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Thermal analysis as an aid to forensics: Alkane melting and oxidative stability of wool

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Abstract

Interdisciplinary methods and thermal analytical techniques in particular are effective tools in aiding the identification and characterization of materials in question involved in civil or criminal law. Forensic material science uses systematic knowledge of the physical or material world gained through analysis, observation and experimentation. Thermal analytical data can be used to aid the legal system in interpreting technical variations in quite often a complex system.

Calorimetry and thermal microscopic methods helped define a commercial product composed of alkanes that was involved in a major law suit. The solid-state structures of a number of normal alkanes have unique crystal structures. These alkanes melt and freeze below room temperature to more than 60°C below zero. Mixtures of specific alkanes have attributes of pure chemicals. The X-ray diffraction structure of a mixture of alkanes is the same as a pure alkane, but the melting and freezing temperature are significantly lower than predicted. The jury ruled that the product containing *n*-alkanes had the appropriate melting characteristics. The thermal-physical properties made a commercial fluid truly unique and there was no advertising infringement according to the law and the jury trial

A combination of thermogravimetry, differential thermal analysis, infrared spectroscopy and macrophotography were used to conduct an extensive modeling and analysis of physical evidence obtained in a mobile home fire and explosion. A person's death was allegedly linked to the misuse of a kerosene space heater. The thermal analytical techniques showed that external heating was the cause of the space heater's deformation, not a firing of the heater with gasoline and kerosene. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Material evidence in a civil or criminal case is quite often evaluated by interdisciplinary analytical methods, including thermal science techniques. These methods are used in order to identify or characterize that material for the sake of a legal judgment. The composition of forensic materials such as polymers, metals, ceramics, composites, alloys, fibers and chemicals can be measured by thermal methods for the purpose of settling intellectual property rights or finding the origin of a material. A common forensic problem is to connect physical evidence found at the scene of a crime, possibly an item overlooked by a criminal, to a similar material. A key issue in dealing with forensic evidence is chain of custody, the 'evidence trail' [1]. Forensic evidence needs to be tracked from collection through disposition. Chain of custody is the process of maintaining a link from, for example, the crime scene or accident, through the analysis or characterization and the return of the exhibit to the police or proper authority.

Thermal techniques are based on using small, milligram samples and have the ability to gather a great deal of technical information [2]. Thermal analysis can be correlated with other analytical techniques, for example, rheology, spectroscopy and separation

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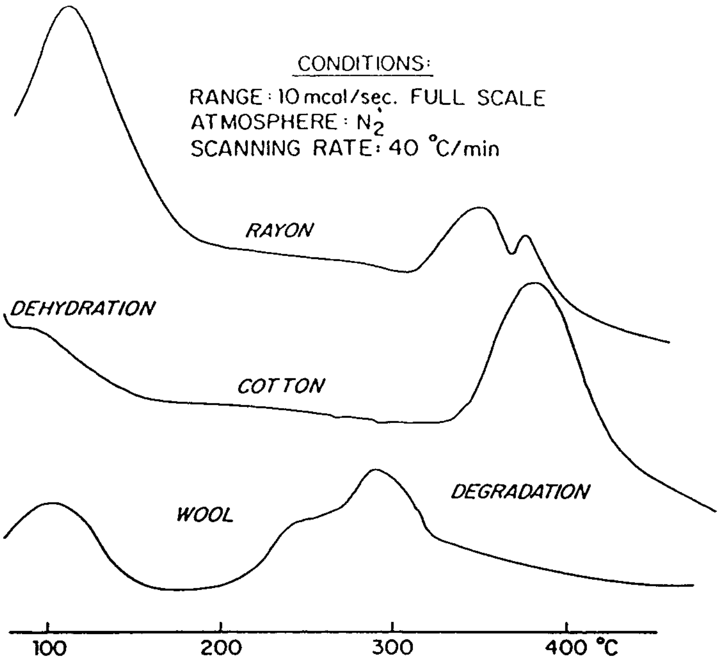

Fig. 1. Identification of fabric material by DSC (after Hall and Cassel [2]).

science. If the evidence is a polymer or plastic contamination from a crime scene, blood, dirt or dust do not interfere with test [2]. Characterization of polymer fibers, from a carpet or fabric, by thermal techniques is moderately easy (see Figs. 1 and 2). Thermal methods, differential scanning calorimetry (DSC) or thermogravimetric analysis (TGA), are useful in comparing materials to determine if they are from the same origin [2,3]. Dyzel has established a number of DSC methods for determining the country of origin for nuts and cheeses [3].

Two case studies employing thermal methods will demonstrate the utility of how physicochemical data can aid legal decisions. The first forensic case deals with phase change alkane materials and the 'legal' definition of the mixed alkane's melt temperature. The solid-state structure of *n*-alkanes at or below room temperature having a triclinic crystal structure [4]. Most of the characteristic 'fingerprint' interplanar spacings of the C_8H_{18} to $C_{22}H_{46}$ *n*-alkanes are the same. These chemicals melt at well-documented temperatures from -57 to $+42$°C.

