

CHROM. 16,982

PRELIMINARY EVALUATION OF THERMAL DESORPTION-GAS CHROMATOGRAPHIC ANALYSIS OF AIRBORNE PARTICULATE MATTER ON DICHOTOMOUS FILTERS

R. L. CROUCH, R. A. HAWLEY-FEDDER and M. L. PARSONS**

Department of Chemistry, Arizona State University, Tempe, AZ 85287 (U.S.A.)

and

F. W. KARASEK

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G7 (Canada)

(First received April 6th, 1984; revised manuscript received June 6th, 1984)

SUMMARY

Direct thermal desorption of organic compounds associated with airborne particulate matter on TeflonTM filters used in dichotomous samplers followed by gas chromatographic analysis provides an approximately 100-fold increase in analytical sensitivity. Comparison between the most sensitive solvent extraction technique and thermal desorption is presented. The apparatus and procedure used for thermal desorption-gas chromatographic analysis are described. Evidence is presented suggesting that no significant thermal degradation of organic compounds occurs under the conditions used. The minimum detectable quantity of organic compounds is estimated to be in the range of sub-pg/m³ of air sampled.

INTRODUCTION

The presence of airborne particulate matter in the environment is a serious problem affecting health and the quality of life. Consequently, much effort has been expended in recent years to achieve accurate and specific determination of the organic compounds associated with such aerosols¹. The analytical methods used have been based on solvent extraction followed by evaporative re-concentration. The estimated detection limit for this method is about 10 pg/m³ of sampled air and is limited both by extraction efficiency and the level of contamination introduced by the solvent¹. The planned changes in the United States Environmental Protection Agency (EPA) air quality regulations reflect the difficulty of analyzing this class of pollutants. To date, no method has been available to determine the extent of human exposure to toxic compounds associated with air particulates and, consequently, current EPA policy is to regulate sources of particulate emissions. We believe the development of advanced sampling and analysis methods based on thermal desorption will allow sub-pg/m³ determination of organic compounds associated with air particulates.

* Present address: Los Alamos National Laboratory, CHM-1, G740, Los Alamos, NM 87545, U.S.A.

This, in turn, will allow a more accurate assessment of the health risks and level of human exposure to this class of pollutants.

Of greatest analytical interest are those particulates having a size range of less than $3.5\ \mu\text{m}$ since these are most likely to be retained in the human lung. The dichotomous sampler² has been developed to classify air particulates into two size fractions, one of less than $3.5\ \mu\text{m}$ and the other of about 3 to $10\ \mu\text{m}$. In this device, the particulates are collected on a TeflonTM membrane filter which can be analyzed for both organic and inorganic chemicals.

The total amount of organic material on a Teflon filter from a dichotomous sampler is usually on the order of $100\ \text{ng}^1$. The amount of individual compounds on the filter is extremely small, since hundreds or thousands of compounds may be present. Previous methods based on Soxhlet or ultrasonic solvent extraction have failed to achieve the required analytical sensitivity. We present here a method of analysis based on direct thermal desorption of organic compounds from air particulates and subsequent analysis by gas chromatography (GC). Evidence is presented suggesting that detection of organic compounds at the sub-pg/ m^3 level of sampled air is achievable.

An improvement in sensitivity of analysis using thermal desorption over solvent extraction methods is expected on purely theoretical grounds. When a compound is dissolved it is diluted to the extent of the solvent volume used. In extraction methods used for air particulates, typically a final solution volume of $100\ \mu\text{l}$ was obtained¹ from which $1\ \mu\text{l}$ was taken for GC analysis. This amounts to a dilution factor of 100 for these methods. On the other hand, direct thermal desorption allows all of the organic material associated with the air particulates to be analyzed at once. A minimum improvement in sensitivity of a factor of 100 is predicted for thermal desorption on this basis.

