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TECHNICAL NOTE

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Comparison of the Effectiveness of Tenax TA® and Carbotrap 300® in Concentration of Flammable Liquids Compounds

ABSTRACT: The aim of research was to compare two adsorbents, Tenax TA® and Carbotrap 300®, to evaluate their usefulness as passive adsorbents of flammable liquids compounds. It was also to determine whether Carbotrap 300® could be used in a passive adsorption mode, contrary to manufacturer recommendations. To compare the adsorption properties and the thermal desorption efficiency for Tenax TA® and Carbotrap, the components of test mixture were adsorbed and then chromatographically analyzed. The analysis was conducted by means of an automated thermal desorber coupled with a gas chromatograph and a mass spectrometer. This research established that although these adsorbents significantly differ from each other in adsorption properties, each of them can be successfully used for passive adsorption of ignitable liquids compounds. Tenax TA® turned out to be more effective for the adsorption of nonpolar, high-boiling compounds, whereas Carbotrap is more effective for polar and volatile compounds. The examined adsorbents differ in their susceptibility to thermal desorption. For Carbotrap 300®, after the analysis an additional treatment is required to remove the remnants of adsorbed compounds. With Tenax TA®, this additional step is not necessary because the thermal desorption is sufficiently effective that this product is immediately ready for re-use.

KEYWORDS: forensic science, ignitable liquids, fire debris, gas chromatography-mass spectrometry, passive adsorption, headspace analysis, Tenax TA®, Carbotrap 300®

The aim of chemical analysis of fire debris is to check for traces of flammable liquids, and if present, to identify them.

One of the initial stages of the analysis is the separation and concentration of the analytes. To achieve this, different techniques can be utilized, but presently the most often used one is headspace analysis with passive adsorption and subsequent thermal desorption of the analytes (1).

Different adsorbents vary in their effectiveness based on the concentration of flammable liquid compounds. They also differ in other properties such as susceptibility to thermal desorption.

When automated thermal desorbers are used, the adsorbent is in the form of an instrument-compatible tube.

A literature search shows that in this case, the best adsorbent for ignitable liquid compounds concentration is Tenax TA® (2–6). However, there is one paper that describes a procedure in which Carbotrap 300® is routinely and successfully used (7).

The information regarding the use of Carbotrap 300® for the passive adsorption of ignitable liquid compound is interesting because, according to information in the paper, it cannot be used for passive adsorption and should be used for active (pumped) sampling only (8). This is due to the structure of the adsorption tube—Carbotrap 300® contains three layers of different carbon adsorbents.

This research was undertaken to better compare the two adsorbents.

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The aim of research was:

- to compare the effectiveness of Tenax TA® and Carbotrap 300® in passive adsorption of flammable liquids compounds in headspace of samples; and
- to examine and compare the efficiency of thermal desorption of flammable liquids compounds using these adsorbents.

Materials and Methods

- The laboratory oven with a thermostat (KBC G65/250, Premed, Warsaw, Poland) was used for heating the samples during adsorption;
- an Auto System XL gas chromatograph (Perkin Elmer Instruments) coupled with a Turbo Mass Gold mass spectrometer (Perkin Elmer Instruments, Norwalk, CT) was used for the chromatographic analysis. An Elite 1 capillary column with an internal diameter of 0.25 mm, a stationary phase film thickness of 1 μm and a length of 30 m was utilized. The mass spectrometer was equipped with a quadrupole analyzer and electron impact ionization. The ionization energy was set to 70 eV and the total ion measurement mode was used;
- an automated thermal desorber ATD Turbo Matrix (Perkin Elmer Instruments) was used to desorb the analytes.

