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Perspective

Workplace monitoring for volatile organic compounds using thermal desorption-gas chromatography-mass spectrometry†‡§

Ardith A. Grote* and Eugene R. Kennedy

Chemical Exposure and Monitoring Branch, Division of Applied Research and Technology, National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention, 4676 Columbia Parkway, Cincinnati, OH 45226, USA

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The interest in the identification of volatile organic compounds in the workplace has been a major focus of many National Institute for Occupational Safety and Health (NIOSH) field studies. A primary technique for sampling and analysis of these compounds is summarized by NIOSH Manual of Analytical Methods (NMAM) 2549. This is a screening method that uses a multi-bed sorbent to trap a wide variety of compounds and compound classes. Thermal desorption techniques are used as a first attempt to characterize potential contaminants in a workplace and to determine what future sampling and analyses must be performed. Field examples are provided to show the versatility of thermal desorption methods and techniques. Due to their sensitivity, thermal desorption tube methods are sometimes required in order to measure the workplace concentrations of unusual compounds. In other situations, the exposures are too high or varied to make thermal desorption tubes practical. In these cases, the identification of contaminants with thermal desorption tubes leads to new method developments for the quantification of specific compounds using more conventional solid sorbent–solvent desorption based methods.

Aim of investigation

One of the functions of the Chemical Exposure and Monitoring Branch in the National Institute for Occupational Safety and Health (NIOSH) is to provide analytical services to NIOSH industrial hygiene groups. As part of this function, pre-survey discussions between chemists and industrial hygienists are encouraged to help to determine which compounds are of interest. These discussions often center on the identification of volatile organic compounds (VOCs) that may be present in the workplace. Usually, there is an initial survey that attempts to screen for VOCs and to determine the major components in the workplace that may be responsible for any reported adverse health effects. In follow-up surveys, the quantities of these compounds are the focus of the sampling and analysis component. This step often requires the development or modification of sampling and analytical methods to address the compounds of interest. The NIOSH approach for the screening of VOCs is summarized in the NIOSH Manual of Analytical Methods 2549.[1] Using this method, samples are collected with a multi-bed thermal desorption tube at 20–50 cm^3 min^{-1} for a total sample volume of 1–10 L. These samples are then analyzed by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) to determine the compounds present. Based on this initial identification, additional method development or modification may be required to quantify the compounds present.

Thermal desorption samples analyzed by TD-GC-MS provide some unusual challenges for routine use in the field. These challenges include dealing with varying concentrations, the identification of multiple components, looking for trace compounds, analytical recovery, humidity effects, compound interactions or decompositions, artifacts, and capacity and migration. Depending on the nature of the workplace and the compounds of interest, these challenges may either make thermal desorption analyses a requirement or a hindrance for quantitative determinations. Several examples are described in this paper that show instances in which either of these two situations exists.

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Experimental

A Perkin-Elmer Automated Thermal Desorber (ATD) 400 thermal desorber, interfaced to a Hewlett Packard 6890 gas chromatograph and a Hewlett Packard 5973 mass selective detector, was used. A 30 m SPB®-1 fused silica capillary column (0.25 mm id and 1 µm film thickness; Supelco, Bellefonte, PA, USA) was used in the chromatograph with helium as the carrier gas. Tubes were desorbed for 10 min at 300 °C with only a minimum outlet split of 20 : 1 (no inlet split) for maximum sensitivity. The internal focusing trap on the ATD unit contained Carbopack® B/Carboxen® 1000 adsorbents. The gas chromatograph was programmed initially at 35 °C (4 min), up to 100 °C at 8 °C min^{-1}, and then ramped to 300 °C at 15 °C min^{-1}. The mass spectrometer transfer line was at 280 °C and the mass spectrometer was set to scan from 20 to 300 atomic mass units (amu).

The sampling tubes (Supelco, Bellefonte, PA, USA) were stainless steel with three beds of sorbent materials: front bed, 90 mg, 40/60 mesh Carbopack® Y; middle bed, 115 mg, 40/60 mesh Carbopack® B; back bed, 150 mg, 40/60 mesh Carboxen® 1003. Tubes were cleaned in the thermal desorber system after each use by heating at 375 °C for 2 h. Cleaned tubes were stored capped in a desiccator.

