Characterization of Ballpoint Pen Inks by Solid-Phase Microextraction Gas Chromatography—Time-of-Flight Mass Spectrometry

Introduction

Time-of-Flight Mass Spectrometry (TOFMS) offers benefits for Gas Chromatography (GC) not available with other mass spectrometers (e.g. quadrupoles and magnetic sectors) because of its fast acquisition rates (up to 500 spectra/second) and the spectral continuity associated with an almost instantaneous mass analysis. Two of these benefits are automated Peak Find and Spectral Deconvolution, algorithms that can be built into the data processing software.

Characterization of ink samples with GC-MS is important for several reasons, including formulation determination for competitive motives, quality assurance and control, counterfeit cases, and cases where age of a document is in question. In this contribution, Solid-Phase Microextraction (SPME) GC-TOFMS, with automated peak find and spectral deconvolution, is used to characterize ballpoint pen inks. In addition, an automated Compare algorithm is employed to identify components associated with aged ballpoint inks in a complex background matrix of volatile compounds generated from the heating of paper to sample the aged ink by SPME.

Experiments

Two experiments were conducted for this work. The first involved characterization of black (8 samples) and blue (5 samples) ballpoint inks for volatile organic compounds (VOCs) with SPME GC-TOFMS. The second was determining VOCs remaining in ballpoint ink from aged scribbles on paper.

Experimental Conditions

Solid-Phase Microextraction
A divinylbenzene/Carboxen/PDMS (50/30 μm) fiber from Supelco was used. 5 mm punched paper holes with ink scribbles were placed into a 4 mL vial that was capped with a PTFE-silicone septum for SPME sampling. Five holes were used for the characterization experiment and eight were used for the ink aging work. The vial was sampled by headspace SPME while either at 22°C (characterization) or 70°C (aging). For the aging work, the vial was equilibrated at 70°C for 10 minutes prior to SPME. A 10 minute SPME sampling time was used to collect ink volatiles. The fiber was desorbed into a 0.75 mm injection sleeve (Supelco) in a split/splitless injector at 270°C either at a 20:1 split ratio (characterization) or splitless with a valve time of 60 seconds (aging).

GC-TOFMS

Column: 20 m x 0.25 mm x 0.71 µm Rtx-TNT (Restek)
Carrier: Helium at 2 mL/min, constant flow
Injection: See above.
Oven Program: 40°C (1 min), 40°/min to 340°
Total Run Time: 9 min

MS: LECO Pegasus TOFMS
Ionization: Electron ionization at 70 eV
Source Temperature: 200°C
Stored Mass Range: 35 to 450 u
Acquisition Rate: 10 spectra/second

Data Processing
LECO ChromaTOF® software with automated peak find and spectral deconvolution.

Results and Discussion

The automated Peak Find algorithm that is integral to ChromaTOF software was used to locate all ballpoint ink VOCs that eluted in a retention range approximately between acetone (not included in tables) and 2-phenoxyethanol (included in tables). Separate reference tables were prepared of major volatiles in black and blue inks. Tables 1 and 2 contain the results for major components of black and blue ballpoint pen inks. All of the values in the table are relative to mixed ink samples and do not necessarily indicate the major volatile component of each ink. Interestingly, all of the ballpoint pen inks, except for black pens 4 and 5, are distinctly different as to their volatile constituents. This was quickly and easily determined through fast GC-TOFMS analysis and the fully automated data processing available with ChromaTOF.

Table 1. Relative component amounts for eight black ballpoint pen inks analyzed using SPME GC-TOFMS.

Compound Name	1	2	3	4	5	6	7	8
Ethylene glycol						930		
Propylene glycol		100	13			310		
Hexylene glycol			630					
Phenol	8	100	82	2	4		52	140
Aniline		150	85			120		
Ethoxy ethoxyethanol	350	3						
2-Ethylhexanol	17	97	170	140	120	35		
Benzyl alcohol		91	120	170	150			
Phenylethanol	170	15	53	85	62			
2-Phenoxyethanol	33	46	41	38	22			75
Phenoxypropanol			210					95

Table 2. Relative component amounts for five blue ballpoint pen inks analyzed using SPME GC-TOFMS.