EXPERIMENTAL

A thermal desorption device was constructed consisting of a heated sample valve (HTA-CV4, Valco Instruments, Houston, TX, U.S.A.), desorption tube ($5\ \text{cm} \times 1/4\ \text{in. O.D.} \times 3\ \text{mm I.D.}$ glass-lined stainless-steel, Scientific Glass Engineering, Austin, TX, U.S.A.) and a heated aluminum desorption oven that was hinged to allow clamping around the desorption tube (Fig. 1). Sample introduction was accomplished by cutting the Teflon filter away from its polyester frame and placing it into the desorption tube. All utensils and glassware were kept cleaned by storage in a 300°C oven and cooled immediately prior to use. All sample loading operations were performed in a Class 100 clean hood (Contamination Control, Lansdale, PA, U.S.A.). A Hewlett-Packard 5830A gas chromatograph with a flame ionization detector was used along with a $50\ \text{m} \times 0.25\ \text{mm I.D.}$ ($0.25\ \mu\text{m}$ film thickness) SE-54 capillary column.

To minimize the possibility of thermal reactions of the analyte compounds at the desorption temperatures used, all tubing downstream from the desorption tube was glass lined.

Fig. 2 illustrates the timing of events required to desorb the sample and condense it into the capillary. The GC oven was brought to -30°C with dry ice. During the 5-min desorption period, all transfer lines and the heated valve were brought to

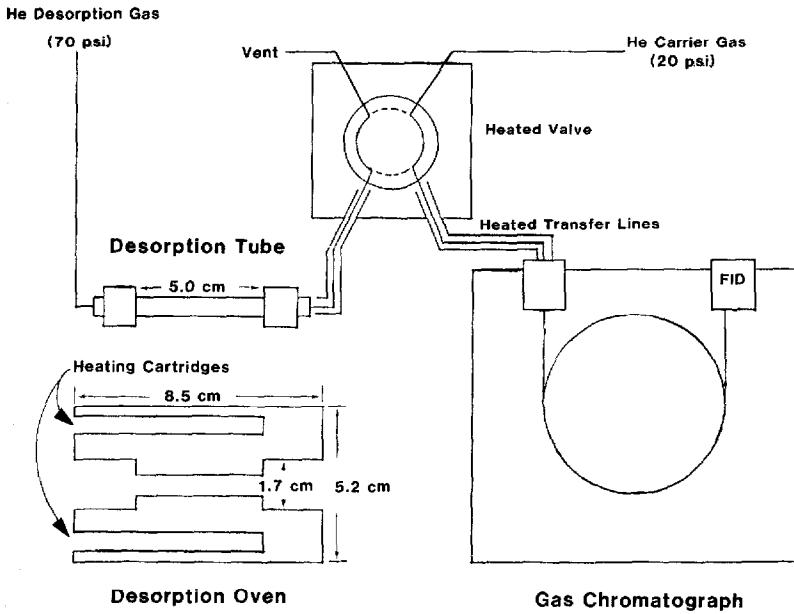


Fig. 1. Diagram (not to scale) of the valve, oven, gas, chromatograph and desorption tube for these experiments. The desorption oven is an aluminum block with hinges to allow manual clamping around the desorption tube.

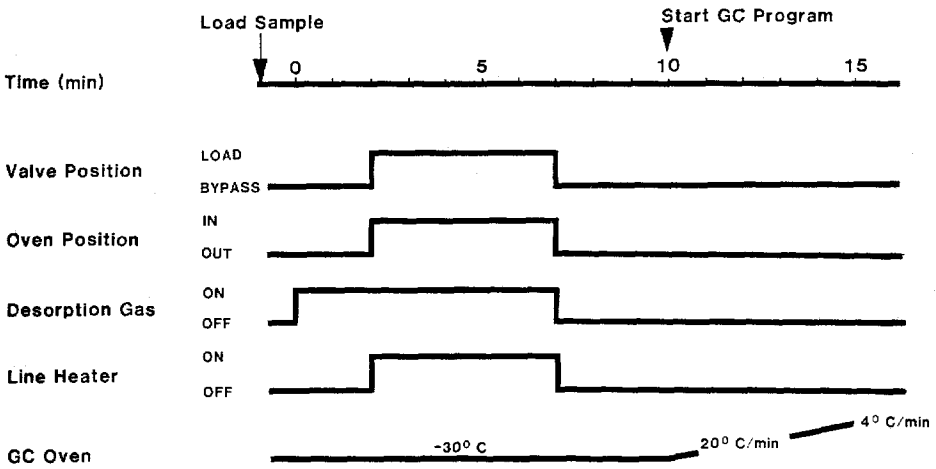


Fig. 2. Timing diagram showing sequence of operations on a typical desorption run.