Standard spiked samples were prepared using 0.1–1 µL aliquots of the analyte dissolved in an appropriate solvent. Carbon disulfide and methanol were the two solvents used most frequently. Two or more stock solutions were prepared and multiple syringes were used to prepare the spiked tube standards. Only 0.5–1.0 µL plunger-in-needle-type syringes were used for accurate spiking at these low volumes. To prepare spiked standards, the injection port of a Hewlett-Packard 5790 gas chromatograph was retrofitted with an adapter for a 1/4 in metal column and set at 120 °C. The thermal desorption tube was connected to the injection port using a 1/4 in Swagelok® nut and a Teflon® ferrule. The helium flow was adjusted to between 50 and 60 $cm^3\ min^{-1}$. After spiking, the tube was allowed to equilibrate in the injection port with helium flow for 5–10 min. Spikes were analyzed in exactly the same manner as the field samples as described above.

Results and discussion

Although thermal desorption is a very powerful technique for the detection of low concentrations of chemicals in the workplace, it is not the only tool that chemists need to use to provide required exposure data. At NIOSH, although TD-GC-MS is a major analytical technique used for field studies, more traditional methods have also been developed and used for the analysis of field samples. Presented below are several examples of sampling and analysis situations in which thermal desorption techniques alone or in combination with solid sorbent–solvent desorption methods have been crucial in addressing industrial hygiene concerns.

Microwave popcorn packaging

NIOSH researchers were recently involved in the study of occupational exposures at microwave popcorn production facilities. The chemical exposures at the plants were suspected of being the cause of reported health problems of the workers, including reduced lung capacity.[2] Thermal desorption tubes were used in the initial surveys to identify the variety of compounds present. However, the concentrations of some of these compounds were so high in these samples that the mass spectrometer was saturated and no useable data were obtained. This emphasized the need for good communication between the laboratory and field researchers to understand the limitations and advantages of thermal desorption analysis. When samples were retaken at lower flow rates and total volumes, chromatograms such as those shown in Fig. 1 were obtained. From these data, the major compounds present in the complaint areas were diacetyl and acetoin. Diacetyl is the compound that provides the buttery flavor to popcorn. The top chromatogram represents a personal sample taken in an area where there were no health complaints. Other compounds identified were acetic acid and 2-butanone. Because of the high concentrations observed with diacetyl and acetoin, a more traditional solvent desorption based method was developed.[3] This method is one of the primary methods used for the collection of data on worker exposure to diacetyl and acetoin in this ongoing study.

Lithographic printing

A recent study in a printing plant found workers to be complaining of blurry vision and halo effects that seemed to subside later in the day or after work and on weekends.[4,5] The chemicals used in the plant were suspected of causing the effect, but there were no data available to prove a direct correlation. Thermal desorption tubes were used to screen the chemicals present in the workplace air. The analytical results from these tubes indicated that several compounds were present at very high concentrations. The major compounds found were dimethylethanolamine and dimethylisopropanolamine. The interesting factor about these exposures is the difference between morning and afternoon sampling, as shown in Fig. 2. These personal breathing zone samples were taken on the same worker. During an initial investigation, only afternoon samples were collected and no tertiary amine compounds were detected, which were suspect causative agents for the reported health effects. Follow-up surveys collected samples during both morning and afternoon shifts as shown here. The morning samples (top chromatogram) displayed high levels of isopropanol, ethyl acetate, dimethylethanolamine and dimethylisopropanolamine. During the afternoon shifts (bottom chromatogram), only isopropanol and ethyl acetate remained as major components.

Due to the high concentrations found in this environment and the number of samples (over 300) proposed for a detailed follow-up investigation, a solvent desorption method was developed for additional air monitoring in order to determine exposure concentrations. The method was based on collection on XAD-7 sorbent tubes, desorption with methanol and analysis by gas chromatography-flame ionization detection (GC-FID).[6]

Chromatograms from thermal desorption tubes collected in the complaint and non-complaint areas contained essentially the same compounds. The major difference noted was in the ratios of the two compounds in the complaint and non-complaint areas. The complaint areas always had higher concentrations of 'total' amines and, in particular, dimethylisopropanolamine. A direct correlation was established between the total amine concentrations and the workers with the eye problems. Although dimethylethanolamine probably contributed to the complaints, the main culprit appeared to be the high concentrations of dimethylisopropanolamine. It was