The following materials and reagents were used:

- a set of stainless-steel adsorption tubes (Supelco, Bellefonte, PA), containing Tenax TA®;
- a set of stainless-steel adsorption tubes (Supelco), containing Carbotrap 300®;

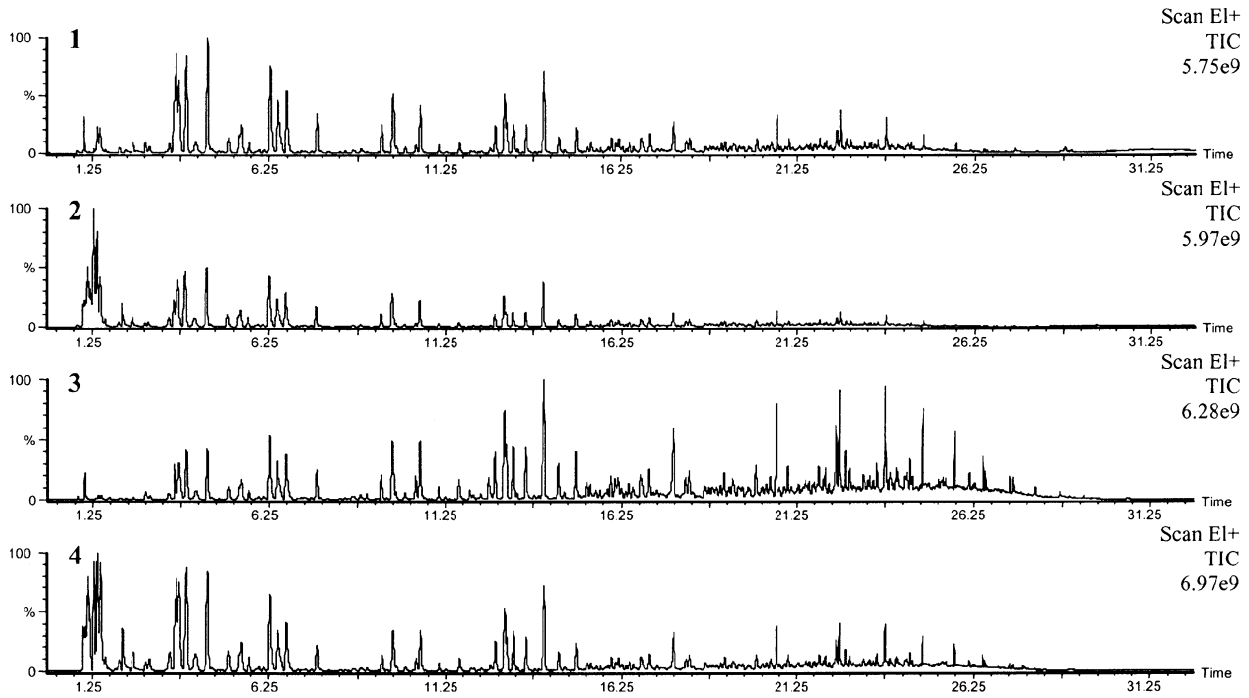

FIG. 1—*Representative chromatograms comparing the effectiveness of Tenax TA® and Carbotrap 300® concentrating ignitable liquid compounds. Chromatograms 1 and 2 show the results of the analysis of the test mixture adsorbed on Tenax TA® (chromatogram 1) and Carbotrap 300® (chromatogram 2) at 60°C. Chromatograms 1 and 2 show the results of the analysis of the test mixture adsorbed on Tenax TA® (chromatogram 3) and Carbotrap 300® (chromatogram 4) at 90°C.*

- Erlenmeyers with polished closing and fitted glass plugs;
- helium (Helium 6.0 Linde Gas AG, Munich, Germany);
- test mixture of methanol, ethanol, acetone, propanol, *n*-butanol, "Benzyna Ekstrakcyjna" (solvent based on volatile alkanes, within the boiling range C5–C8), gasoline, and diesel fuel. These compounds were mixed in a volume ratio of 1:1:1:1:1:5:5:5. To prepare the test mixture, the following reagents were used:
- methanol (cz. Chempur, Piekary Śląskie, Poland),
- ethanol (Polmos Kraków, Krakow, Poland),
- acetone (cz.d.a. Polskie Odczynniki Chemiczne, Gliwice, Poland),
- *n*-propanol (cz. Polskie Odczynniki Chemiczne),
- butanol (a.r. Roanal, Budapest, Hungary),
- "Benzyna Ekstrakcyjna" (Dragon, Polska, Poland),
- gasoline (U95, Orlen, Plock, Poland), and
- diesel fuel (Orlen).

