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TECHNICAL NOTE

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A Simple MicroThermal Desorption Device

ABSTRACT: A new method for thermal desorption of small samples is presented. The method uses a solid phase microextraction (SPME) holder with the fiber removed. The sample—for example, an ink sample on paper—is simply placed inside the needle of the holder, where normally an SPME fiber is positioned. The thermal desorption is then performed on any kind of gas chromatograph in a manner similar to that for SPME analysis. The needle of the SPME holder penetrates the injector septum; the temperature of the thermal desorption is simply the temperature of the injector. No solvents or liquid nitrogen cooling are used. The paper sample is kept inside the holder needle during the analysis. After the analysis is completed, the sample is removed from the needle by pushing forward the steel wire inside the needle in the way normally used to perform sampling with the SPME fiber. The desorbed compounds were analyzed by gas chromatography with a flame ionization detector or by gas chromatography-mass spectrometry. The optimum temperature for desorption of ink samples on paper was 200°C. The influence of the paper matrix is negligible at that temperature. Laboratories lacking the commercial device for thermal desorption can use this cheap device for the analysis of, for example, writing ink, printing ink, and inkjet ink samples on paper. Other types of samples can be investigated but the size of samples suitable for analysis is limited.

KEYWORDS: forensic science, thermal desorption, ink analysis, document examination

Thermal desorption is a widely used technique for extracting and isolating volatile and semivolatile compounds from various matrices. Almost any sample containing volatile organic compounds can be analyzed by using some variation of this technique. The method is well established in forensic science, for example, for headspace analysis of accelerant vapors in arson analysis. Automated thermal desorption units are commercially available.

Recently, the thermal desorption technique was used for chemical analysis of ink solvents and resins directly on paper (1). This technique avoids the use of solvents and also the risk for contamination of the sample during the preparation. It represents an important complement to other methods for chemical analysis of inks. The temperature of the thermal desorption is optimized to desorb volatile compounds in inks as well as volatile fragments from dyes and binder resins. The decomposition of the sample matrix—paper background—is, on the other hand kept very low or negligible. The equipment used is commercially available and consists of a thermal desorption unit connected to an injector with a liner equipped with a liquid nitrogen cooling unit.

In this study, a simple and cheap device for thermal desorption of small samples is presented. The technique uses a commercial solid-phase microextraction (SPME) holder, available in most laboratories today. No solvents or liquid nitrogen cooling units are necessary. As with the SPME technique, this device can be used in connection with any kind of gas chromatographic equipment having a straight inlet liner. This "poor man's microthermal desorption" is demonstrated here for comparative analysis of inks, printing inks and inkjet inks on paper.

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Materials and Methods

SPME Holder Modified for Microthermal Desorption

A conventional Supelco SPME fiber holder for manual use was modified to a microthermal desorber. For SPME work, a replaceable SPME fiber assembly is attached to the holder. The fiber is kept completely inside the septum-piercing needle when not used for sampling or desorption. The SPME fiber consists of an approximately 1 cm long silica fiber coated with an appropriate stationary phase. The fiber is connected to a plunger using a stainless-steel wire (fiber attachment needle) and a tensioning spring. The plunger is pushed downward or upward to move the SPME fiber outside or inside the needle. The SPME fiber is fragile and can easily be broken. It can happen accidentally (which was the case with one of our SPME fibers) when the sampling is not carefully performed and for example, the fiber bends or touches some object. By removing the fiber, the outermost part of the needle (about 1.3 cm in length) remains empty. The remaining part of the needle is blocked by the fiber attachment needle. The plunger can push the fiber attachment needle about 2 cm forward or backward. If a small sample is placed inside this empty space, it can be introduced into an injector of any kind of gas chromatographic equipment having a straight inlet liner. The septum-piercing needle penetrates the gas chromatography (GC) inlet septum with the sample inside the needle. In the injector liner, the sample will immediately be heated up to the injector temperature and thermal desorption will occur. The sample is kept inside the needle for the whole procedure. The time for the thermal desorption is given by the time the needle is kept inside the liner. Afterwards, the needle is withdrawn from the injector and the sample can be easily removed from the needle by pushing the plunger forward. Similar to the SPME analysis, the liner used for microdesorption should have a small inner diameter as a splitless

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analysis is normally carried out. Large volume liners will cause a broadening of peaks in the resulting chromatogram.