Compound Name	1	2	3	4	5
Propylene glycol		38			160
Hexylene glycol		81			
Phenol	48			30	
Aniline		29	130		
Methoxy methylethoxy propanol 1	550	15	62		
Ethoxy ethoxyethanol	520				
Methoxy methylethoxy propanol 2	530				
Dimethoxy propane	620				
Benzyl alcohol	780				
Phenylethanol	900				
2-Aminotoluene			130		
2-Phenoxyethanol	71	16	18	38	
Diethylaniline				100	

An example of the automated peak find capability of ChromaTOF for a complex ink sample is seen in Figure 1. Each vertical line with a number represents a found peak, and even where there are significant coelutions (some of the peak apexes are only ms apart), peaks were easily located.
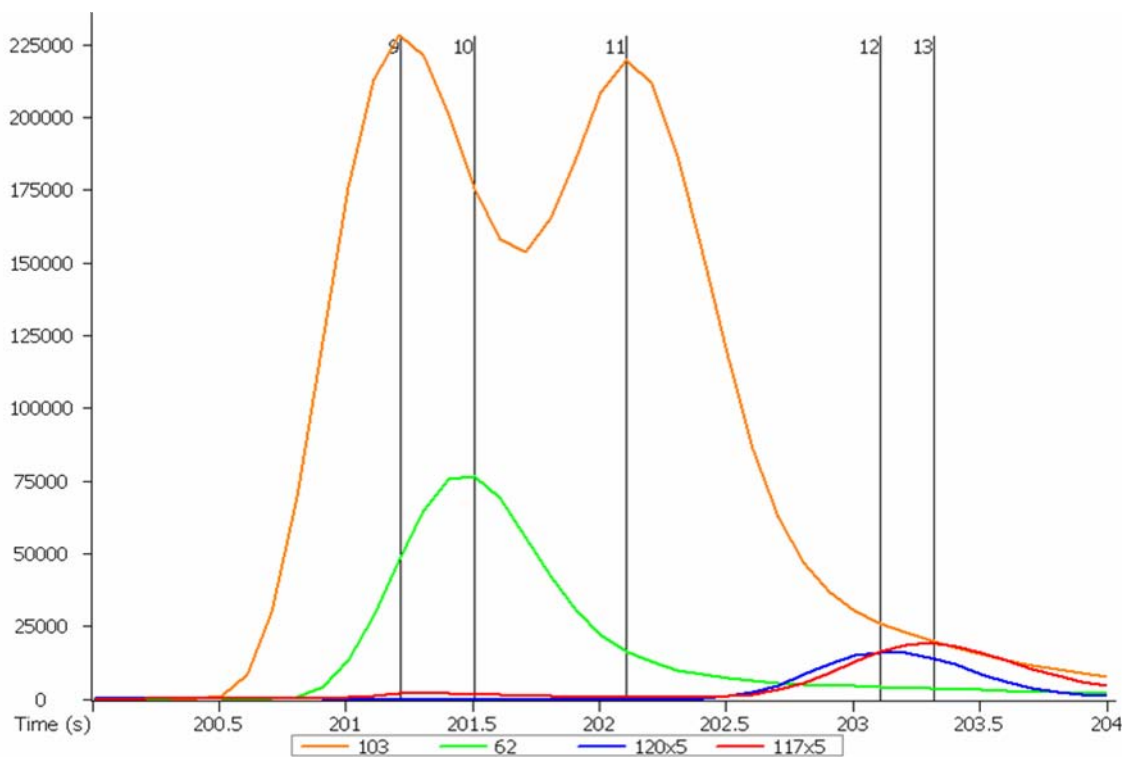

Figure 1. *Automated peak find with ChromaTOF. Each numbered vertical line is a peak marker. Even though there are obvious coelutions, ChromaTOF located the peaks.*