the desorption temperature. The desorption oven was kept at a constant temperature of 350°C. The temperature ramping characteristics of the thermal desorption tube and heated transfer line were measured with copper-constantan thermocouples. The first 2 min of the procedure involved flushing the desorption tube free of air at *ca.* 30 ml/min. When the desorption period was started, the column back pressure of 70 p.s.i. resulted in a volumetric flow-rate of *ca.* 30 ml/min measured at the detector.

When the column back pressure was returned to 20 p.s.i. at the end of the 5-min desorption period, 3 min were required to return the column flow to its normal 0.9 ml/min (55 cm/sec calculated). The complete GC program is -30°C to 70°C at $20^{\circ}\text{C}/\text{min}$ then 70°C to 250°C at $4^{\circ}\text{C}/\text{min}$ then isothermal at 250°C for 30 min.

RESULTS AND DISCUSSION

The first discovery made from running blank filters was that significant contamination exists on the filters as received from the manufacturer (Membrana Corp., Pleasanton, CA, U.S.A.). Fig. 3 shows a comparison of blank, raw filters analyzed by thermal desorption and ultrasonic extraction. The large contaminant with retention time *ca.* 40 min is 1-octadecanol and is believed to be a component of the polyester frame used to support the Teflon filter. The other prominent feature in the ultrasonic extraction chromatogram is a high molecular weight phthalate ester at retention time *ca.* 73 min for which the exact structure has not been determined. This compound is also believed to originate from the frame. Extractable contaminants from the frame are clearly a problem with extraction methods. Since no part of the frame is used for thermal desorption, such contaminants should be absent using this method. The 1-octadecanol has sufficient volatility that its presence in the thermal desorption chromatogram may be accounted for by vapor phase migration from the frame during manufacture or storage. We have found that pretreating the filters in a vacuum oven (water aspiration) at 190°C for 2 h removes the majority of contaminants, as shown in Fig. 4. Also illustrated in Fig. 4 is the fact that no significant thermal decomposition of the Teflon filter occurs under the conditions used.

To illustrate the dramatic increase in analytical sensitivity afforded by thermal desorption, a comparison of organic compounds on air particulates sampled in the

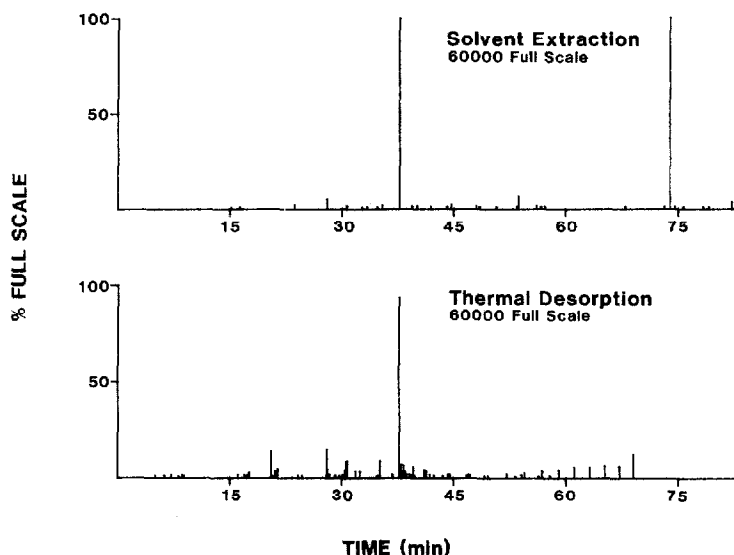


Fig. 3. Comparison of ultrasonic extraction (ref. 1) and thermal desorption analysis of blank filters as received from the manufacturer. Full scale value is in area counts. (Reconstructed chromatograms using a Digital Equipment MINC 23 minicomputer).

