Analysis of Currency with SPME and GCxGC-TOFMS—Advanced Data Processing with Classifications

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Key Words: GCxGC, TOFMS, SPME, Classifications

1. Introduction

Interest in the analysis of currency has included its authenticity based upon ink analysis, the identification of cocaine and methamphetamines, as well as the nature of origin based upon targeted compounds. Recent interest by the Department of Homeland Security has included the detection of money at airport screening facilities. In this study, solid phase microextraction (SPME) was used to collect volatile and semivolatile compounds in the headspace of a single United States $1 bill. The analysis was performed on a comprehensive two-dimensional gas chromatograph coupled to a time-of-flight mass spectrometer (GCxGC-TOFMS). Data processing was performed with LECO ChromaTOF® software utilizing Classifications.

2. Experimental Conditions

Pegasus® 4D GCxGC-TOFMS
Primary Column:
 30 m x 0.25 mm x 0.25 µm Rtx-1 (Restek)
Secondary Column:
 1 m x 0.10 mm x 0.20 µm Rtx-Wax (Restek)
Primary Oven:
 30°C for 0.5 minute, 7°C/minute to 220°C
Secondary Oven:
 40°C for 0.5 minute, 7°C/minute to 230°C
Modulation:
 Quad-jet, dual-stage
Modulation Period:
 5.0 seconds
Carrier Gas:
 Helium at 1.5 mL/minute constant flow

TOFMS Conditions
Ionization: EI at 70 eV
Source Temp: 200°C
Acquisition Rate: 100 spectra/second
Mass Range (u): 35 to 400

Sample Preparation and Introduction

A single $1 bill was placed in a 20 mL vial and closed with a septum screw-top. The SPME fiber (75 µm Carboxen – PDMS, Supelco) was exposed to the headspace around the bill for 60 minutes with the vial at a temperature of 30°C. The fiber was then desorbed in a 225°C GC inlet for 15 seconds.

3. Results and Discussion

This simple and relatively fast (27 minutes) GCxGC analysis of currency identified more than 300 compounds. The separation power and enhanced detectability of GCxGC are shown by the separation of the alkanes, aldehydes, and alcohols throughout the two-dimensional retention plane. Figure 1 shows the GCxGC chromatogram (contour plot) for the SPME analysis of money and Table 1 contains the data for identified n-alkanes, n-ketones, and n-alcohols found in the sample.

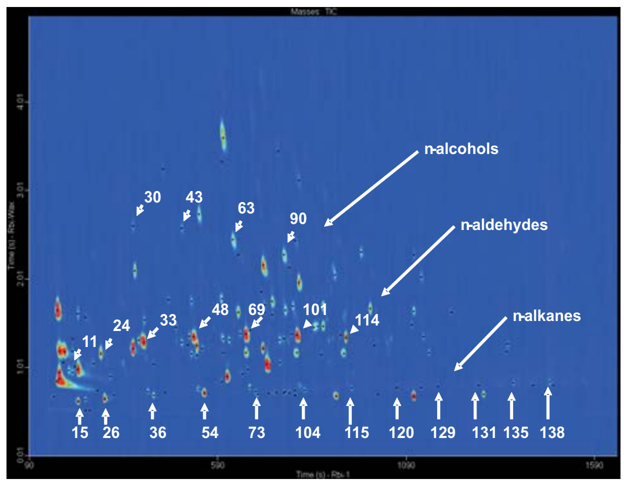

Figure 1. GCxGC chromatogram (contour plot) of SPME analysis of a $1 bill. The total ion count (TIC) is shown with red being the most intense color. More than 300 compounds were detected by the TOFMS with a run time of less than 30 minutes. The numbered compounds, representing n-alkanes, n-aldehydes, and n-alcohols were identified by ChromaTOF software and are listed in Table 1.

Table 1. Identified n-alkanes, n-aldehydes, and n-alcohols.

Peak #	Name	R.T. (s)	UniqueMass	Area %
11	Butanal	205 , 0.960	72	0.07
15	Hexane	220 , 0.630	41	0.69
24	Pentanal	280 , 1.170	58	0.42
26	Heptane	300 , 0.670	58	0.00
30	1-Pentanol	365 , 2.610	42	0.15
33	Hexanal	395 , 1.300	56	1.78
36	Octane	420 , 0.700	41	0.14
43	1-Hexanol	495 , 2.590	56	0.16
48	Heptanal	525 , 1.360	70	0.97
54	Nonane	555 , 0.720	57	0.92
63	1-Heptanol	630 , 2.460	70	0.35
69	Octanal	665 , 1.390	41	1.98
73	Decane	690 , 0.740	41	0.05
90	1-Octanol	765 , 2.290	56	0.33
101	Nonanal	800 , 1.380	57	1.52
104	Undecane	820 , 0.760	57	0.10
114	Decanal	930 , 1.350	57	0.39
115	Dodecane	945 , 0.780	57	0.07
120	Tridecane	1065 , 0.790	57	0.03
129	Tetradecane	1175 , 0.800	57	0.03
131	Pentadecane	1280 , 0.810	57	0.04
135	Hexadecane	1375 , 0.840	57	0.08
138	Heptadecane	1470 , 0.850	57	0.09