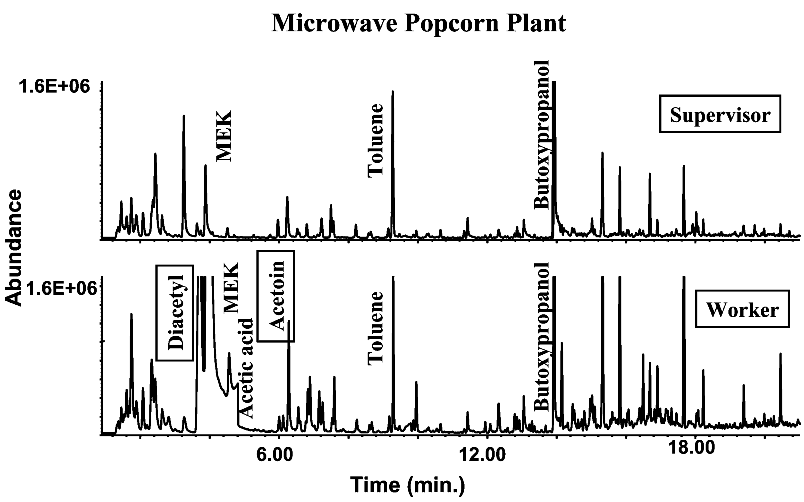

Fig. 1 Chromatograms from thermal desorption tubes collected on workers at a microwave popcorn packaging plant in complaint (bottom) and non-complaint (top) areas.

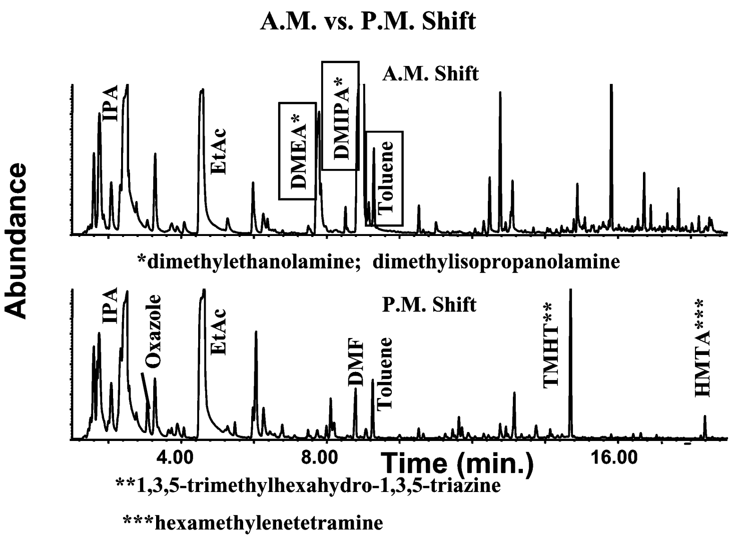

Fig. 2 Personal thermal desorption tube samples collected on the same worker during morning and afternoon shifts at a lithographic printing facility.

found that dimethylisopropanolamine was only used in one solution in the plant. When the solution was diluted, all heath complaints ceased.

Plastic projection lens production

NIOSH researchers were requested to study a plant that produced plastic lenses used for projection television systems.[7] One of the additives present in the plastic pellets used for the injection molding of the lenses was cyclohexylmaleimide (CHMI). The plant asked NIOSH to measure this compound down to the 0.6 μg m^{-3} level. As a first step, a sample of the plastic pellets was heated in the thermal desorber in a glass tube to try to identify any volatile components that might be released during the injection molding process. The sample was heated at the same temperature as used in the process, 250 °C. The results showed that CHMI could indeed be released by heating and did pose a potential exposure problem to the workers. When thermal desorption tube samples were collected in the plant around the injection molding process, it was verified that CHMI was present in the workplace (Fig. 3). The next step was to evaluate the sampling and analytical approach for the quantification of CHMI by thermal desorption. A solution of CHMI in acetone was prepared and known aliquots of the solution were spiked onto thermal desorption tubes. A calibration curve from 4 to 1500 ng per sample was prepared, and so it was possible to measure extremely low levels of CHMI in personal breathing zone samples. The linearity of the curve indicated that the recovery of the CHMI from the sorbent was constant. Personal samples taken in the plant indicated that employees were exposed to levels ranging from 0.21 to 3.8 μg m^{-3}.

