Scientific Instruments
Sales & Service, LLC www.sci-instruments.com
2200 Spanish Oak Trail Tel: 512/259-8298
Round Rock, Texas 78681 Fax: 512/259-8296

UNAMBIGUOUS CONFIRMATION BY GCMS AND LARGE VOLUME INJECTION OF RESIDENTIAL SOOT CONTAMINATION FROM THE BURNING OF CANDLES

LD Garretson[1], Owner and ED Golla[2], phD, CIH.

[1]Scientific Instruments Sales & Service, LLC, Round Rock, TX
[2] Texas Research International, Austin, TX

ABSTRACT
The complaints are generally the same; black markings on carpets and baseboards, black particulate dusting appliance surfaces and bathroom fixtures, darkened HVAC filters and supply registers and sooty deposits on furniture, draperies and clothing. Typically, this occurs in newer homes, often under manufacturer's warranty. Candles are not the only source of soot production, but in many recent investigations, candles were related to the appearance of staining. In addition to the physical damage caused to the home, there is also some concern that the presence of these fine soot particles may present an indoor air quality health hazard. This paper will describe an unambiguous technique utilizing Gas Chromatography-Mass Spectroscopy (GCMS) combined with Large Volume Injection/Microextraction to confirm the presence of paraffin in the soot particles. While there are many sources of hydrocarbons in new residences, the unique pattern and distribution of aliphatic hydrocarbons found in petroleum-derived paraffin (candle wax), provide evidence of the source of contamination.

INDEX TERMS
Determination of paraffin, Candle wax determination, Residential soot contamination, Fuel pollutants, Combustion pollutants, Material damage.

INTRODUCTION
Residential indoor air is potentially a complex matrix. In order to unambiguously confirm the presence of paraffin contamination, a technique is required which can distinguish the unique characteristics of candle soot contamination from other potential interferences. In addition to the analytical technique developed to perform this analysis, other physical factors from the home are also examined. Theses physical factors include heavy soot contamination found on walls, furnishings, ceramic fixtures, air conditioning registers and ductwork, HVAC return air filters, carpet, leading edges of ceiling fans and clothing. Figure 1 shows where some of the soot deposition points may occur. The combination of the analytical data and physical evidence provide valuable information regarding the source of the contamination.

There is an extensive body of work presenting the results of investigations into the physical characteristics common to paraffin soot contamination of households[1] (Frank Virgil, 1998). This paper will primarily focus on the Large Volume Injection/Microextraction and GCMS technique developed to provide chemical confirmation of the presence of petroleum-derived paraffin (candle wax).