Just as important as locating the peaks in a complex sample, is producing deconvoluted mass spectra that are fully library searchable. Figures 2 and 3 demonstrate this for two of the peaks from Figure 1. When viewing the figures, notice that shared ions between the compounds, represented by extracted unique ions 103 (orange) and 62 (green), are properly proportioned by the ChromaTOF Spectral Deconvolution algorithm. This guarantees that library search results will be accurate.
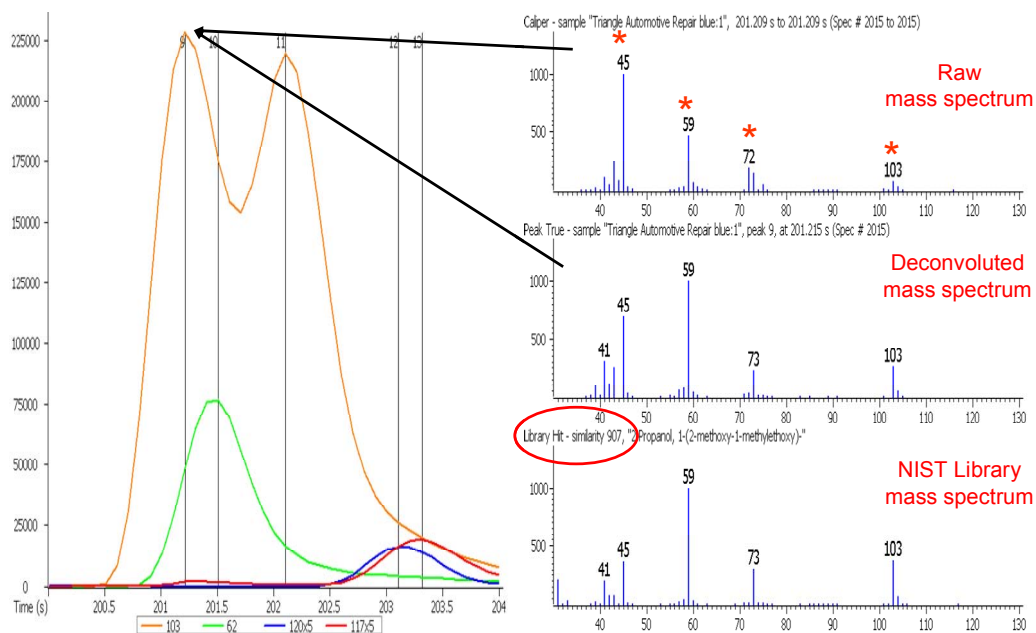

Figure 2. *Automated peak find and spectral deconvolution for methoxy methylethoxy propanol in a blue ballpoint pen ink. The raw mass spectrum is a combination of ions (including those that are shared, marked with red asterisks) from the coelutions. The deconvoluted spectrum has a similarity of 907 (out of 999) with the library spectrum.*
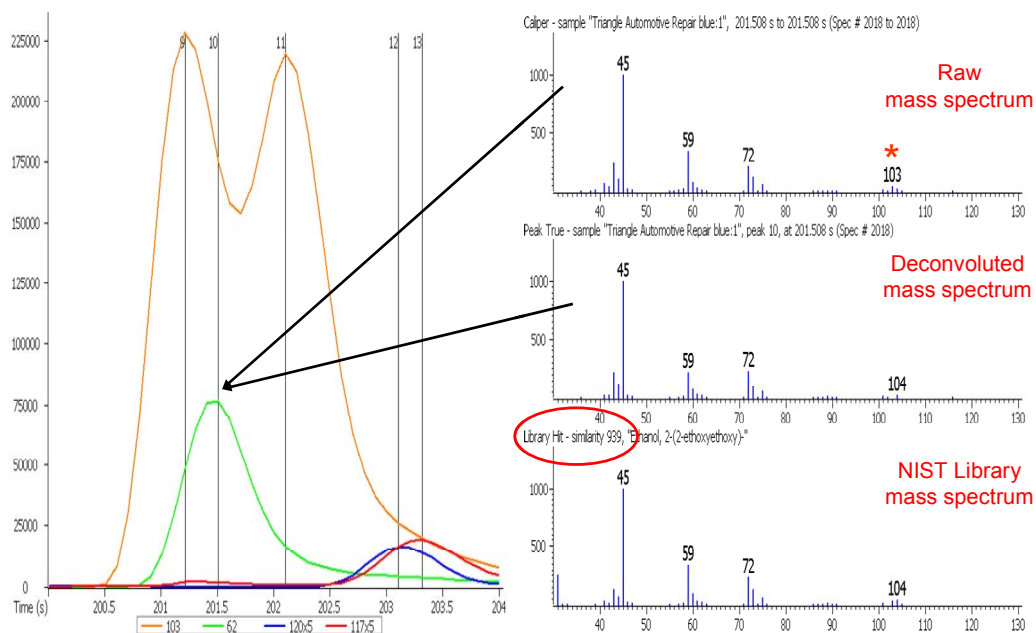

