J Forensic Sci, September 2009, Vol. 54, No. 5
doi: 10.1111/j.1556-4029.2009.01104.x
Available online at: www.blackwell-synergy.com

TECHNICAL NOTE

Jan Andrasko,[1] *Ph.D.*

Some Examples of Applications of a Microthermal Desorption Device in the Forensic Laboratory

ABSTRACT: Several applications of a microthermal desorption device for analysis of small forensic samples are presented. The method uses a solid phase microextraction holder with the fiber removed. In addition to samples of inks on paper, this device was successfully used for analysis of toners, various stains on bank notes, and lipstick stains on paper. Other small items encountered in a forensic science laboratory were also analyzed: particles of smokeless powder, particles of coffee, and automotive clear topcoat layer. The desorbed compounds were analyzed by gas chromatography with a flame ionization detector or by gas chromatography–mass spectrometry. This device can be used in connection with any kind of gas chromatograph. By selection of different injector temperatures, fractionated thermal desorption of samples is achieved. The procedure was demonstrated on samples of ballpoint pen ink of various age.

KEYWORDS: forensic science, microthermal desorption, gas chromatography/mass spectrometry, lipsticks, propellants, inks, coffee, toners, fractionated thermal desorption

Thermal desorption is a widely used technique for extracting and isolating volatile and semivolatile compounds from various matrices. The method is well established in forensic science, for example, for headspace analysis of accelerant vapors in arson analysis. This technique avoids the use of solvents and also the risk of contamination of the sample during the sample preparation.

The thermal desorption technique was used for chemical analysis of ink solvents and resins directly on paper (1). Recently, we presented a simple and cheap device for thermal desorption of small samples (2). A conventional Supelco SPME fiber holder for manual use was modified to a microthermal desorber ("microTD"). This device was used for comparative analysis of inks, printing inks, and inkjet inks on paper.

The usefulness of the microthermal desorption device is not limited to analysis of inks on paper. The technique was tested in casework on many different types of materials. It is not linked to any specific equipment; the analysis is performed on any kind of gas chromatograph in a manner similar to that for solid phase microextraction (SPME) analysis. In this study the use of microthermal desorption is demonstrated on some other forensic samples encountered in casework.

Materials and Methods

SPME Holder Modified for Microthermal Desorption

A modification of a Supelco SPME fiber holder (Sigma-Aldrich, St. Louis, MO) for manual use to a microthermal desorber was described earlier (2). By removing the SPME fiber, the outermost part of the needle belonging to the holder (about 1.3 cm in length) remained empty. A small sample was placed inside this empty space and was introduced into an injector of any kind of gas chromatographic equipment having a straight inlet liner. The temperature of the thermal desorption was given by injector temperature and the time was given by the time during which the needle was kept inside the liner. After finishing the analysis the sample was removed and the device was ready for the next analysis.

In some applications, thermal desorption is carried out at different temperatures using the same sample (fractionated desorption). The microdevice described here can be used for different desorption temperatures in a similar manner, such as performing desorption at lower injector temperature, withdrawing the sample from the injector, increasing the injector temperature, and performing next analysis.

Gas Chromatography

The desorbed compounds were analyzed by gas chromatography with a flame ionization detector (GC-FID) or by GC–mass spectrometry (MS) (Hewlett-Packard 5972 series MSD detector). For GC-FID, the column was a HP-5, 30 m × 0.32 mm × 0.52 μm, with an average He gas flow rate of 1.0 mL/min. The analytical conditions were initial temperature of 45°C held for 1 min, ramp of 8°C/min to 280°C, and final time of 10 min. For GC–MS, the analytical conditions were the same but the column used was a DB-35ms, 30 m × 0.25 mm × 0.25 μm. The liner used was open with 1.5 mm inner diameter. All the analyses were performed in a splitless mode. The temperature of the thermal desorption was given by the temperature of the injector, normally 200°C if not otherwise stated.

Results and Discussion

Ink on Paper

The great advantage of thermal desorption of inks on paper is the possibility of analyzing the ink with minimum decomposition of the paper background. This application has been described in the literature (1,2). The temperature of 200°C seems to be optimal for thermal desorption. At this temperature the decomposition of paper

[1]National Laboratory of Forensic Sciences, SE 581 94 Linköping, Sweden.

Received 11 June 2008; and in revised form 3 Sept. 2008; accepted 28 Sept. 2008.

matrix is negligible. In addition to samples of various inks on paper, we have also encountered quite some different materials deposited on paper matrix.