Samples were analyzed according to standard procedure, which, in brief, is as follows: adsorbed compounds are thermally desorbed (Tenax conditions: 330°C for 20 min; Carbotrap conditions: 360°C for 20 min) and concentrated on a cold trap—a quartz tube containing a small quantity of Tenax TA® and cooled down to − 30°C. Afterwards, they are quickly thermally desorbed again (conditions 330°C for 20 min) and carried to a gas chromatograph by a heated transfer line (200°C). For the identification of analytes, a gas chromatograph coupled to a mass spectrometer is used.

The GC-MS analysis is conducted according to the following temperature program: initial temperature: 30°C maintained for 5 min; increase 5°C/min to 120°C, increase 15°C/min to 270°C; and final temperature: 270°C maintained for 5 min.

The research concerning the comparison of adsorption properties of Tenax TA® and Carbotrap 300® included adsorption of test mixture compounds at temperatures of 60°C and 90°C and subsequent thermal desorption and GC-MS analysis of the desorbed compounds.

Six adsorption tubes containing Tenax TA®, six tubes with Carbotrap 300®, and a filter disk spiked with 5 µL of the test mixture were placed in Erlenmeyer flasks with air-tight closures. The flasks were sealed and placed in the oven, at selected temperatures (60°C and 90°C) for 16 h.

Following this, the adsorption tubes were placed on the thermal desorber carousel and the analysis was carried out according to the previously described procedure.

To compare the thermal desorption efficiency for Tenax TA® and Carbotrap 300® six Tenax TA® adsorption tubes, six Carbotrap 300® adsorption tubes, and a filter disk spiked with 5 µL of test mixture were placed in an Erlenmayer with an air-tight plug. The sealed flask was placed in the thermal examination chamber at 90°C for 16 h.

Thermal desorption was carried out as previously described.

Every sample tube was analyzed twice, that is, after thermal desorption and GC-MS analysis the process of thermal desorption and GC-MS analysis was repeated for the same adsorption tube to determine whether all compounds were totally desorbed during the first analysis.

The desorption temperature was established based on the manufacturer's recommendation (8). Thermal desorption for Tenax TA® was conducted at 330°C and at 360°C for Carbotrap 300®.

Results

Adsorption Properties of Tenax TA® and Carbotrap 300®

Examples of obtained chromatograms are shown in Fig. 1.

From among isolated compounds, 18 were chosen as representative for all flammable liquids. There were divided into four