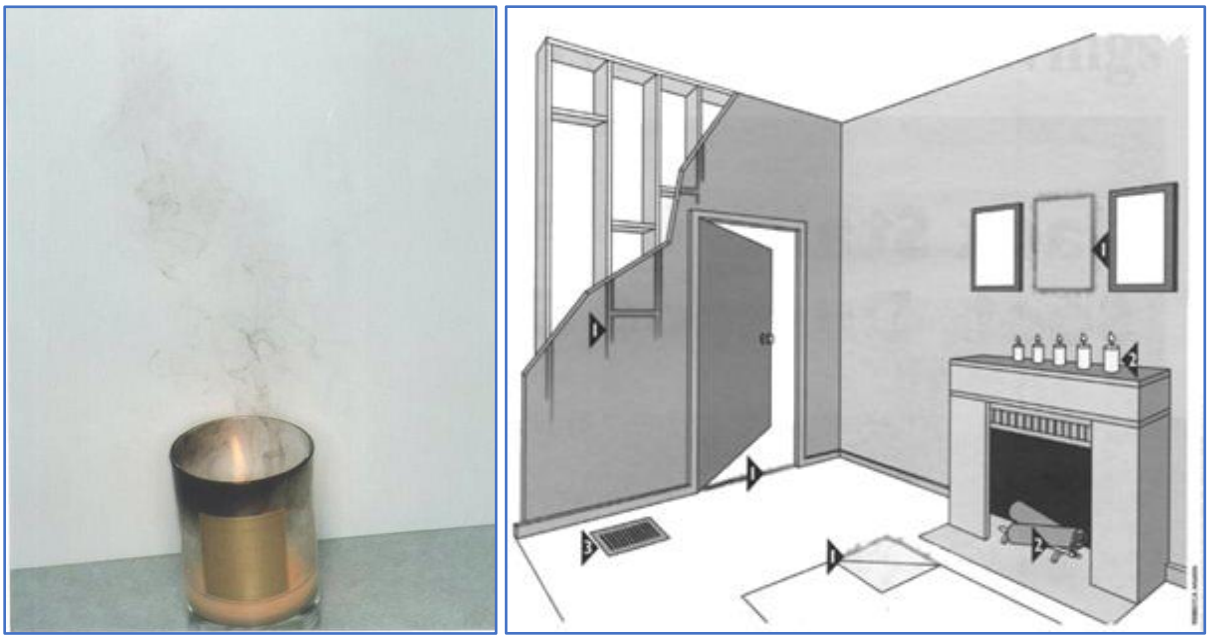

Figure 1: Soot production from candle burning and possible points of deposition (Frank Virgil, 1998).

METHODS

The soot particles emitted during the candle burning process contain charged hydrocarbon particles that are extremely small, typically 0.045 – 0.2 microns[2] (J. David Krause, 1999). These charged particles are carried throughout the home via air currents and the central HVAC system. As the particles move through the air, they attract other airborne particles and increase in weight. The soot particles then begin the process of collecting on the surfaces and areas previously described. The soot deposits in contaminated homes contain varying amounts of paraffin resulting from the incomplete combustion of the candle wax. Samples for GCMS confirmation analysis are collected utilizing sterile gauze wipes, cotton tipped swabs or portions from the HVAC return air filter. Figure 2 shows return air filters sampled for GCMS analysis.

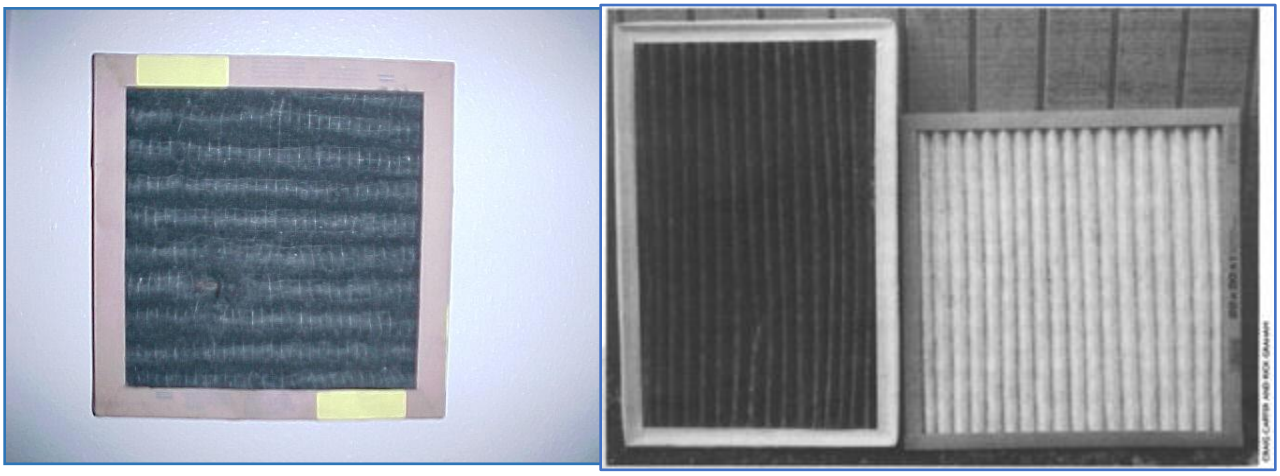

Figure 2: Return air filters sampled from residential contamination investigation.

The wipes, swabs or a portion of the filter (approximately one gram) are then placed in a pre-cleaned, glass, Teflon-lined capped container and extracted with an appropriate amount of Methylene Chloride ($MeCl_2$), typically about ten milliliters. The sample is then vigorously vortexed for several minutes and allowed to settle.

The confirmation of paraffin soot contained in a wipe or filter sample is based on the presence of specific hydrocarbons typically found in petroleum-derived wax. These hydrocarbons are present in a specific ratio and produce a unique pattern when measured by GCMS. The paraffin soot reference material is generated by collecting soot from a burning candle by placing a porcelain dish approximately 8-10 inches above the flame of an aromatic candle. A wipe sample of soot from the blackened area created by candle burning is taken and then prepared in identical fashion as the unknown wipe or filter material. Figure 3 presents the type of porcelain crucible utilized to produce the reference material.