Lipstick on Paper

A lipstick was used to write part of a threatening letter to a person. Control sample of lipstick of a similar shade, to be compared with the suspect sample, was supplied by police. Lipsticks are known to contain fatty materials, oils, and other compounds with such volatility that they may be analyzed by GC–MS. A small sample, about 5 mm in length and 0.3 mm in width, was cut out from the letter and analyzed by microthermal desorption. The control sample was also transferred to paper and analyzed in the same manner. The results are shown in Fig. 1. There was a clear difference between the two lipstick samples. Additionally, five samples of lipsticks from various manufacturers were analyzed by this technique and all of them were found to be clearly distinguishable from each other (Fig. 2). The differences between the lipstick samples were qualitative. When semiquantitative differences are observed, several analyses on each sample should be performed to evaluate the homogeneity of the samples. The reproducibility of microthermal desorption is very good if the samples analyzed are homogeneous.

Toner on Paper

Toners from copy machines or laser printers are another type of material which is found suitable for analysis by microthermal desorption. Traditionally, when two or more samples of toners are compared, the samples are analyzed first by Fourier transform infrared spectrophotometry followed, if necessary, by pyrolysis GC–MS (3,4). Although less sensitive, microthermal desorption is an alternative to pyrolysis for laboratories lacking a pyrolysis device or due to simpler sample preparation. The desorption temperature of 200°C worked well. Figure 3 shows a comparison of results achieved for black toners from three different copy machines (Canon GP 220, Xerox 5614, and Canon NP 6025) and one laser printer (HP LaserJet 4250n). All these toner materials could easily be distinguished. Most of the peaks detected, for e.g., Xerox 5614 toners, contained benzene ring but generally did not match well to the compounds in our mass spectra library.

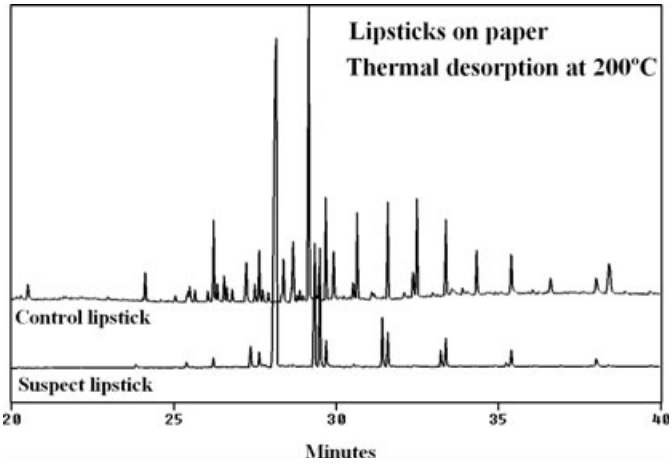

FIG. 1—*Chromatograms (GC–MS) obtained by microthermal desorption of suspect and control sample of lipsticks in casework. The two samples were found to be completely different. GC–MS, gas chromatography–mass spectrometry.*

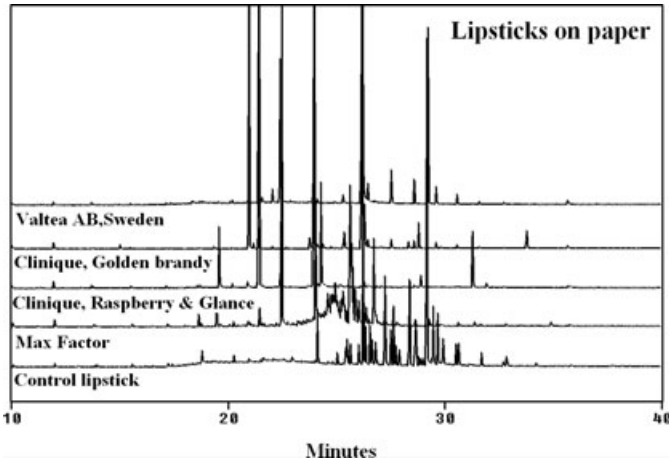

FIG. 2—*Chromatograms (GC–MS) recorded for five samples of lipsticks from different manufacturers. The microTD was applied to weak smears of these lipstick samples on paper. One of the samples was the control sample from casework in Fig. 1. The manufacturer was unknown to us. GC–MS, gas chromatography–mass spectrometry.*