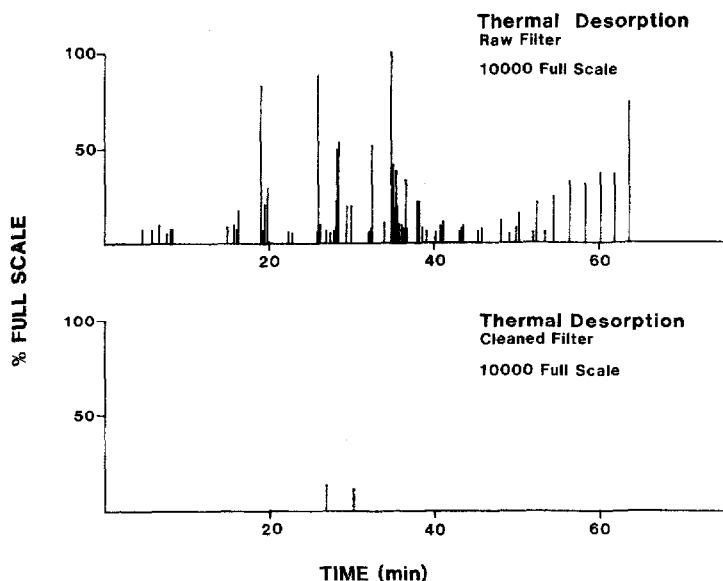


Fig. 4. Comparison of thermal desorption analysis of a filter as received from the manufacturer with one cleaned according to the text. Full scale value is area counts.

Houston metropolitan area³ is presented in Fig. 5. No attempt has been made to optimize the chromatography in this comparison. Both filters analyzed contained fine particles of less than $3.5 \mu\text{m}$ size range. The total area counts for the thermal desorption run are about 100 times that found from extraction. This result is in agreement with the 100-fold increase in sensitivity predicted on theoretical grounds

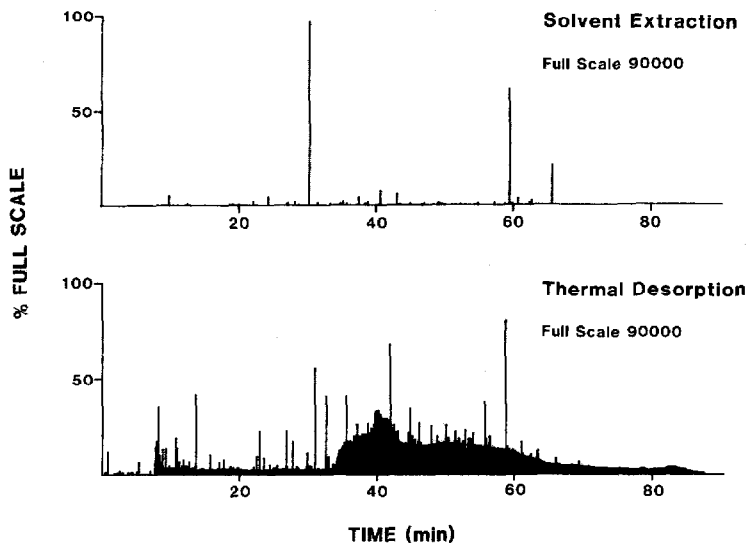


Fig. 5. Comparison of solvent extraction and thermal desorption analysis of fine particle Teflon filters from the Houston metropolitan area (ref. 3). Full scale value is area counts. Total area counts are 2.65×10^7 for filter No. 215517F (bottom) and 2.12×10^5 for filter No. 215510F (top).