The space available for the sample is limited. The inner diameter of the septum-piercing needle is 0.3 mm and the length of the sample should not exceed 1.3 cm. In a splitless mode, the sensitivity of the analysis is generally very good because the whole sample is analyzed in a single desorption step. The small sample dimension is, however, advantageous for rapid thermal desorption. The volatile compounds, which evaporate from the sample, will be introduced directly into the chromatographic column. The size and form of this device is suitable for analysis of samples on paper—i.e., various writing and printing inks.

Microthermal Desorption of Ink on Paper

Ink samples on paper were cut out using a scalpel. The samples were normally about 1 cm long and 0.3–0.4 mm wide. It was found advantageous to cut out samples and remove most of the paper backside with tweezers. The paper backside is normally easily removed by slicing it off as from a sandwich. The thinner ink sample is then easier to introduce into the holder needle. The process of putting the sample inside the needle requires some training at the beginning, but is normally quite rapid. Sharp-edged tweezers are used and the sample handling is carried out under a microscope. By small sideward movements of the sample kept in tweezers, the sample is transferred into the needle step by step. To facilitate this transfer, a steel wire, 0.2 mm in diameter, can be used for pushing the sample. If the paper sample is wider than 0.3 mm, it may also be slightly bent with tweezers and formed according to the walls of the needle. It is also possible to divide the sample into several parts, which can be transferred into the needle separately.

The temperature of the thermal desorption was conferred by the temperature of the injector, normally 200°C if not otherwise stated. When changing the injector temperature, the system was left for 3 min to reach equilibrium before the introducing of next sample. The desorbed compounds were analyzed by gas chromatography with a flame ionization detector (GC-FID) or by gas chromatography-mass spectrometry (GC-MS, Hewlett-Packard 5972 series MSD detector, Hewlett-Packard, Palo Alto, CA). For GC-FID, the column was an 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 as follows: initial temperature 45°C held for 1 min, ramp 8°C/min to 280°C, and final time 5 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 a 1.5 mm inner diameter. All the analyses were performed in a splitless mode. The thermal desorption was carried out for 3 min if not otherwise stated. After this time, the SPME holder containing the sample was withdrawn from the injector. The aim of this study was to show the functionality of the proposed microdesorption device; the type of column and GC conditions were not so important.

Results and Discussion

Performance of the Device

The great advantage of thermal desorption of inks on paper is the possibility of analyzing the ink with minimum decomposition of the paper background (1). By varying the injector temperature, the optimum conditions for the analysis of a particular sample can be selected. Figure 1 shows the microdesorption of an ink on paper sample performed at four different desorption temperatures,

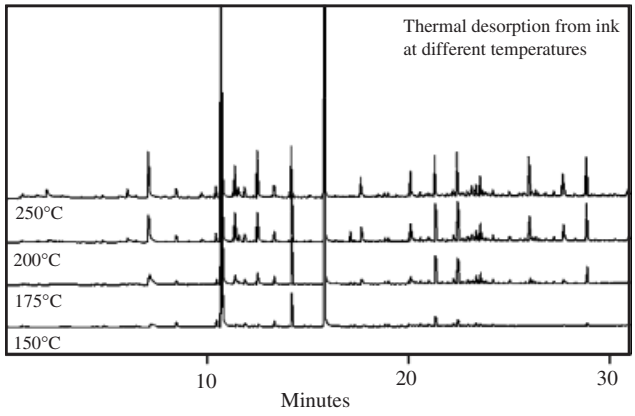

FIG. 1—*Microthermal desorption of an ink on a paper sample (Solstar ink) at four different temperatures: 150°C, 175°C, 200°C, and 225°C. At temperatures below 200°C, the yield of desorption is poor.*