Figure 3. *Automated peak find and spectral deconvolution for ethoxy ethoxyethanol in a blue ballpoint pen ink. The deconvoluted spectrum has a similarity of 939 (out of 999) with the library spectrum.*

A more dramatic example of automated peak find and spectral deconvolution is seen in Figure 4 where a minor peak (diethylaniline) is buried underneath a huge peak. Not only was this minor compound located underneath the large 2-phenoxyethanol peak, but a deconvoluted mass spectrum was produced that had excellent similarity with a library mass spectrum.
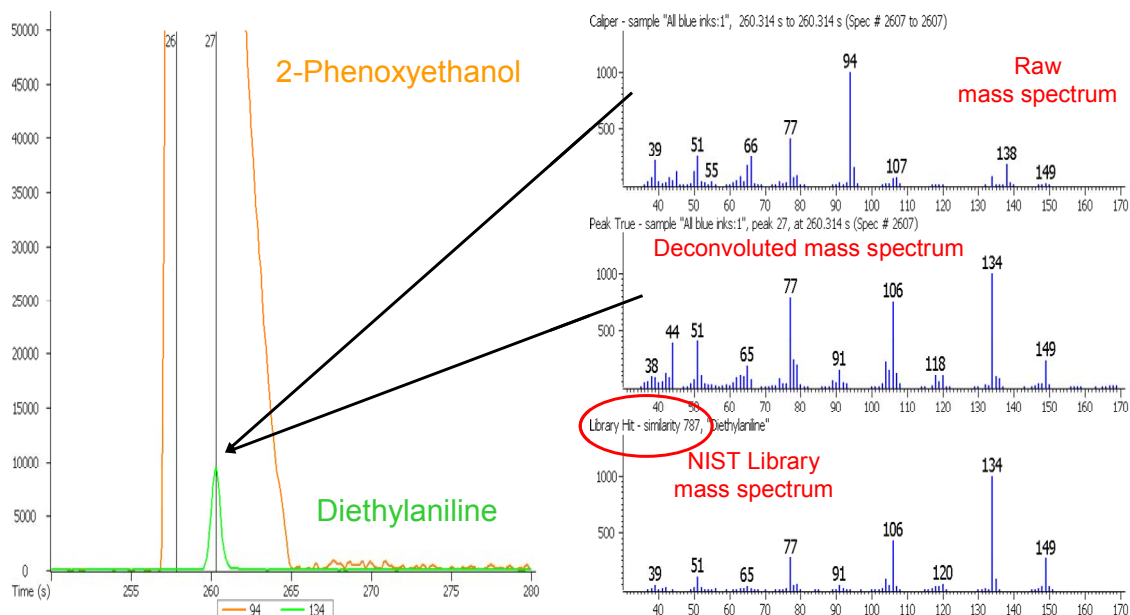

Figure 4. *Automated peak find and spectral deconvolution for diethylaniline in the presence of 2-phenoxyethanol in a mix of blue ballpoint pen inks. Note that the raw mass spectrum taken at the peak apex for diethylaniline is characteristic of 2-phenoxyethanol due to its high concentration. The deconvoluted spectrum for diethylaniline matches well with the library spectrum.*