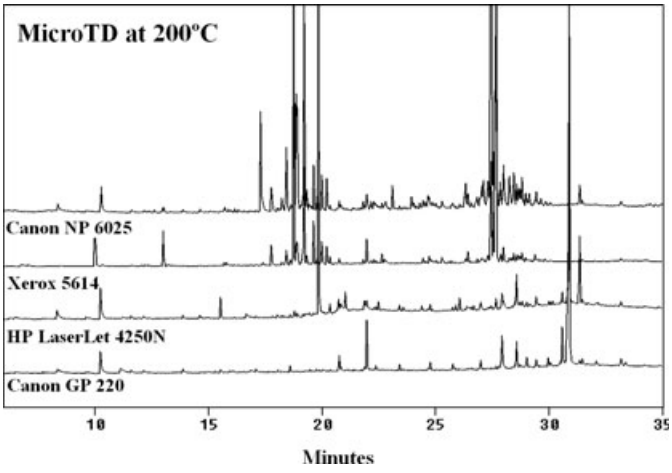

FIG. 3—*Chromatograms (GC/FID) obtained by microthermal desorption of toner material on paper. Three photocopiers and one laser printer were analyzed. The desorption temperature was 200°C. GC/FID, gas chromatography/flame ionization detector.*

Security Dye on Paper

Another application of microthermal desorption in our laboratory is an analysis of the red and the black security dye employed in Sweden for staining of stolen bank notes. These dyes are strongly adsorbed on the bank note background and difficult to analyze by thin layer chromatography or high performance liquid chromatography (HPLC). By cutting small stained pieces of a suspect bank note, microthermal desorption detects the solvents used in the security dyes. This analysis alone is not sufficient for the identification of the security dyes but microTD is a useful contribution for this purpose.

Clear Coat

Microthermal desorption can be employed for analysis of small items and is not limited to samples on paper. For such items, the desorption temperature used can be higher than that for samples on paper. The size of the sample is, however, restricted by the

dimensions of the inner part of the needle. The analysis has the advantage of the SPME technique in that the sample is desorbed into a limited vapor volume. An example of the acceptable quality of the resulting chromatograms is shown in Fig. 4. This chromatogram was obtained by microdesorption (3 min at 225°C) of a small amount of the automotive clear topcoat layer. Even the peaks with short retention times were well resolved. The thermal desorption analysis gives information about the analyzed item complementary to that obtained by pyrolysis gas chromatography. Small samples chosen for analysis must be introduced to the inner part of the holder needle. Sharp-edged tweezers are used and the sample handling is carried out under a microscope. During the analysis, the sample will be preserved inside the needle. Afterwards, the sample can easily be removed from the needle by pushing the plunger forward.

Smokeless Powder

One category of samples suitable for this analysis we encountered in our casework were flakes of smokeless powder. Stabilizers, softeners, and solvents (in unfired propellant) were detected and identified in a single analytical step (Fig. 5). Figure 6 shows the comparison of propellant flakes collected from the inside of a pistol and from clothing, respectively. The shooting distance was about 50 cm, from a Walther 7.65 mm caliber pistol using Remington ammunition. The particles were partially burnt but one single particle was sufficient for an analysis. The agreement in composition of propellant particles was generally qualitative, as a single particle did not generally represent the whole propellant in composition quantitatively (5). For quantitative comparison, methods such as HPLC or LC/MS are more suitable and several particles are needed.

Coffee Particles

An interesting application of microTD was encountered in a case where coffee particles were the evidential material. The case was a robbery and it was important to find coffee grains in the back seat of a car used for escape. By careful search, five very small brown particles were collected from the seat. It was decided to analyze each particle separately. As reference material, grains of a roasted coffee were analyzed. The first two suspect particles were not identified, but they were not composed of coffee. The third and the fourth particle were found to contain high content of caffeine and also some other compounds typical for coffee, such as pyridinol, furfuryl alcohol, and quinic acid. The chromatogram obtained for the third particle is depicted in Fig. 7. The agreement with reference material is good considering that the reference particle was not of the same brand of coffee and that the suspect particles were collected after a long time of airing and sample handling. The particles were identified as particles of coffee.