between 150°C and 225°C. It can be seen that the amount of ink-volatile compounds and also compounds formed by the decomposition of ink components increase with the desorption temperature. Below 200°C, the yield of desorption is poor. The desorption of pure paper matrix is shown in Fig. 2. The peaks marked 1 and 2 represent nonanal and decanal, respectively, and are the strongest peaks in the chromatograms obtained for temperatures below 225°C. These peaks are also detected as very weak peaks in Fig. 1. After complete thermal desorption, the paper samples were removed from the SPME holder. At temperatures up to 200°C, there was no change in the color. At 225°C, the paper became slightly yellow, indicating some decomposition of the paper material. For ballpoint pen inks on ordinary white paper, a temperature of 200°C seems to be optimal for thermal desorption, which is in agreement with the results reported previously (1). An example of thermal desorption at 200°C for the sample of Solstar ink on paper is shown in Fig. 3. For comparison, thermal desorption of a paper matrix (approximately the same amount of sample in both analyses) is also shown. The influence of the paper matrix is negligible.

The applicability of the microdesorption for the analysis of ink on paper is depicted in Fig. 4. In this figure, five different ballpoint inks have been analyzed. The desorption temperature was 200°C. The peaks shown in Fig. 4 are mostly representing the various

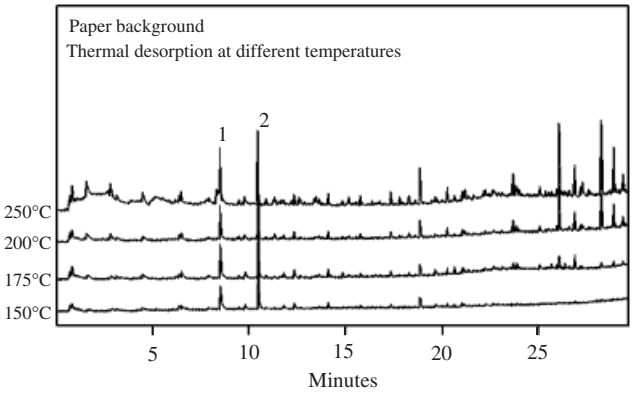

FIG. 2—*Microthermal desorption of paper background at four different temperatures. The peaks marked 1 and 2 were identified as nonanal and decanal, respectively, and are the strongest peaks at desorption temperatures up to 200°C. At higher temperatures, some decomposition of paper material occurs, but is still not considerable at 225°C.*

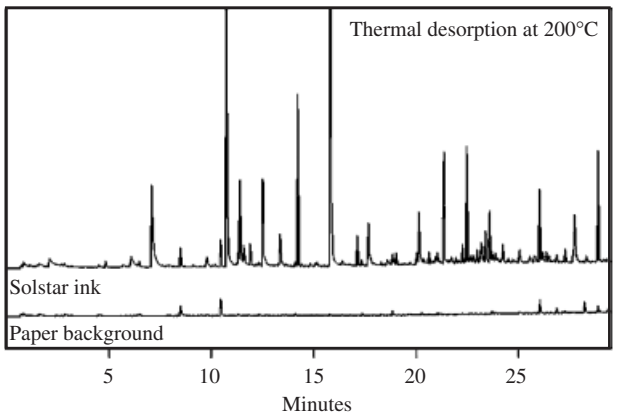

FIG. 3—*Thermal desorption at 200°C of Solstar ballpoint ink on paper. The influence of paper matrix is negligible.*

volatile compounds present in inks. The latter part of the chromatograms contains peaks corresponding to fragments of binder polymers and, possibly, decomposition products of ink dyes. Figure 5 shows this part of the resulting chromatograms and, together with Fig. 4, illustrates the possibility of distinguishing between different inks. The aim of this study was not to identify the various volatile components of binder polymers and ink colorants detected by thermal desorption; this was described earlier by Bügler et al. (1). It is useful to examine the inks after the analysis. For example, investigating blue inks—some inks do not change color significantly, some inks turn green and some inks contain colorants that are completely removed by the thermal desorption. It would be interesting to investigate this phenomenon in detail.

On aging, the content of volatile compounds in inks such as phenoxyethanol decreases. When inks on paper samples of different age are compared, the comparison should be mostly of a qualitative nature. However, the resin polymer fragments and volatile fragments of dyes seem to remain essentially unchanged over longer periods of time as shown in Fig. 6.