on going from solvent extraction to thermal desorption, assuming equivalent flame ionization detector responses between both runs. This assumption of equivalent flame ionization detector response factors (RF) between thermal desorption and direct injection methods is based on the determination of RF for *n*-alkanes, polynuclear aromatic hydrocarbons (PAHs), oxy-PAHs and nitro-PAHs. Response factors have been measured of 14.42 ± 0.25 (mean \pm standard deviation, expressed as area counts per ng), 13.47 ± 0.77 , 11.90 ± 0.90 , 9.83 ± 0.46 , and 10.04 ± 2.5 , respectively, for *n*-alkanes C₁₄-C₃₂, PAHs C₁₂-C₂₂ including isomers and methyl PAHs (twenty-two compounds), oxy-PAHs C₁₃-C₁₅ (four compounds), nitro-PAHs C₁₀-C₁₄ (five compounds) and phthalate esters (four compounds)⁴. Thus, the use of a single averaged response factor to estimate the amount of each compound class present appears to be an acceptable approach for the comparison of complex mixtures. The major organic compound classes associated with air particulates are alkanes, phthalate esters, PAHs fatty acid esters and nitrogen containing polyaromatics⁵. Since these groups should be present in both filters analyzed in Fig. 5, the direct comparison of total area counts is a valid indication of relative sensitivity. The roughly 100-fold increase in sensitivity based on comparison of area counts is a clear indication of the advantage of thermal desorption. The largest variation in response factors measured is a factor of three (4.54 for hexachlorobenzene to 14.78 for C₂₁H₄₄). Since material is not created during possible thermal degradation, such processes cannot account for the increase in total area counts measured for the Houston thermally desorbed sample in Fig. 5.

The possibility of decomposition of thermally unstable compounds under the conditions employed must be examined further. Fig. 6 shows the temperature ramping characteristics of the thermal desorption tube and heated transfer line under analysis conditions. The desorption tube temperature ramps quickly from room temperature to about 210°C in 20 sec and then increases more slowly (roughly 10°C/min) to about 265°C, the maximum reached at the end of the 5-min desorption period. The volumetric desorption gas flow-rate is 30 ml/min and the desorption tube volume is 0.35 ml. This results in the desorption tube volume being swept every 0.7 sec and yields a low residence time for volatilized compounds. Provided that no catalytic surface is present, these conditions are mild enough to prevent thermal reactions of many compounds. This is illustrated in Fig. 7 which shows a direct thermal desorption of a standard mixture placed in the desorption tube. No extraneous peaks are observed compared to direct injection and the area counts for each peak are in accordance with the flame ionization detector response measured for our instrument for the amount of each compound present.

It appears that the predominant peaks in solvent extraction are from extractable contaminants and not from organic material associated with air particulates. Also, these results suggest that thermal desorption is more sensitive to a wider range of compounds than solvent extraction. The roughly 100-fold increase in sensitivity obtained by thermal desorption presents a significant advancement in the analysis of organic compounds on air particulates. With the further improvement of mass spectrometric detection with selected ion monitoring, detection limits could be lowered by an additional factor of 10-100, allowing quantitation and identification of the extremely low levels of material expected from dichotomous samplers. Since the estimated limit of detection for the ultrasonic extraction is 10 pg/m³ of air sampled,