Other materials were subjected to microTD, e.g., red particles intended to be mixed with hash. Also suspected coffee smears on bank notes were analyzed by this technique. Generally, microthermal desorption provides information about the analyzed item

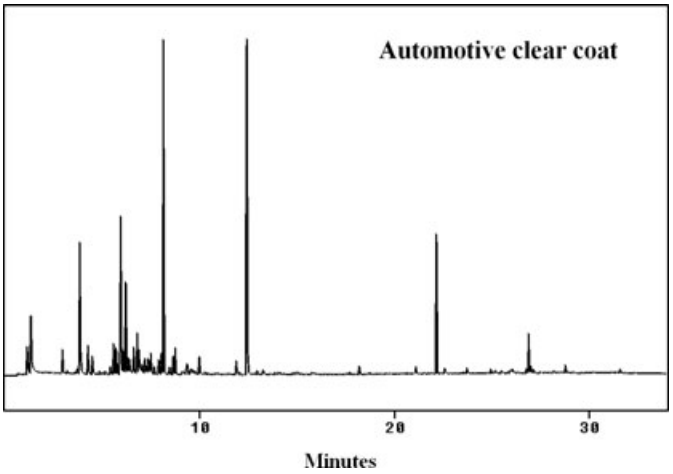

FIG. 4—*A well-resolved chromatogram (GC/FID) obtained by the microthermal desorption of automotive clear coat No. 10264. GC/FID, gas chromatography/flame ionization detector.*

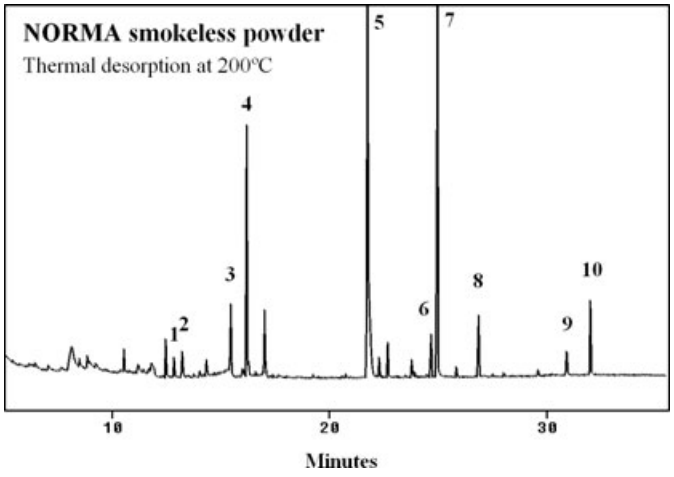

FIG. 5—*Thermal desorption GC–MS of a single grain of smokeless powder manufactured by NORMA. Solvents, softeners, and stabilizers are detected. Some identified peaks: 2-(2-butoxyethoxy) ethanol (1), o-nitrotoluene (2), N-methylaniline (3), 2-(2-butoxyethoxy) ethylacetate (4), diphenylamine (5), N,N-diphenylformamide (6), centralite (7), 2-nitrodiphenylamine (8), 4-nitrodiphenylamine (9), and bis(2-ethylhexyl) phthalate (10). GC–MS, gas chromatography/mass spectrometry.*

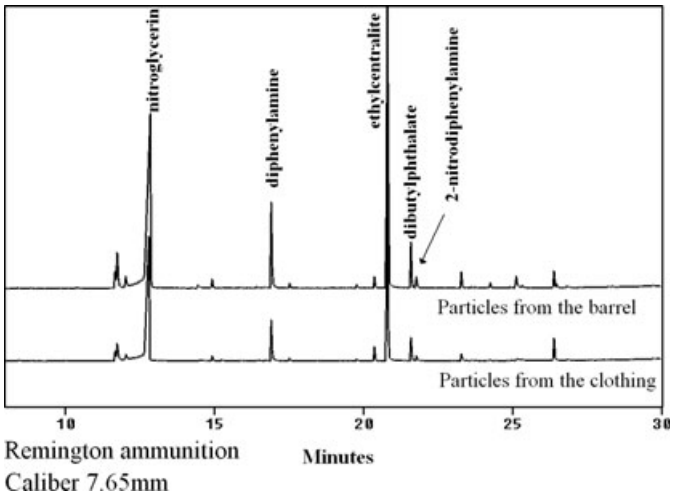

FIG. 6—*The composition of grains of smokeless powder collected from the inside of a Walther caliber 7.65 mm pistol (Remington ammunition) and from clothing, respectively. The shooting distance was about 50 cm. GC/FID chromatograms are shown. The agreement in composition as obtained by microTD of single particles is evaluated mainly qualitatively. GC/FID, gas chromatography/flame ionization detector.*