The usefulness of a microthermal desorption device is not limited to ballpoint pen inks. Also, other types of inks on paper may be analyzed and compared. The analysis of black printing

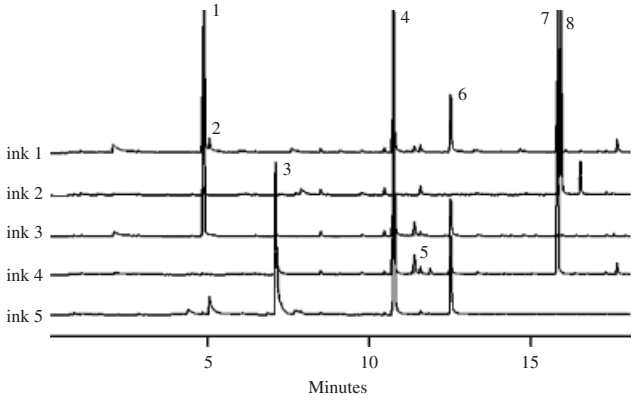

FIG. 4—*Desorption of five different blue ballpoint inks on paper. The initial part of the observed chromatograms, containing various volatile compounds present in inks, is depicted. Some of the peaks detected are marked 2-methyl 2,4-pentanediol (1), 2,2-dimethyl 1,3-propanediol (2), benzylalcohol (3), 2-phenoxyethanol (4), 2-ethyl 2-hydroxymethyl 1,3-propanediol (5), phthalic anhydride (6), 2-(2-phenoxyethoxy)ethanol (7), and 2-naphtol (8).*

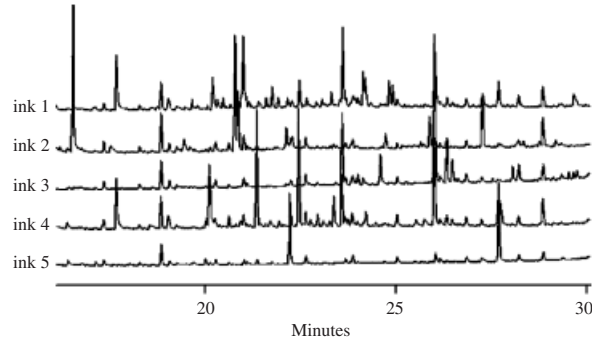

FIG. 5—*Latter parts of the chromatograms shown in Fig. 6. The various peaks correspond to volatile fragments of binder polymers and of ink colorants. All the inks are clearly distinguishable.*

inks from three different manufacturers is shown in Fig. 7. Figure 8 depicts an analysis of two different black inkjet inks from the same manufacturer.

The microthermal desorption can also be useful for analysis of materials other than inks on paper. We have carried out analyses of single grains of smokeless powder. Stabilizers, softeners, and solvents were detected and identified in a single analytical step. Also, automotive clear topcoat layers can be analyzed by this technique giving well-resolved peaks, even those with short retention times.

Limitations of the Proposed Device

The proposed device is very cheap, normally available in every laboratory having the SPME technique. It can be used in connection with every kind of GC. The temperature of thermal desorption is given by the temperature of the injector. The range of temperatures is dependent on the possibility of temperature programming and keeping a set temperature constant during the analysis.

The microdevice has the advantage of the SPME technique in that the sample is desorbed into a limited vapor volume. Performing the thermal desorption directly inside the liner without collecting the volatile components in a cooled trap can, however, result in broadening of chromatographic peaks if the desorption process is slow, for example, at low desorption temperatures. At 200°C, as mostly used in this study, the broadening of chromatographic peaks was not serious and the resulting chromatograms were of acceptable quality. The tailing of very polar compounds,