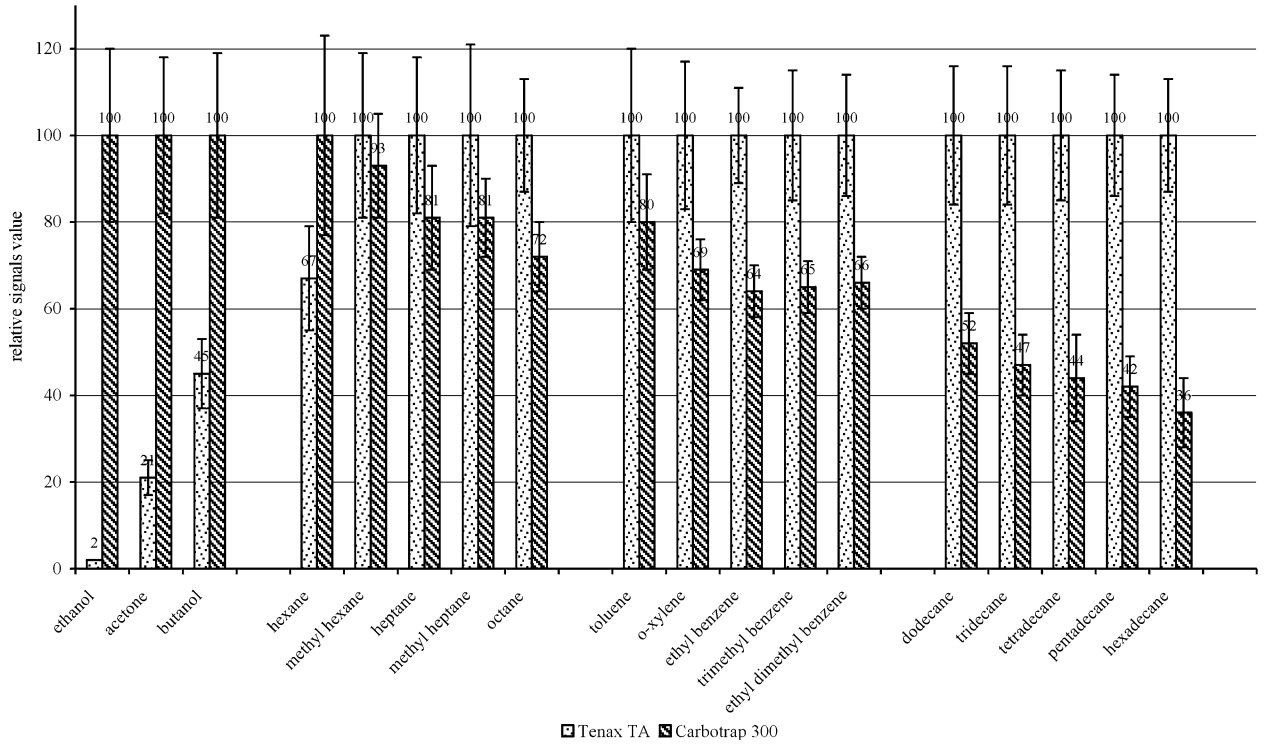

FIG. 2—*The bar graphs illustrate the effectiveness of Tenax TA® and Carbotrap 300® in the adsorption of target compounds at 60°C.*

groups based on their physicochemical properties*: volatile polar compounds* (ethanol, acetone, butanol), *volatile nonpolar compounds* (hexane, methyl hexane, heptane, methylheptane, octane), *benzene derivatives* (toluene, *o*-xylene, ethyl benzene, trimethylbenzene, ethyldimethylbenzene), and *heavy nonpolar compounds* (dodecane, tridecane, tetradecane, pentadecane, and hexadecane).

The range of physicochemical properties of the chosen compounds covers the range of physicochemical properties of flammable liquids compounds likely to be encountered in casework. Evaluating the adsorption efficiency of the two adsorbents for these compounds allows one to estimate their suitability for the analysis of evidence samples.

The GC peaks of 18 analyzed compounds were integrated (their areas were calculated). The peak areas are directly proportional to each compound's mass.

The results for a given compound, adsorbent, and adsorption temperature were averaged for all six analyses and the uncertainties were calculated as a standard deviation.

To make the comparison of adsorption efficiency of investigated adsorbents easier, the mean signal value for a given compound, adsorbent, and adsorption temperature were presented in a relative form. The relative value was calculated by dividing the mean signal of the given compound and adsorbent by the mean signal of the same compound and adsorbent that turned out to be more effective (where the signal for given compound with this adsorbent was higher)

$$\text{Relative signal value} = \frac{x}{y} \times 100$$

where x is the mean signal value for the given compound and investigated adsorbent (at a specific adsorption temperature); y is the mean signal value for the same compound, the same temperature, and adsorbent that turns out to be more effective with relation to this compound. The uncertainty of the obtained relative signal values was calculated on the basis of the standard deviation of means.

The results obtained are presented graphically. Figure 2 presents the results for a temperature of 60°C and Fig. 3 for a temperature of 90°C.

Neither Tenax TA® nor Carbotrap 300® adsorbed methanol (the most polar from among investigated compounds) at the temperatures used, so it was not shown on graph bars.

Thermal Desorption Efficiency for Tenax TA® and Carbotrap 300®

Representative chromatograms obtained as a result of this research are shown in Fig. 4.

For the compounds that were not totally thermally desorbed (as evidenced in the chromatograms resulting from the second analysis), the thermal desorption efficiency was calculated as a percent of adsorbed compound mass that was thermally desorbed during the analysis.