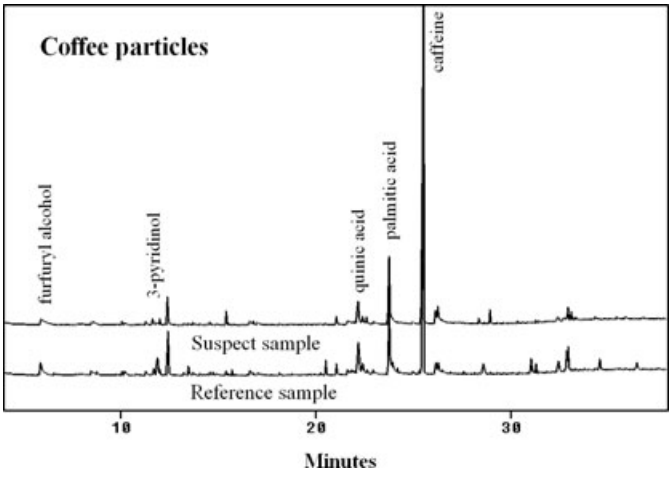

FIG. 7—*Microthermal desorption GC–MS of a suspect coffee particle collected from the back seat of a car. Caffeine is the main compound detected in the resulting chromatogram. A comparison with an analysis of a particle of roasted coffee is also shown. GC–MS, gas chromatography–mass spectrometry.*

complementary to that obtained by pyrolysis GC and both techniques may be combined. Sample preparation is limited to use of scalpel and tweezers; no solvents and liquid nitrogen cooling units are necessary.

Ink Dating

As mentioned above, the microTD device can easily be used for fractionated thermal desorption analysis. The sample inside the holder is gradually exposed to several different temperatures and chromatograms are recorded at every temperature. We have employed the device for fractionated TD of ballpoint pen inks and inks from inkjet printers. Fractionated TD may be useful for distinguishing between fresh and old inks. Solvents such as phenoxyethanol, phenoxypropanol, etc. will be liberated at lower temperatures from fresh inks in comparison to old ink samples. Table 1 illustrates the use of fractionated TD for a sample of ballpoint ink of different age. The desorption was performed at injector temperatures of 100°C, 150°C, 200°C, and 225°C, respectively. The table shows clearly how the relative amount of phenoxyethanol liberated at 100°C and 150°C decreases with the age of the ink. The results are mass independent as the same sample is used for all the temperatures and the amount of phenoxyethanol is expressed as a percentage. The total amount of phenoxyethanol liberated at these four temperatures is assumed to be 100%.

Conclusion

The described device for microthermal desorption has been shown to be suitable for an analysis of various types of forensic samples. Some examples of analyses from casework are presented. In addition to samples of inks on paper, this device was successfully used for analysis of toners, various stains on bank notes, and lipstick stains on paper. Also other small items, not attached to paper, can be analyzed. The reproducibility of the method is very good if the sample analyzed is homogeneous. It was demonstrated in our previous study on ink samples (2). This device can also be used for fractionated thermal desorption analysis, a method suitable for distinguishing between fresh and old inks.

TABLE 1—*Fractionated thermal desorption of a ballpoint pen ink.*

	Amount of Phenoxyethanol Liberated at Different Temperatures			
Ink Age	100°C	150°C	200°C	225°C
1.5 month	17.6%	35.1%	36.8%	10.5%
6 months	7.7%	32.5%	44.8%	15.0%
1 year	2.7%	23.5%	52.6%	21.1%
2 years	0%	18.3%	53.8%	27.9%
3 years	0%	7.2%	55.6%	37.1%

The same sample of ink was desorbed at four different temperatures (100°C, 150°C, 200°C, and 225°C) and the relative amount of 2-phenoxyethanol liberated at each temperature was measured.

References

1. Bügler JH, Buchner H, Dallmayer A. Characterization of ballpoint pen inks by thermal desorption and gas chromatography-mass spectrometry. J Forensic Sci 2005;50:1209–14.
2. Andrasko J. A simple microthermal desorption device. J Forensic Sci 2006;51:925–8.
3. Egan WJ, Morgan SL, Bartick EG, Merrill RA, Taylor HJ. Forensic discrimination of photocopy and printer toners. II. Discriminant analysis applied to infrared reflection-absorption spectroscopy. Anal Bioanal Chem 2003;376:1279–85.
4. Egan WJ, Galipo RC, Kochanowski BK, Morgan SL, Bartick EG, Miller ML, et al. Forensic discrimination of photocopy and printer toners. III. Multivariate statistics applied to scanning electron microscopy and pyrolysis gas chromatography/mass spectrometry. Anal Bioanal Chem 2003;376:1286–97.
5. Andrasko J. Characterization of smokeless powder flakes from fired cartridge cases and from discharge pattern on clothing. J Forensic Sci 1992;37:1030–47.

Additional information and reprint requests:
Jan Andrasko, Ph.D.
SKL, National Laboratory of Forensic Science
Linköping SE-581 94
Sweden
E-mail: chemistry@skl.police.se