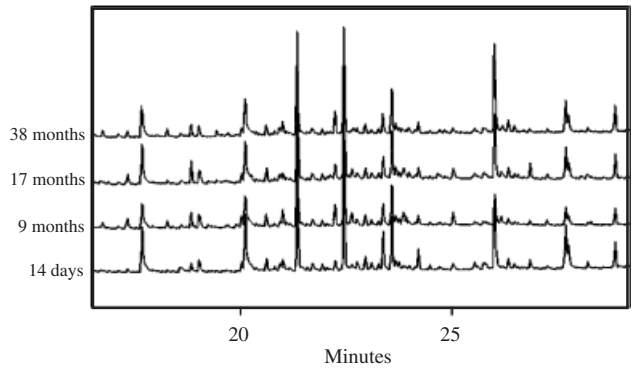

FIG. 6—*Latter part of the chromatograms obtained for a ballpoint ink of varying age, between 14 days and 38 months old. No essential changes are observed. Solvent peaks (phenoxyethanol, benzylalcohol) appearing in the initial parts of these chromatograms and not shown in this figure decrease with age.*

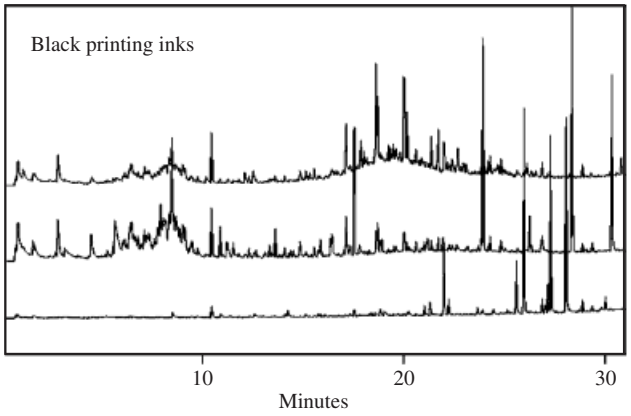

FIG. 7—*Microthermal desorption of three different black printing inks on paper.*

such as phenoxyethanol, can be minimized by using a clean, deactivated liner and column.

The size of samples suitable for analysis is also limited. The main application of the device is the analysis of inks on paper and for this purpose, the sensitivity of the analysis is sufficient. To increase the sensitivity, several pieces of paper containing ink may be introduced into the needle of the SPME holder.

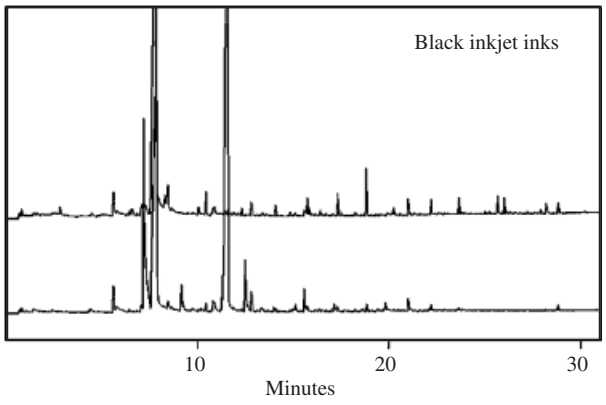

FIG. 8—*Microthermal desorption of two black inject inks (on paper) from the same manufacturer. HP OfficeJet Pro 1170C (upper trace) and HP DeskJet 6122 (lower trace).*

Like in an ordinary SPME analysis, the septum-piercing needle will transfer a small amount of air together with the sample into the injector liner. We have not noticed any problems connected with this fact, and the reproducibility of the method is good.

The SPME holder used was designed for manual analysis. It should also be removed from the GC injector after a certain time to restrict the desorption time.

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 a lower injector temperature, withdrawing the sample from the injector, increasing the injector temperature, and performing the next analysis.

After completing the analysis, the sample is removed and the device is ready for the next analysis. We have not noticed any carry-over of an ink sample to the next analysis. Before the first analysis, we usually conditioned the device by a blank analysis at 200°C with the fiber attachment needle pushed maximally forward inside the injector. Possible residues of compounds desorbed in previous analyses and deposited in the space between the fiber attachment needle and needle inner walls are removed in this way. If necessary, the septum-piercing needle of the SPME holder may simply be cleaned by washing with a suitable solvent.

Conclusions

The proposed microdevice for thermal desorption has been shown to be suitable particularly for an analysis of various types of inks on paper. Although it has some limitations such as limited sample size, it is very cheap and applicable to any kind of gas chromatographic equipment. It is easy to keep this device clean and thus minimize the risk for contamination.

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