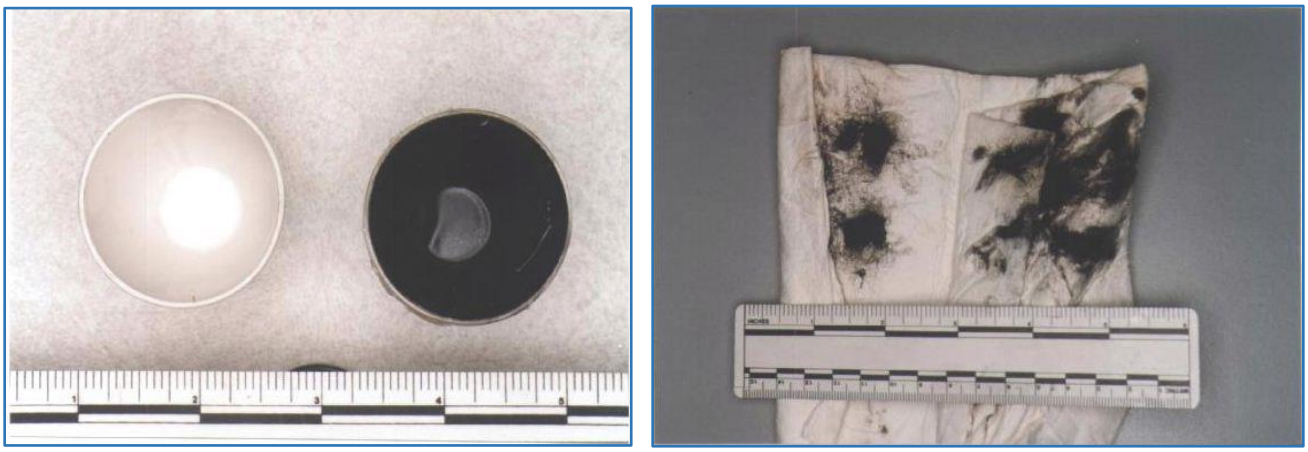

Figure 3: Porcelain Crucible for Collecting Soot Reference Material and Wipe from Ceiling Fan

The extracts are next subjected to GCMS analysis utilizing a specialized injector system known as an OPTIC 2 Inlet[3]. This temperature programmable vaporizing inlet is operated in the large volume injection mode. Fifty microliters of the sample extract is injected under cool, splitless, large volume conditions then separated by high-resolution gas chromatography interfaced to an Agilent Technologies Model 5973 mass selective detector operating in the full scan acquisition mode. GCMS determination of residual paraffinic hydrocarbons is performed based on the presence of the typical paraffin profile of aliphatic hydrocarbons listed in Table 1. These hydrocarbons are present due to the commercial refining process of petroleum crude oil used to generate paraffin-containing products.

GCMS Identification	Retention Time Reference	Retention Time Wipe	Molecular Weight
Docosane ($C_{22}H_{46}$ aliphatic hydrocarbon)	18.04	18.04	310
Tricosane ($C_{23}H_{48}$ aliphatic hydrocarbon)	18.76	18.76	324
Tetracosane ($C_{24}H_{50}$ aliphatic hydrocarbon)	19.45	19.45	338
Pentacosane ($C_{25}H_{52}$ aliphatic hydrocarbon)	20.11	20.11	352
Hexacosane ($C_{26}H_{54}$ aliphatic hydrocarbon)	20.75	20.75	366
Heptacosane ($C_{27}H_{56}$ aliphatic hydrocarbon)	21.37	21.36	380
Octacosane ($C_{28}H_{58}$ aliphatic hydrocarbon)	21.95	21.96	394
Nonacosane ($C_{29}H_{60}$ aliphatic hydrocarbon)	22.54	22.54	408
Triacontane ($C_{30}H_{62}$ aliphatic hydrocarbon)	23.16	23.16	422
Hentriacontane ($C_{31}H_{64}$ aliphatic hydrocarbon)	23.86	23.85	436
Dotriacontane ($C_{32}H_{66}$ aliphatic hydrocarbon)	24.62	24.62	450
Tritricontane ($C_{33}H_{68}$ aliphatic hydrocarbon)	25.50	25.50	464