Laser coding operations

A plant that performed laser coding of various materials requested NIOSH assistance in the characterization of emissions that resulted from the use of a 100 W carbon dioxide laser.[8] A variety of materials, such as polyethylene, polyvinyl chloride, glass and cardboard, were etched by the laser. The operation only lasted a few seconds and so the potential exposures were intermittent. Thermal desorption samples were collected with a total volume of less than 1 L. Over 200 compounds were identified in these samples. Each of the different matrices provided a different chemical signature. The results from this study show the versatility of thermal desorption in handling a variety of different chemical classes and volatilities. When coding was performed on high density polyethylene, a range of hydrocarbons from C_6 to C_{20} were observed in the sample, as shown in Fig. 4. This demonstrates a very wide range of volatility for the approach. When polyvinyl chloride was the coding substrate, compounds such as hydrochloric acid, acetic acid, methyl methacrylate and some polynuclear aromatic compounds were detected (see Fig. 5). Polyethylene terephthalate substrate gave off benzene, styrene,

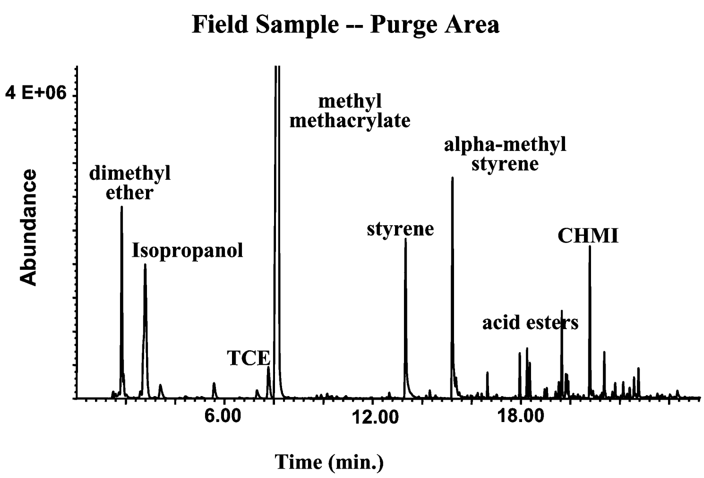

Fig. 3 Area sample collected on a thermal desorption tube at a plastic lens production company.

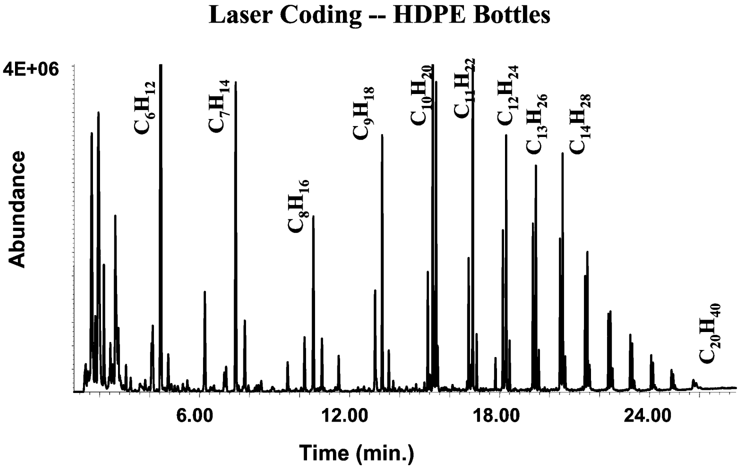

Fig. 4 Thermal desorption tube collected over laser coding on high density polyethylene (HDPE).

acetophenone, isobutyrophenone and benzoic acid, as might be expected from the thermal decomposition of the base material (see Fig. 6).

Indoor environment quality studies (IEQs)

IEQs always pose interesting challenges when it comes to VOCs. Normally, concentrations are very low and so thermal desorption tubes are often the best choice. Thermal desorption tubes can be used to show a visual map of the different VOC exposures encountered throughout an entire office building. Fig. 7 shows the results from thermal desorption tubes for a multi-floor office building. Thermal desorption tubes were collected on each floor and at different areas within a floor. The top chromatogram was sampled in a general area near a drinking water fountain. The high levels of Refrigerant 11,