The aging of documents created or signed with ballpoint pens is often done by "calibrating" how certain ink components decrease over time. For the aged ink experiment in this work, 2-phenoxyethanol was chosen for monitoring because it is the principal solvent in many ballpoint ink formulations. Preliminary experiments showed that the 2-phenoxyethanol concentration in an ink scribble (as sampled by ambient temperature SPME) dropped rapidly and stabilized (Figure 5). This observation was confirmed with older ink samples also, as shown in Figure 6.
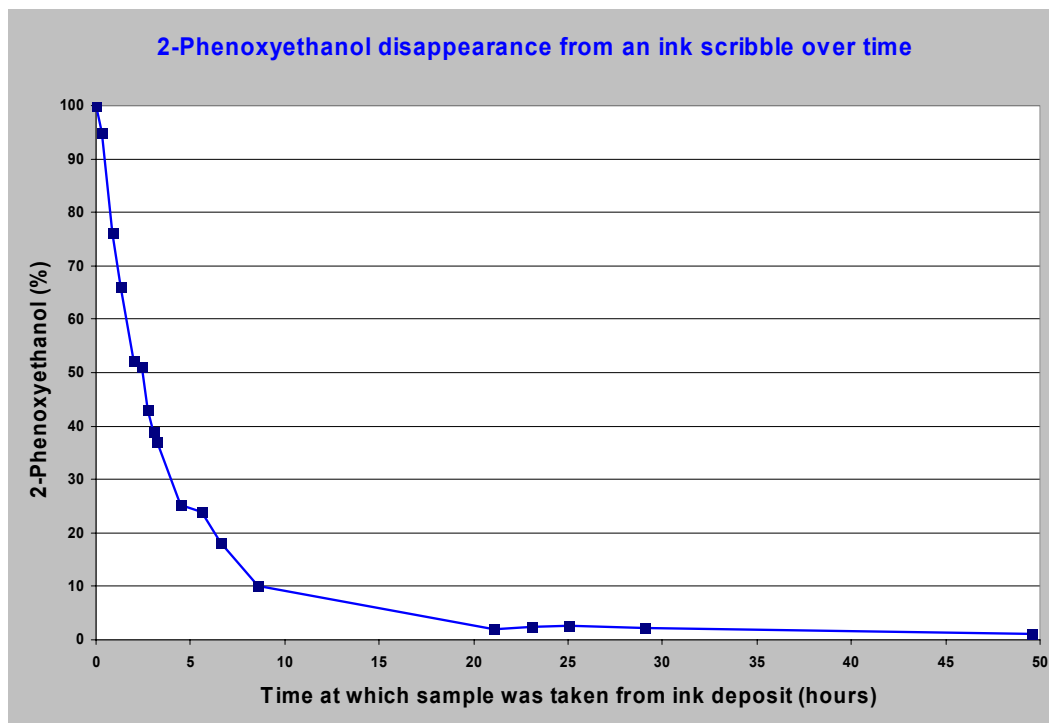
Figure 5. *2-Phenoxyethanol disappearance from an ink scribble over time as determined by SPME and fast GC-TOFMS. The concentration of 2-phenoxyethanol that can be determined by SPME GC-TOFMS stabilizes after about 20 hours.*
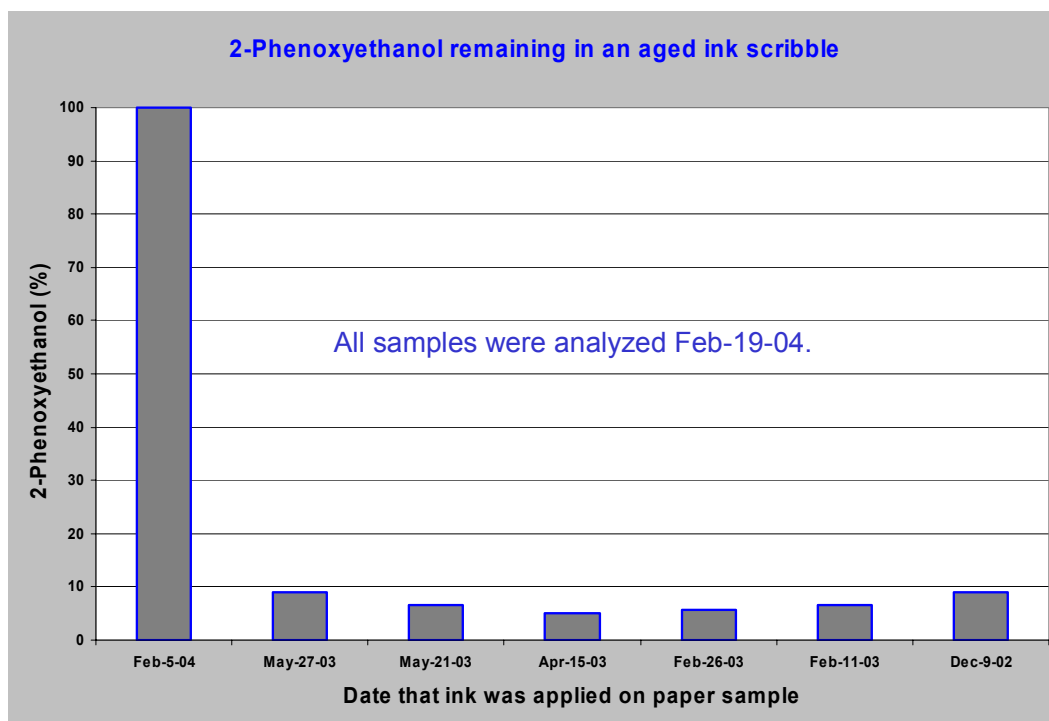

