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PO-CON1407E

Simultaneous Analysis of ppb and % Level Components by Headspace GC and Peak Splitting

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Jeff Parish, Field Tech Support,
Shimadzu Scientific Instruments

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Introduction

What follows is an application for simultaneous analysis of ppb and % level components by headspace GC and peak splitting. The work was performed on a Shimadzu GC-2010 Plus fitted with a Shimadzu HS-20 headspace autosampler.

HS-20 + GC-2010 Plus

Background

It is frequently desirable to quantitate very low levels of one component while simultaneously quantitating very high levels of another component. Such an analysis is useful in many industries, including the pharmaceutical industry where both an active ingredient and impurities need to be documented for regulatory agencies. It is also useful in the food industry where an accurate value for both major and minor components needs to be determined for proper process control.

Summary of Methodology

In this work, two classes of components are introduced by automated headspace analysis from a single vial filled with 1 mL. of beer and separated on a single GC column. The peaks are then split at a ratio of 40:1, with the large fraction going to an Electron Capture Detector (ECD) in order to analyze butanedione and pentanedione down to 10 ppb, and the smaller fraction going to a Flame Ionization Detector (FID) to analyze ethanol up to 15%. Calibration curves were generated for both detectors and replicate injections were performed to confirm that the technique is both linear and reproducible.

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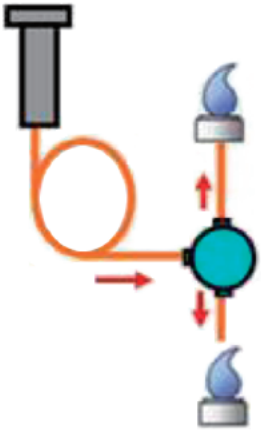
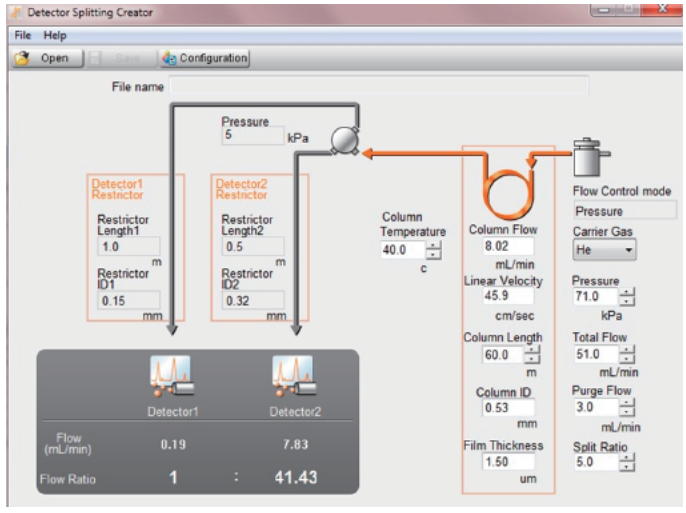
Peak Splitting

Peak splitting is done post-column by attaching a 3-way union to the column outlet and then using a length of blank capillary tubing to connect to each detector. Different lengths and diameters of tubing can be used to achieve various split ratios between the detectors.



A calculator such as Shimadzu's Advanced Flow Technology tool can be used to determine the optimum capillary lengths and diameters to achieve the desired absolute flows and ratio of flows to the detectors.



Instrumental Conditions

GC Parameters

Instrument	: Shimadzu GC-2010 Plus
Column	: Restex RTx-5 60m x 0.53mm ID, 1.5um film
Injection Mode	: Split
Flow Control Mode	: Constant Linear Velocity
Linear Velocity	: 47.1 cm/sec
Split Ratio	: 5
Oven Temp Program	: 60C for 2 min. 20C/min to 150C, hold for 0 min 30C/min to 200C, hold for 0.83 min
ECD Temp & Current	: 150C and 1.2 nA
FID Temp	: 250C

Headspace Parameters

Instrument	: Shimadzu HS-20
Oven Temperature	: 60°C
Sample Line Temperature	: 200°C
Transfer Line Temperature	: 200°C
Vial Pressurization	: 6.4 psi
Sample Loading Time	: 0.2 min.
Injection Volume	: 1 mL.
Injection Time	: 1.0 min.
Needle Flush Time	: 8.0 min.
Vial Volume	: 20 mL.
Liquid in Vial	: 1 mL.