Table 1: Typical Hydrocarbons Present in Petroluem-based Paraffin

RESULTS

Analytical reference materials, utilized to confirm the presence of residual paraffin in soot-containing samplse, are produced by taking a wipe sample from soot produced from the burning of an aromatic candle. The soot wipe is then extracted with Methylene Chloride in the same fashion as the unknown sample. This reference material is then subjected to GCMS analysis identical to that utilized for unknown sample extracts. Results of this analytical reference material analysis are presented in Figure 4. Figure 5 presents the results from the GCMS analysis of the A/C filter element. In order to more precisely speciate suspected paraffinic hydrocarbons, the characteristic mass of 71 (Extracted Ion Current Profile – EICP) was utilized to profile the twelve hydrocarbons listed in Table 1. The compounds selected as indicative of the presence of paraffin in the reference material and sample, belong to a class of chemical compounds known as "saturated aliphatic hydrocarbons." This class of compounds is typically found in specific ratios, resulting from the refining process of petroleum, that produces the material generically referred to as "wax." One of the sources of these compounds, often detected in residential soot containing samples, would be from (but not limited to) the incomplete combustion of paraffin associated with the routine burning of aromatic candles.

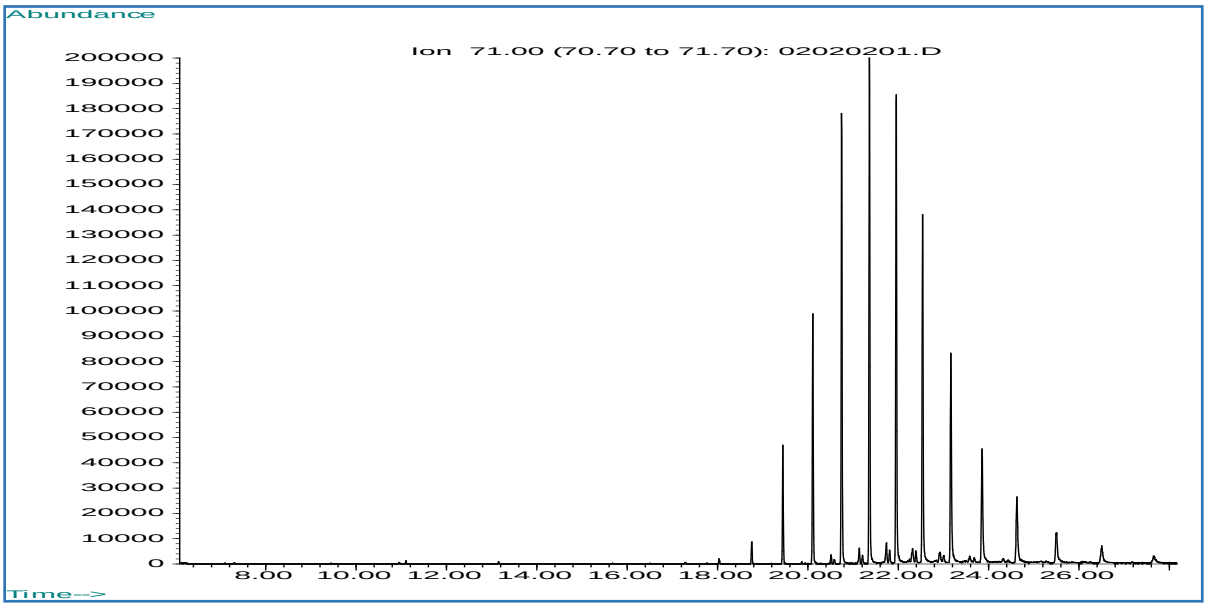

Figure 4: GCMS EICP of Mass 71 from Candle Soot Reference Material

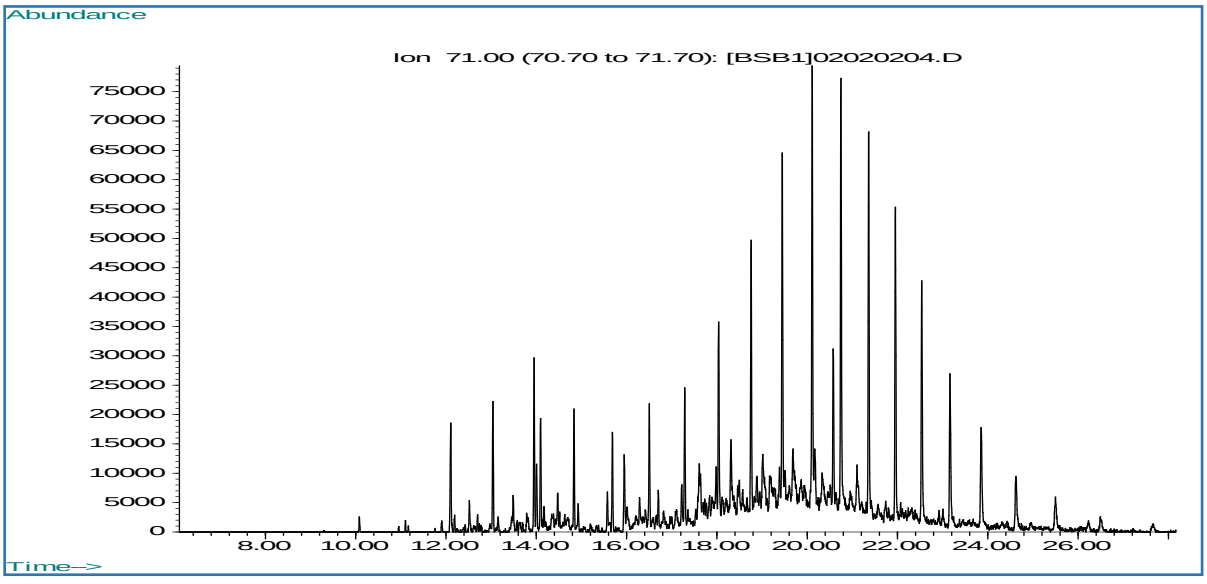

Figure 5: GCMS EICP of Mass 71 from AC Filter Element

DISCUSSION

Figures 6 & 7 compares the Extracted Ion Current Profile (EICP) for the characteristic mass 71 from the soot reference material and the EICP of mass 71 from the A/C filter sample extracts. This zoomed overlay comparison provides evidence that the saturated aliphatic hydrocarbon pattern is present in the GCMS analyzed sample. The comparison also offers visual reference as to the similarity of the characteristic pattern match of the speciated hydrocarbons present. Based on these inspections, it is determined that the air filter element contained significant contamination of the dark soot material. The aliphatic hydrocarbon pattern match was very similar to the pattern observed in the soot reference material. Based on this inspection and the presence of physical contamination found in the residence, it was determined that the heavy soot deposit contained on the air filter element resulted from the incomplete combustion of paraffin products, such as candle burning.

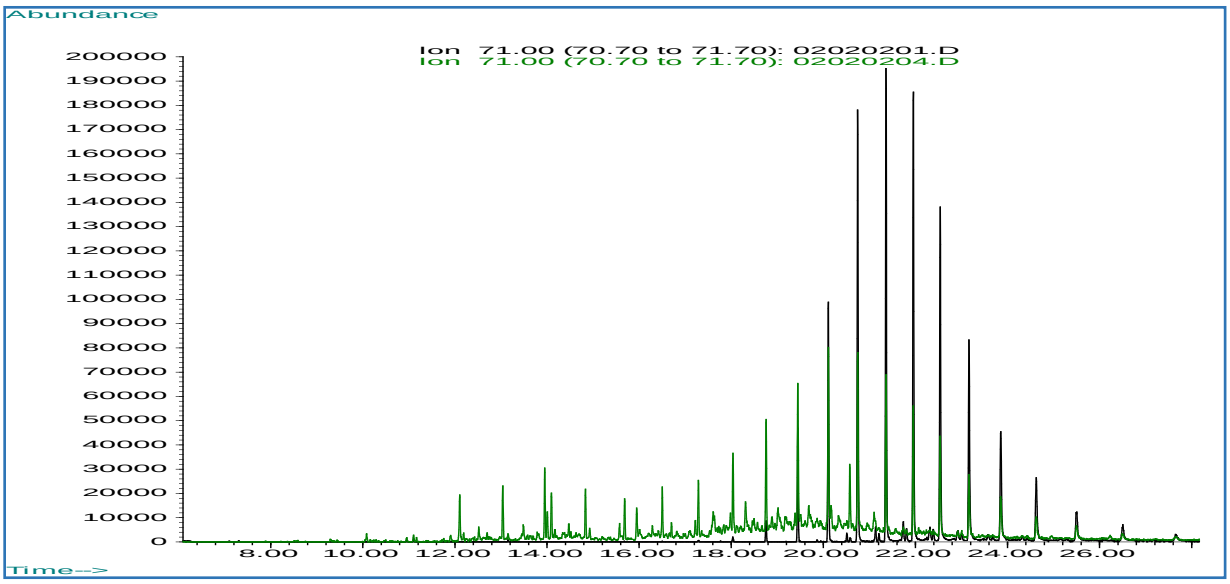

Figure 6: GCMS EICP Overlay of Mass 71 from Soot Reference Material and Air Filter Element (Black trace = Candle Soot Reference material. Green trace = A/C Filter Extract profile).