Figure 6. *2-Phenoxyethanol disappearance from aged ink scribbles as determined by SPME and fast GC-TOFMS. The SPME vial was heated to 70°C prior to sampling. 2-Phenoxyethanol concentration differences as determined by SPME GC-TOFMS are indistinguishable for 2003 and 2002 samples.*

Based on the results seen in Figure 6, it was concluded that documents could not be aged past 8 months using SPME GC-TOFMS and 2-phenoxyethanol concentrations. It was theorized that using a less volatile component, one that might stay in the paper longer than 2-phenoxyethanol, could be used to age ballpoint pen ink documents. Unfortunately, diphenylamine gave similar results to 2-phenoxyethanol (Figure 7). Although the results are not shown here, the ratio of less- to more-volatile compounds, as analyzed by SPME GC-TOFMS, was no help in determining ballpoint pen ink age either.
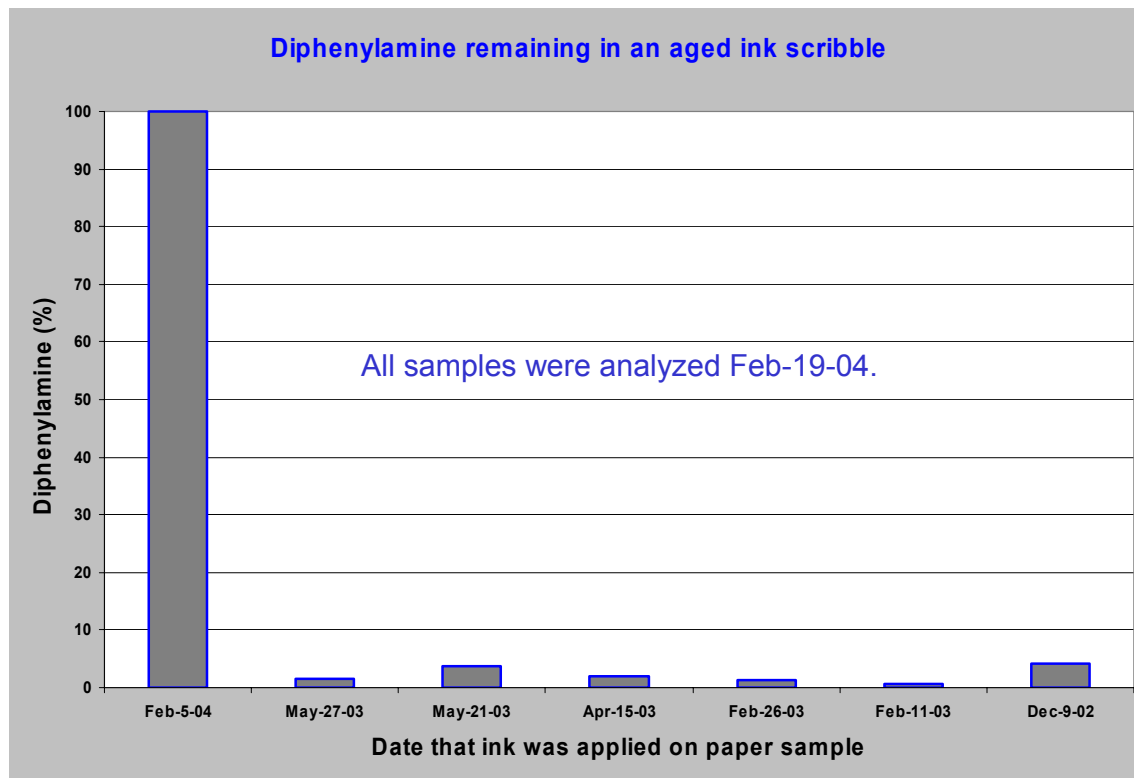