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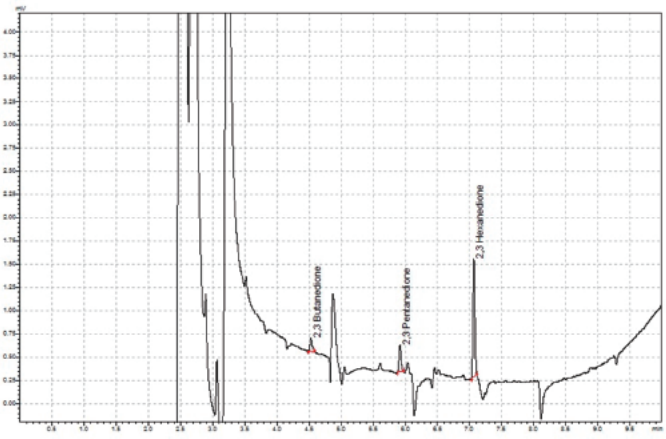
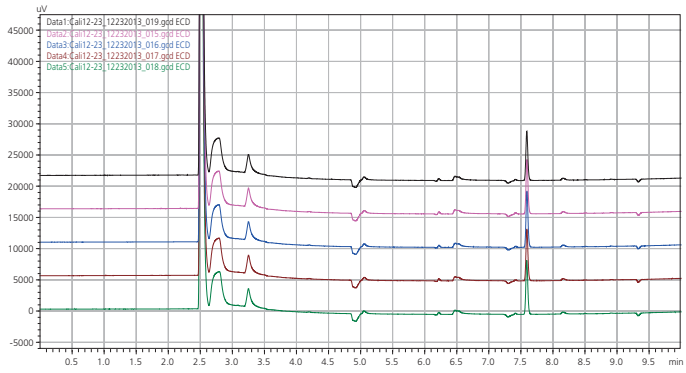
ECD Chromatogram 10ppb

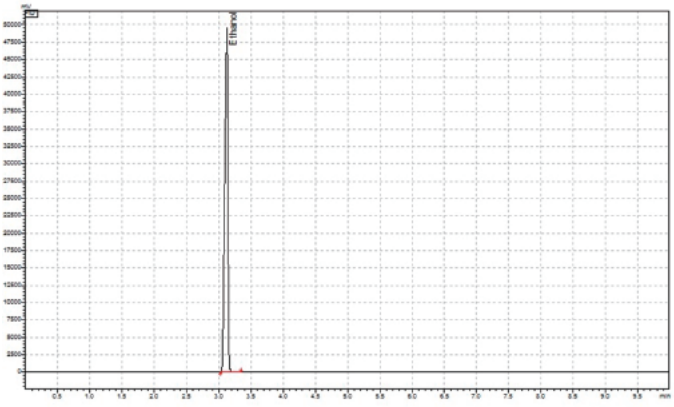


ECD Chromatogram Reproducibility

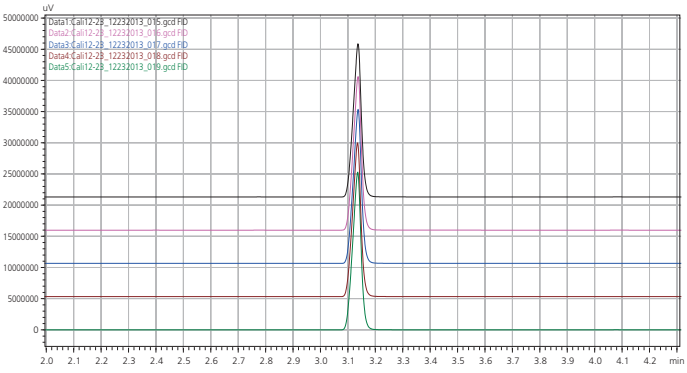


Overlay of 5 sequential injections.
Matrix and internal standard only.