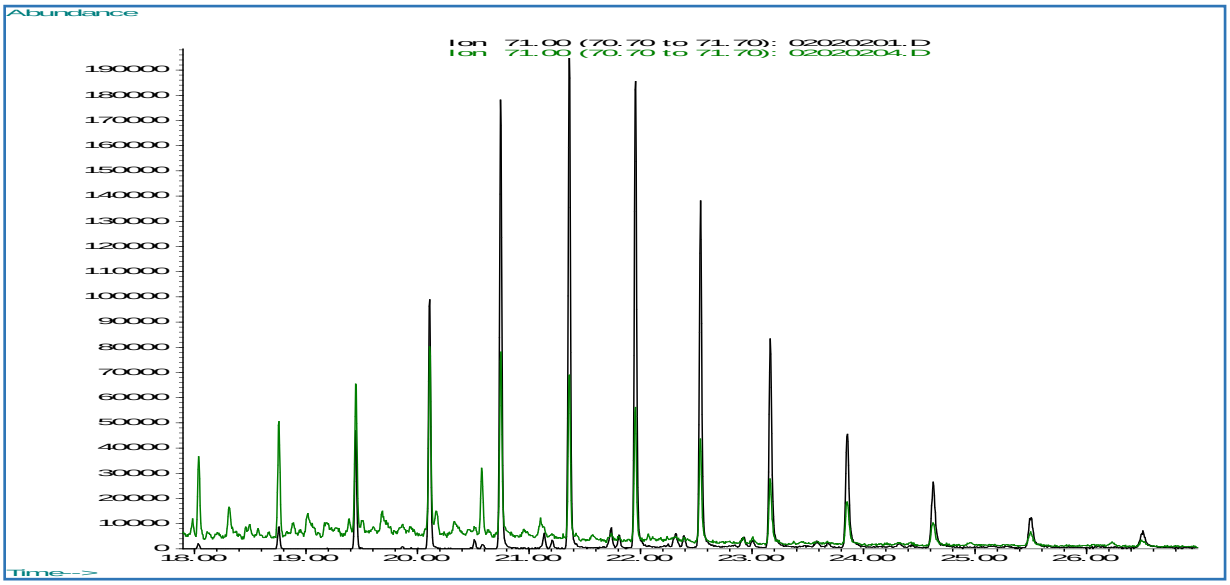

Figure 7: GCMS EICP Expanded Overlay Between 18 & 25 minutes of Mass 71 from Soot Reference Material and Air Filter Element (Black trace = Candle Soot Reference material. Green trace = A/C Filter Extract profile).

While these hydrocarbons may have other sources, the pattern match, distribution of the twelve individual compounds identified and the physical inspection of contaminated household furnishings, suggest they originated from a refined petroleum hydrocarbon source, such as candles.

CONCLUSION

The amount of evidence supporting the routine burning of candles as a source of residential soot contamination is growing (F.D. Stephen, C. H. Stineman, P.W. Jonmaire, W. Kelly, 1999). The costs associated with remediation from soot contamination can be significant. Homebuilders, home warranty agencies and even HVAC contractors have been adversely affected by claims that result in expensive clean-up activities. On many occasions, litigation is required to determine responsible parties and amount of financial settlement required to remediate (Simmons, Clement & Eastman, LLP, 2001). Additional studies are currently underway to determine if soot particles may also pose a health risk to occupants and present inhalation hazards due to the generation of volatile organic compounds, lead and sub-micron particles.

REFERENCES

[1]Frank Virgil 1998. Black Stains in Houses: Soot, Dust, or Ghosts?" *Home Energy Magazine*, January/February 1998.

Ibid.

[3] OPTIC 2: Ohmically Programmable Temperature Inlet for Chromatography, ATAS International, The Netherlands (www.atas.nl).

[2]J. David Krause 1999. Characterization of Scented Candle Emissions and Associated Public Health Risks. *The Journal of The LEAD*. Volume 7, No. 4, 1999-2000.

[3]F.D. Stephen, C. H. Stineman, P.W. Jonmaire, *et al*. 1999. Risk Analysis of Candles. *Emissions, Ecology and Environment, Inc.,* from Newsletter presented at http://www.litigation.support.ene.com/candle_emissions2.htm.

[4]Simmons, Clement & Eastman, LLP 2001. The Burning of Wax Candles Can Cause Soot Damage. From the November 22, 2000 Decision of Justice Whalen Brennan vs. Economical Mutual Insurance Company. *Insurance Law Update*, Winter 2001.