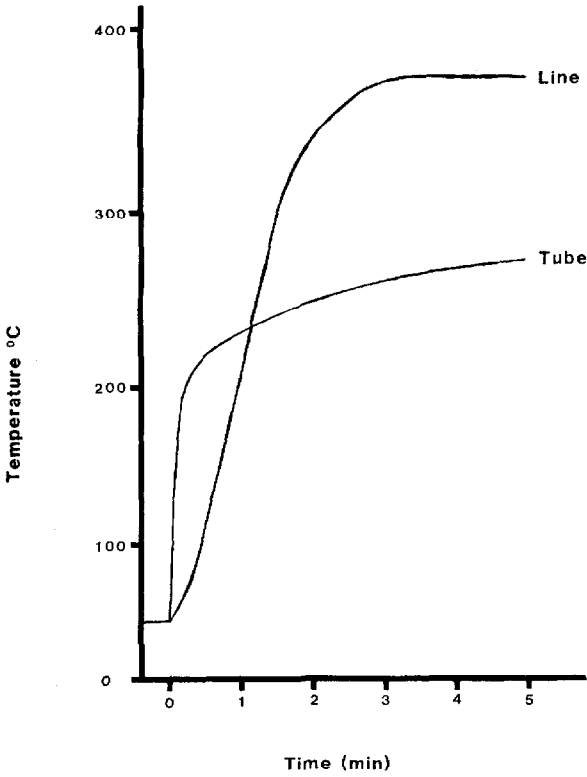


Fig. 6. Temperature ramping characteristics of the thermal desorption tube and heated transfer lines during a typical desorption run.

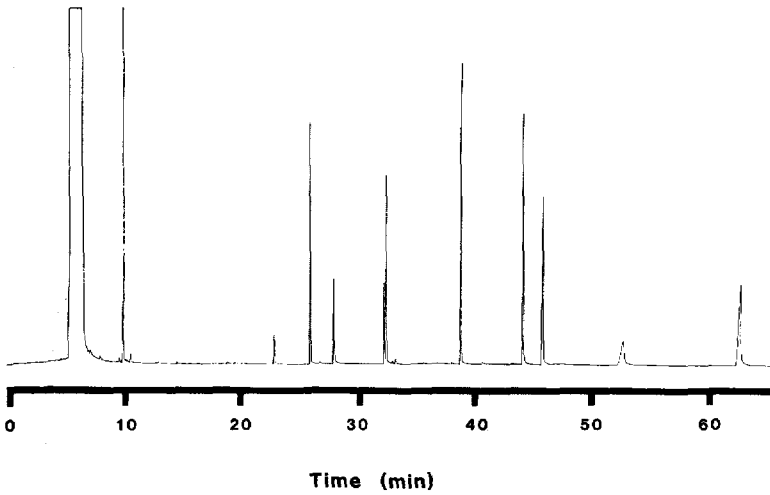


Fig. 7. Direct thermal desorption of standard mixture. Peaks in order of increasing retention time are cyclohexane solvent, biphenyl, dimethyl phthalate, fluorene, diethyl phthalate, tetradecanol, octadecane, hexadecanol, fluoranthene, eicosane, tetracosane and hexacosane.

the expected limit of detection after optimization of the thermal desorption method is in the range 0.01–1 pg/m³ of sampled air.

CONCLUSIONS

Thermal desorption shows great promise for improving the sensitivity with which organic compounds associated with airborne particulate matter can be analyzed. No thermal decomposition of a standard containing *n*-alkanes, PAHs and phthalate esters is observed under the conditions employed, nor is there significant degradation of the Teflon membrane filters used in dichotomous air particulate samplers. Based on theoretical arguments, an estimated 100-fold increase in sensitivity is expected using thermal desorption. Analysis of air particulate samples from the Houston metropolitan area shows this to be true. With the addition of a mass selective type detector the expected detection limit is in the range of sub-pg/m³ of air sampled.

ACKNOWLEDGEMENTS

This work was supported in part by a grant to R.L.C. from the Graduate Student Association of Arizona State University.

REFERENCES

- 1 R. A. Hawley-Fedder, W. D. Bowers, M. L. Parsons and F. W. Karasek, *J. Chromatogr.*, 269 (1983) 161–170; and references cited therein.
- 2 A. R. McFarland, C. A. Ortiz and R. W. Bertch, *Environ. Sci. Technol.*, 12 (1978) 679.
- 3 F. W. Karasek and M. L. Parsons, *Analysis of Houston Aerosol Samples by GC/MS Methods, Final Report, EPA Report EPA-600/2-80-071*, U.S. Environmental Protection Agency, Washington, DC, April 1980.
- 4 H. Y. Tong and F. W. Karasek, *Anal. Chem.*, (1984) in press.
- 5 W. Cautreels and K. Van Cauwenberghe, *J. Chromatogr.*, 131 (1977) 253–264.