FID Chromatogram 15%

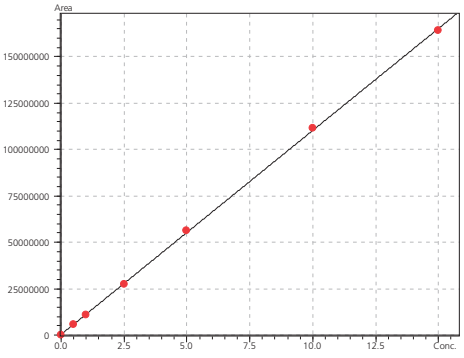


FID Reproducibility



Overlay of 5 sequential injections.

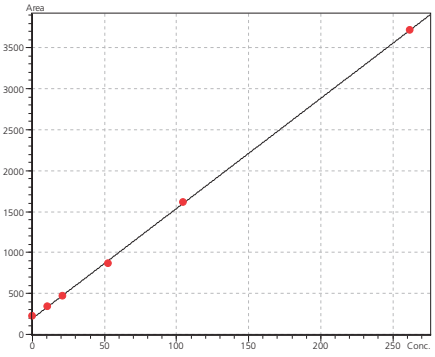
Ethanol Calibration Curve



Conc.	Area
0.0%	6841
0.5%	5679917
1.0%	10983659
2.5%	27594094
5.0%	56222776
10.0%	111427698
15.0%	164299018

Y = mX + b
m = 1.09970e+007
b = 330647
R^2 = 0.9998554

Butanedione Calibration Curve



Conc.	Area
0.0 ppb	218
10.5 ppb	339
21.0 ppb	469
52.4 ppb	866
104.8 ppb	1615
261.9 ppb	3716

Y = aX + b
a = 13.4347
b = 195.121
R^2 = 0.9997949

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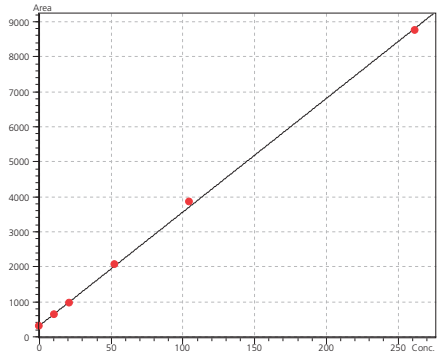
Pentanedione Calibration Curve



Conc.	Area
0.0 ppb	289
10.5 ppb	619
21.0 ppb	961
52.4 ppb	2057
104.8 ppb	3861
261.9 ppb	8757

$Y = aX + b$
$a = 32.4270$
$b = 322.770$
$R^2 = 0.9994278$

Conclusion and Future Development

While this application has demonstrated the feasibility of simultaneously analyzing both ppb levels of one class of components and percent levels of another class, there is still room for improvement and the methodology will continue to be developed.

- The split can be adjusted to allow for less of the major component and more of the trace component so that the detection limit of the trace component can be lowered. This could be done by replacing the 0.32 mm ID capillary with a short length of the 0.53 mm ID analytical column.
- Headspace oven temperature could be optimized. A temperature of 80°C may be optimal for this analysis based on the boiling points of the components versus that of the matrix.
- While the preliminary reproducibility of all components appears to be less than 2%RSD, it needs to be rigorously tested and confirmed.
- Finally, additional components that could be analyzed on either an ECD or FID could be added to the analysis.

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