minimal, and quantification can be easily accomplished using external standards. Very little dilution (split) of the analytes occurs before entering the GC column, so this technique can provide very low detection limits, even with the relatively small sample size used.

References

[1] http://www.thegoodscentscompany.com