Data Processing with Classifications

Classifications provide a way to process GCxGC data more efficiently by grouping compounds of similar chemical functionality. Classifications consist of compounds that are grouped into classes and regions based on user-defined geography. Regions are manually drawn for peaks on the contour plot using the mouse. Once Classifications have been created, a new data processing method which includes the Classification reference can be used to process acquired samples. Furthermore, the peak table can be filtered to display the identified compounds within one or more of the Classification regions. Figure 2 displays the GCxGC chromatogram of money while selectively showing the Classification regions for alkanes, aldehydes, and alcohols. Table 2 displays the filtered peak table sorted by Classification of alcohols.

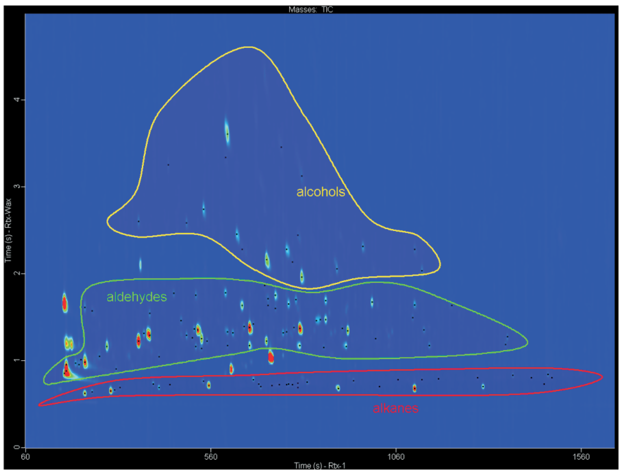

Figure 2. GCxGC chromatogram displaying the TIC and the Classification regions for the alkanes, aldehydes, and alcohols. Notice only peaks within the Classification regions are displayed with black peak markers. The use of Classifications not only aids in compound identification but also provides the analyst with a more efficient way to view the processed data.

Table 2. Filtered peak table for SPME of money displaying the Classification region for alcohols only. Note the calculated area percent for each compound is relative to the alcohol region only, whereas the total area percent for the peak table is representative of the filtered alcohol region relative to the entire area percent of the sample. (Some of the compounds in the alcohol Classification region are not actually alcohols, but because they elute within the boundary of the region, they are included here. A way to further classify compounds based on the mass spectra of compounds within Classifications, called Scripts, will be discussed in another application note.)

Peak #	Name	Classifications	R.T. (s)	UniqueMass	Area %
29	1-Pentanol	alcohols	365 , 2.610	42	1.82
37	2-Pentanone, 4-hydroxy-4-	alcohols	445 , 3.260	43	2.45
42	1-Hexanol	alcohols	495 , 2.590	56	2.01
51	Ethanol, 2-butoxy-	alcohols	540 , 2.750	57	9.14
56	Acetone alcohol	alcohols	600 , 3.340	43	1.72
59	Benzaldehyde	alcohols	605 , 3.610	77	22.87
62	1-Heptanol	alcohols	630 , 2.460	70	4.36
64	1-Octen-3-ol	alcohols	645 , 2.290	57	0.77
76	1-Hexanol, 2-ethyl-	alcohols	710 , 2.170	57	29.51
84	Acetophenone	alcohols	750 , 3.460	105	1.07
89	1-Octanol	alcohols	765 , 2.290	56	4.10
93	Furan, 2-butyltetrahydro-	alcohols	780 , 2.140	71	0.89
98	6-Methyl-3,5-heptadiene-2	alcohols	795 , 2.450	109	1.63
101	11.32 LINALOOL	alcohols	805 , 1.970	71	9.55
102	Furan, 2-methyl-	alcohols	805 , 3.130	82	1.24
109	L-(-)-Menthol	alcohols	900 , 2.060	71	1.13
115	L(-)-Carvone	alcohols	970 , 2.320	82	3.07
123	2,2,4-Trimethyl-1,3-pentan	alcohols	1110 , 2.290	71	1.21
125	Propanoic acid, 2-methyl-,	alcohols	1130 , 2.040	71	1.43
				Total	7.97

4. Conclusions

SPME combined with GCxGC-TOFMS is a powerful analytical technique for headspace analysis of various solid, liquid, and complex samples that contain volatile and semivolatile compounds. The results from this work demonstrate the ability of the LECO Pegasus 4D to identify hundreds of compounds found in a headspace sample from currency. Utilizing the Classification feature in the ChromaTOF software allows the analyst to visually and qualitatively display selected regions of the GCxGC chromatogram for more efficient data analysis.

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