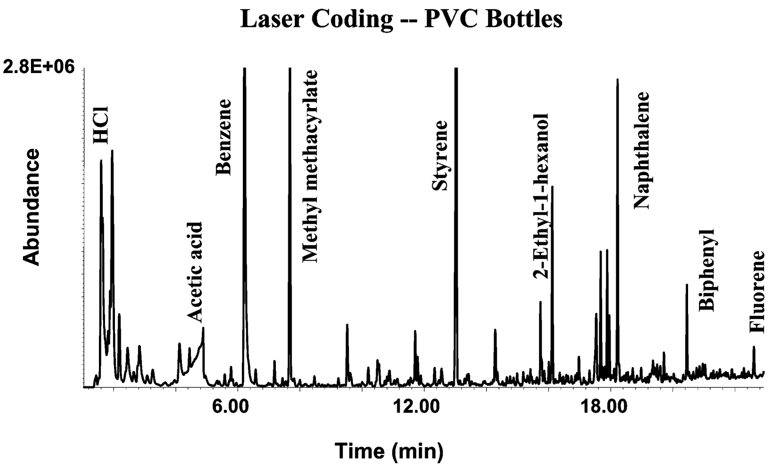

Fig. 5 Thermal desorption tube collected over laser coding on polyvinyl chloride (PVC).

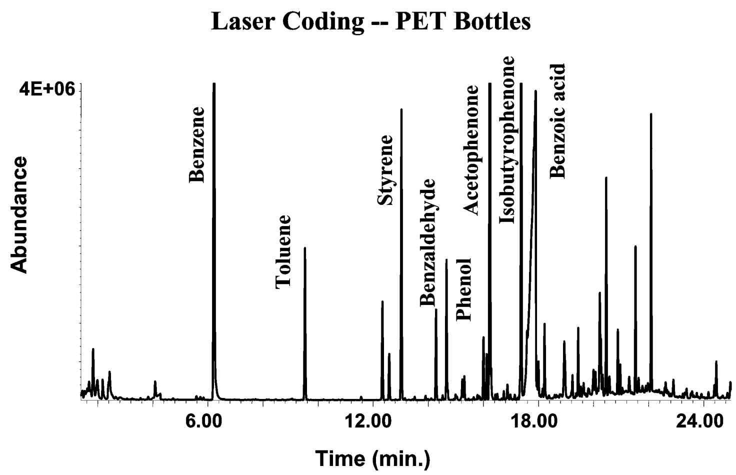

Fig. 6 Thermal desorption tube collected over laser coding on polyethylene terephthalate (PET).

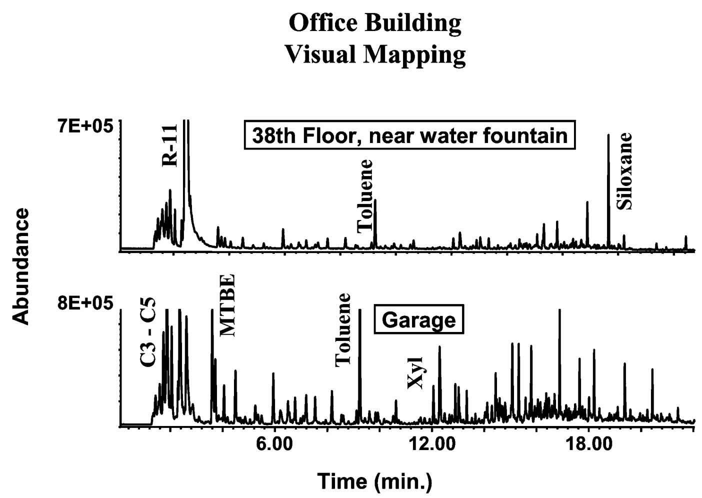

Fig. 7 Indoor environment quality (IEQ) samples from different locations in a multi-floor office building. MTBE, methyl *tert*-butyl ether; R-11, Refrigerant 11; Xyl, xylene.

trichlorofluoromethane, may indicate a possible Freon leak from the water cooler. The bottom chromatogram was collected in the basement garage of the same office building, where delivery vehicles were often left with their engines running. The presence of methyl *tert*-butyl ether (MTBE) is predominant here, together with higher levels of C_3–C_5 hydrocarbons, benzene, toluene, xylene and other aliphatic and aromatic hydrocarbons. MTBE is a gasoline additive and hydrocarbons are present in gasoline or diesel fuels. Showing visually what compounds are present at different locations often helps the industrial hygienist in trying to evaluate the health complaints.