The thermal desorption efficiency was calculated according to the following equation:

$$\text{Thermomdesorption efficiency} = \frac{a}{a+b} \times 100\%$$

where a is the signal (peak area) of the given compound for the first analysis; b is the signal of the same compound for the second analysis.

Values obtained for all six adsorption tubes were averaged and the uncertainty (standard deviation) was calculated.

From among 18 compounds, which were chosen as representative for flammable liquids, seven remained in an average amount of about 13% of their initial mass after the first analysis with Carbotrap 300®. Only one compound (hexane) remained on Tenax TA® in an amount of about 10% of its initial mass (Table 1).

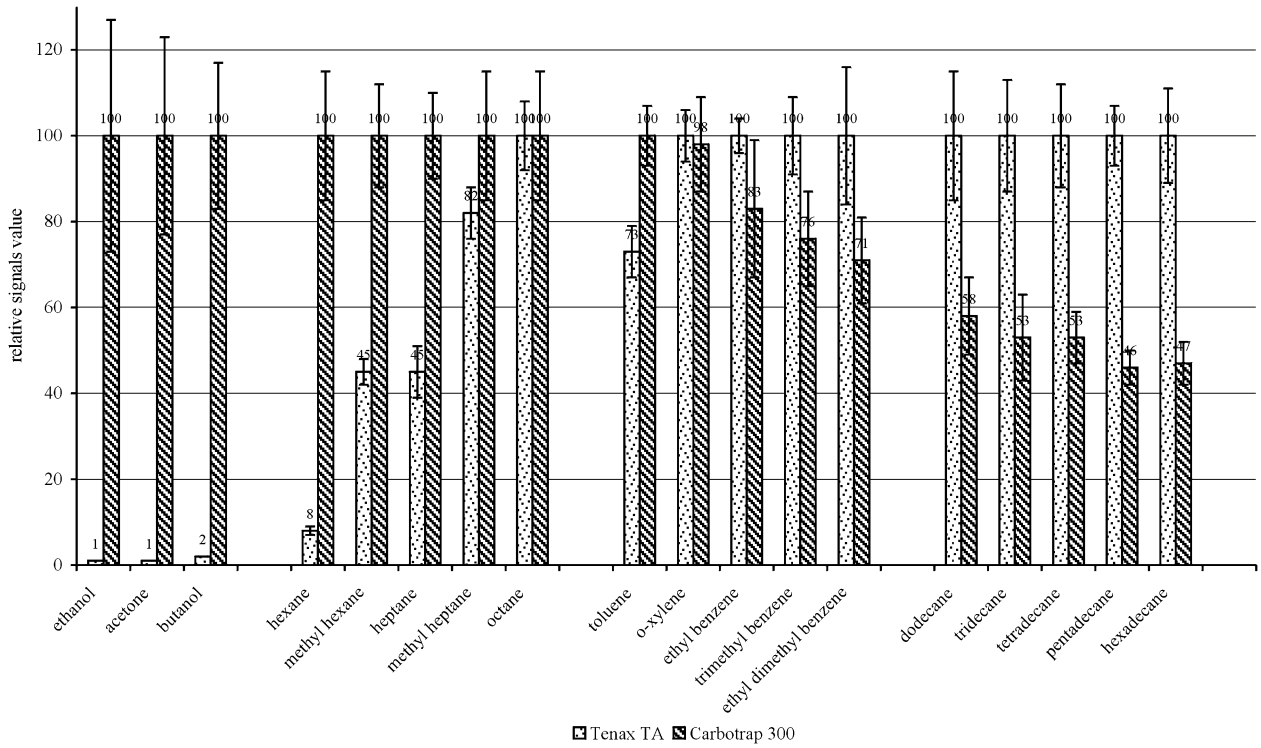

FIG. 3—*The bar graphs illustrate the effectiveness of Tenax TA® and Carbotrap 300® in the adsorption of target compounds at 90°C.*

The average thermal desorption efficiency for all 18 compounds was 95% for Carbotrap 300® and 99.5% for Tenax TA®.