Figure 7. *Diphenylamine disappearance from aged ink scribbles as determined by SPME and fast GC-TOFMS. The SPME vial was heated to 70°C prior to sampling. Diphenylamine concentration differences as determined by SPME GC-TOFMS are indistinguishable for 2003 and 2002 samples.*

When heating the ink scribbles to 70°C for headspace sampling by SPME, most of the volatile contribution is from the paper, and the chromatogram is quite complex. It becomes a challenge to determine which compounds can be attributed to the ballpoint ink. To simplify the data processing for these samples, a feature specific to ChromaTOF, "Compare", was used. This algorithm provides a quick and fully automated way to compare two samples on a GC peak-by-GC peak, mass spectrum-by-mass spectrum basis. As an example in this work, a Reference was created using blank paper (that with no ink line on it) from the February 5, 2004 sample, and then Compare was used to analyze the same sample paper that contained ink lines.

The Compare procedure starts with automated peak find, spectral deconvolution, library searching of the Peak Table, and calculating peak area/height for each compound (for the Reference sample). For the paper used here, over 200 compounds were located and library searched in less than 2 minutes! When Compare is used against the sample (ink scribbles), a Peak Table containing four analyte types is generated.

- Match (compound found and within user-defined concentration range)

- Out of Tolerance (compound found but outside user-defined concentration range)

- Contaminant (compound not in Reference)

- Not Found (compound not in sample, versus Reference)

A Peak Table can be filtered such that any or all of the analyte types is displayed in the table. In the present case, the Contaminants, which can be defined as ink compounds, are of highest interest. Table 3 shows the Contaminants (ink compounds) illuminated through the use of Compare that had spectra in the NIST library. Another five compounds were located, but their spectra were not in the library, and are therefore not included in the table. The Compare data processing time, which included automated peak find, spectral deconvolution, calculation of area/height, matching of results, and library searching of unmatched compounds, took less than a minute.

Table 3. Ink compounds (Contaminants from Compare) in an aged ink scribble.

Retention time (sec.)	Compound Name
175.4	2-Butoxyethanol
192.0	Benzaldehyde
195.5	Phenol
201.6	2-(2-Ethoxyethoxy)-ethanol
205.5	2-Ethoxyethanol
219.4	Phenylethanol
258.4	2-Phenoxyethanol
264.3	Phenoxypropanol
342.1	Diphenylamine