Headspace sampling

Several times a year, wastewaters from various sources, such as coal mines or sewage treatment plants, are submitted for analyses of VOCs. To determine if any VOCs are present, thermal desorption tubes are used in a very simple set-up. A vial containing the wastewater is covered with foil, and a thermal desorption tube is positioned directly above the solution. The solution is gently aerated, and a headspace sample is collected with the thermal desorption tubes. Fig. 8 shows a headspace sample generated from a sludge sample collected in a subway tunnel.[9] Sulfides were detected: dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide and butylbenzenesulfonamide.

Fire scenes

A request was received to determine arson inspectors' exposures as they investigated the causes of fires.[10] As smoldering debris is often still present, the potential for detecting numerous VOCs is high. Fig. 9 shows the results from a thermal desorption tube sample collected on an arson investigator. Compounds of interest included dichlorotetrafluoroethane, furfural, MTBE, phenol, styrene, benzene, naphthalenes and polynuclear aromatic hydrocarbons (biphenyl, acenaphthylene, fluorene, phenanthrene). Most of the major compounds are thermal decomposition products of various building materials, such as plastics, wood and paper.

Conclusions

The examples presented above show the advantages and limitations of TD-GC-MS in the evaluation of workplace exposures. Although the technique cannot provide the ultimate solution for all circumstances, it does provide very useful information on chemical identity. One of the key factors is the experience of the analyst with the technique. As instrumentation increases in computing power, it can provide more and more information. However, the information is only as good as its interpretation, which ultimately lies in the hands of the analyst and the industrial hygienist.

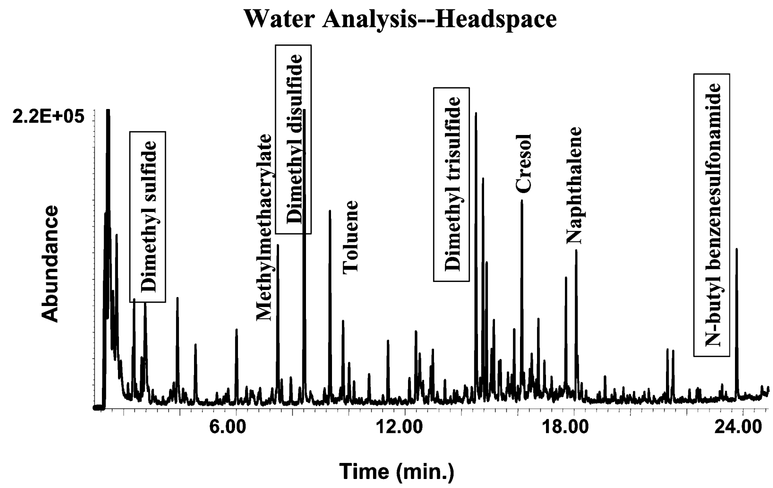

Fig. 8 Headspace sample collected above a sludge sample from a subway tunnel.

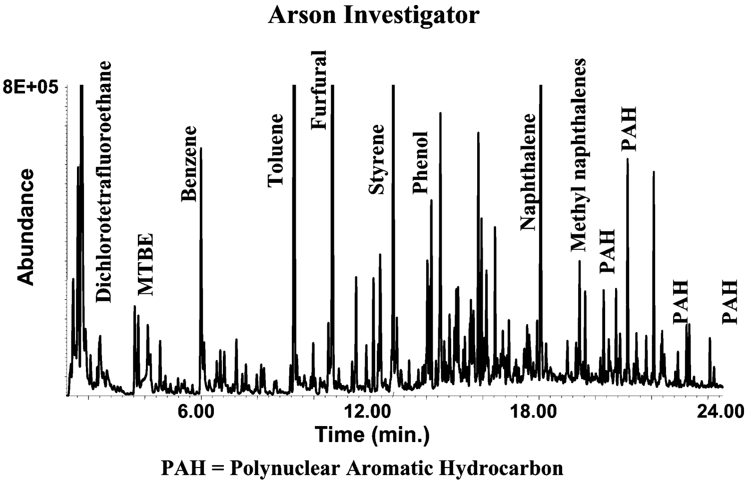

Fig. 9 Personal thermal desorption tube sample from an arson investigator. MTBE, methyl *tert*-butyl ether.

Disclaimer

The mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

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