Compounds that were not totally thermally desorbed from Carbotrap 300® belonged to the "volatile polar compounds" group. None of the compounds from this group was totally desorbed. Two of the five "volatile nonpolar compounds" partially remained on the adsorbent. As for Tenax TA®, only one of the "volatile nonpolar compounds (hexane)" remained after the first analysis.

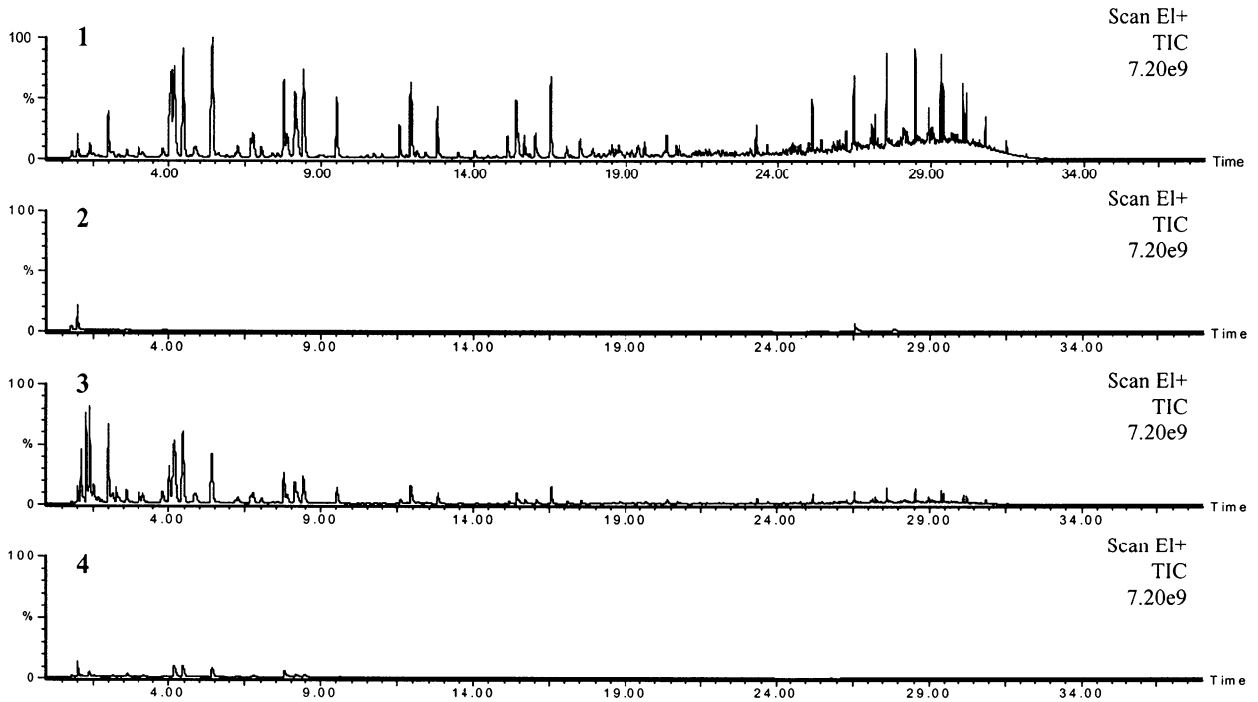

FIG. 4—*Representative chromatograms comparing the effectiveness of thermodesorption of ignitable liquid compounds for Tenax TA® and Carbotrap 300®. Chromatograms 1 and 2 show the result of the analysis of the test mixture adsorbed on Tenax TA® (chromatogram 1) and repetitive analysis of the same adsorption tube (chromatogram 2). The second analysis was conducted to check whether all compounds were thermodesorbed during the first analysis. Chromatograms 3 and 4 show the result of the analysis of the test mixture adsorbed on Carbotrap 300® (chromatogram 3) and repetitive analysis of the same adsorption tube (chromatogram 4).*

TABLE 1—*Results of the calculations of thermodesorption effectiveness for the compounds that were not totally thermodesorbed during the first analysis.*

Adsorbent	Compound	Thermodesorption Efficiency (Mean) (%)	Standard Deviation
Carbotrap 300®	Hexane	79	7
Carbotrap 300®	Methyl hexane	84	5
Carbotrap 300®	Heptane	83	7
Carbotrap 300®	Methyl heptane	90	5
Carbotrap 300®	Octane	92	8
Carbotrap 300®	Toluene	84	7
Carbotrap 300®	Xylene	95	5
Tenax TA®	Hexane	90	1

Conclusion

The two adsorbents differ significantly in adsorption properties.