Figure 8 graphically illustrates the Compare results by overlaying chromatograms for the paper and the paper/ink scribble samples. Diphenylamine, marked with a blue asterisk, is one ballpoint ink compound located with Compare. Although it may be possible to visually locate major compounds of interest through inspecting overlaid total ion chromatograms (TICs), the automated way is faster, and often leads to location of important compounds that may be buried beneath the TIC.
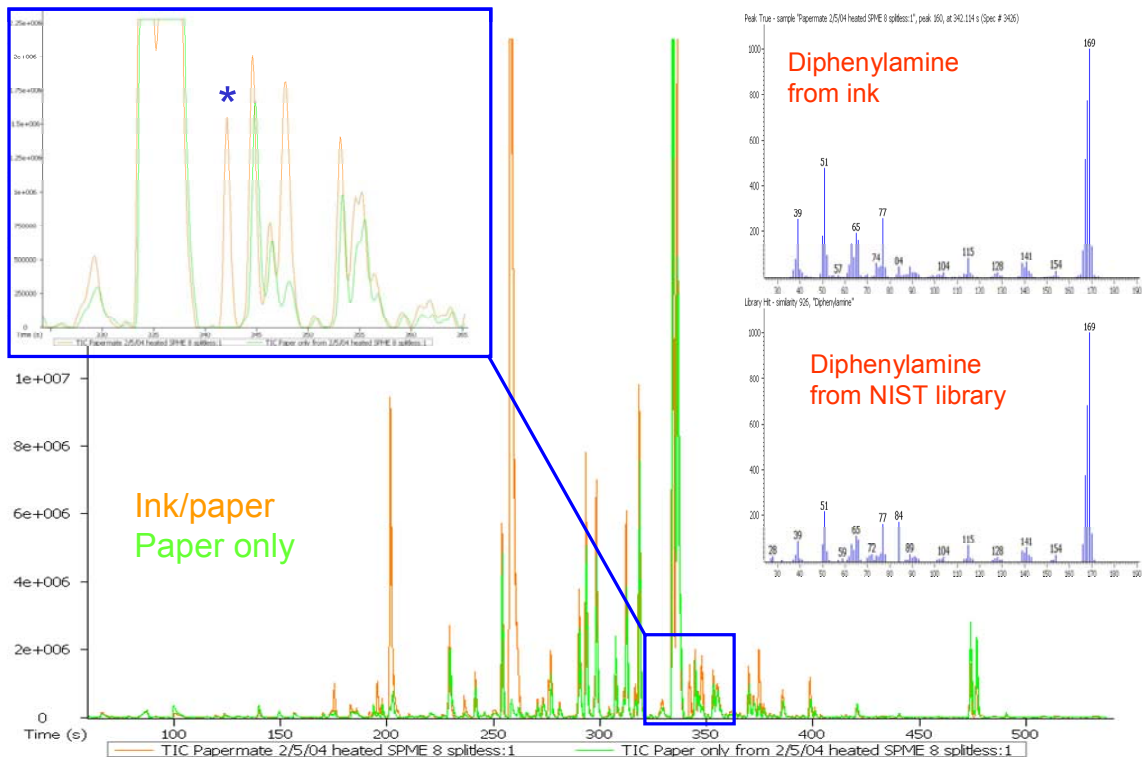
Figure 8. *Overlaid TICs of paper, and paper with ink scribbles, as analyzed using SPME GC-TOFMS. Diphenylamine (blue asterisk, inset chromatogram), which was located automatically with a Compare feature of ChromaTOF, can be attributed to the ballpoint pen ink.*

Conclusions

SPME GC-TOFMS is a fast and powerful way to characterize the volatile organic composition of ink samples, especially due to automated peak find and spectral deconvolution. Compare, a feature unique to ChromaTOF software, simplifies data reduction for complex samples, and quickly highlights (and identifies) compounds that can be considered as "Contaminants" when compared to a Reference. SPME needs further investigation as an ink dating technique for samples more than eight months old.

References

G.M. LaPorte, J.D. Wilson, A.A. Cantu, S.A. Mancke, and S.L. Fortunato, The Identification of 2-Phenoxyethanol in Ballpoint Inks Using Gas Chromatography/Mass Spectrometry—Relevance to Ink Dating*, J. Forensic Sci.*, Jan. 2004, Vol. 49, No. 1

V.N. Aginsky, Current Methods for Dating Ink on Documents

http://www.rileywelch.com/Aginsky_article.pdf

Acknowledgment