When using Tenax, we noted that higher molecular weight, nonpolar compounds displace volatile and polar compounds. As the temperature increases, this effect is more pronounced. Therefore, when using Tenax to isolate compounds with significantly different volatility and polarity, the adsorption temperature must be optimized to ensure that both polar and nonpolar analytes are adsorbed. A previous research proved that the optimal temperature is 60°C (9). Tenax TA® turned out to be more effective for the adsorption of nonpolar, high-boiling compounds and less effective than Carbotrap for polar and volatile compounds.

Thermal desorption from Tenax TA® is so effective that after desorption, the adsorbent is ready for reuse.

If the adsorption temperature is properly optimized, Tenax TA® was found to be the more suitable adsorbent for trace amounts of common ignitable liquids.

In our study, we found that Carbotrap 300® can be successfully used for passive adsorption of ignitable liquids traces with subsequent thermal desorption. It was especially effective for polar and volatile compounds. When using Carbotrap, adsorption should be conducted at the highest possible temperature. This is because the effect of displacement of more volatile and polar compounds for Carbotrap 300® did not take place. However, while establishing the appropriate adsorption temperature, safety considerations must also be taken into account. High temperatures, especially applied to wet samples, can cause a significant increase in pressure and result in an explosion of the sample container. This is why 90°C seems to be the most proper adsorption temperature for Carbotrap.

Before reuse, Carbotrap 300® must be additionally conditioned to remove the compounds that remained after the desorption procedure. This lengthens the analysis time and correspondingly decreases the number of analyses that can be conducted.

Carbotrap 300® turned out to be especially useful for isolation and concentration of volatile oxygenated compounds e.g. ethanol or acetone.

There are little data to determine adequately the frequency with which the volatile oxygenated compounds are used in arsons. Some reports indicate that the incidence of use may be underestimated (10).

References

1. Borusiewicz R. Fire debris analysis—a survey of techniques used for accelerants isolation and concentration. Problems Forensic Sci 2002;50:44–63.
2. Jackowski JP. The incidence of ignitable liquid residues in fire debris as determined by a sensitive and comprehensive analytical scheme. J Forensic Sci 1997;42:828–32.
3. Kärkkäinen M, Seppälä I, Himberg K. Detection of trace levels of gasoline in arson cases by gas chromatography–mass spectrometry with an automatic on-line thermal desorber. J Forensic Sci 1994;39:186–93.
4. Russel LW. The concentration and analysis of volatile hydrocarbons in fire debris using Tetax-GC. J Forensic Sci Soc 1981;21:317–26.
5. Fernanes MS, Lau CM, Wong WC. The effect of volatile residues in burnt household items on the detection of fire accelerants. Sci Justice 2002;42:7–15.
6. Lang T. A study of contamination in fire debris containers. Can Soc Forensic Sci J 1999;32:75–83.
7. Touron P, Malaquin P, Gardebas D, Nicolai JP. Semi-automatic analysis of fire debris. Forensic Sci Int 2000;110:7–18.
8. Supelco. Users guide for prepacked sample tubes. Supelco Park Bellefonte, PA: SUPELCO, 1999.
9. Borusiewicz R, Ziêba-Palus J, Zadora G. Application of head-space analysis with pssive adsorption to the chromatographic detection and identification of accelerants in the ATD–GC–MS system. Problems of Forensic Sciences 2002;51:87–105.
10. Bertsch W, Ren Q. The chemical analysis of fire debris for potential accelerants. In: Bogusz MJ, editor. Handbook of analytical separations, Vol 2: forensic sciences. Amsterdam: Elsevier, 2000. pp. 617–78.

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