The melting and freezing profiles of normal alkanes and paraffins are well documented [5–11]. The melt and crystallization temperature of the normal alkanes from octane to docosane is apparently dependent on the *c*-axis dimension of its unit cell, the (001) miller index [7]. The melting temperatures of these alkanes are not dependent on the 'finger print' major interplanar spacings (010) and (011) crystallographic orientations. However, the melting temperature of the alkanes is dependent on the 'minor' dimension, (001) [7,8].

A key objective of this study was to develop an XRD protocol where one can rapidly cool the alkanes and measure their crystal spacings. The X-ray diffraction (XRD) solid structure of the pure alkanes was recorded. The alkanes were studied by DSC and the American Society of Testing and Materials (ASTM) melt temperature was determined [4]. An alternate objective was to study mixtures of hexadecane and tetradecane and determine the XRD, DSC and thermal microscopy properties.

Mixtures of $C_{14}H_{30}$ and $C_{16}H_{34}$ *n*-alkanes have attributes of pure chemicals and their solid-state structure appears to be an orientational solid solution. The XRD solid-state structure of the mixture is the same as a pure alkane. The melting and freezing of these normal alkanes by DSC and thermal microscopy have been discussed in detail elsewhere [5,12].

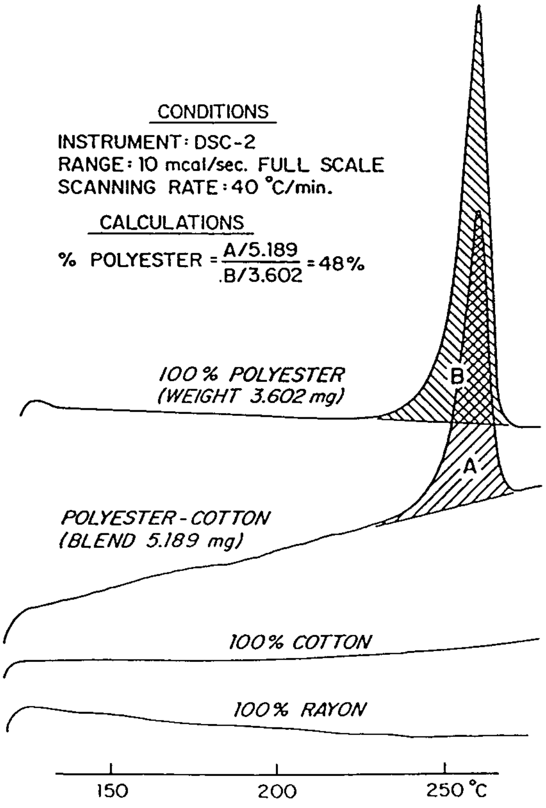

Fig. 2. Blend samples (after Hall and Cassel [2]).

The second forensic case deals with how a kerosene space heater deformed during a mobile home fire, either by explosion or an external source. Physical evidence was passed to the thermal analyst in the form of the kerosene space heater and various materials of deterioration, singed, charred, melted etc. from the area around the fire-damaged space heater by a plaintiff's attorney. The chain of custody of the evidence was unbroken from the time of transmittal for analysis to its return to plaintiff's attorney. Extensive TGA/DTA modeling and analysis of the physical evidence revealed significant implications as to the character of the so-called 'gasoline–kerosene' alleged explosion.

2. Experimental procedures

2.1. Case I. Mixed alkanes melt temperature

A TAI 2910 DSC was used to determine the ASTM melt temperature, the extrapolated onset temperature, ASTM E794 [13] and the crystallization temperatures. The DSC procedure was to cool at 2°C/min to 30°C below crystallization, then heat at 2°C/min to 30°C above the melt temperature. The melt temperature, the crystallization temperature and the heat of fusion and crystallization were determined from the DSC curve and TAI analysis software.

Thermal microscopy was accomplished with a Bausch and Lomb Polarizing Microscope fitted with a Koffler hot or cooling stage. The heating and cooling were viewed at 100× magnification. The microscope stage was enclosed and cooled with liquid nitrogen allowing for a cooling and heating rate of ≈1°C/min.

A Phillips X-Pert XRD System was used to record the crystal spacings of the alkanes. The following XRD conditions were used: CuK_α radiation, 1.5406 Å, a proportional counter, monochromatic X-rays, angular scan from 4 to 30°2θ and the thin film low back ground holder was used to support the crystallized alkanes. The International Crystallographic Diffraction Data is a resource for the standard crystal patterns [4].

A special insulated cell fabricated with a rubber coated petri dish was fitted into the horizontal diffraction sample holder. A columnar stainless-steel microscope cooling plate, 7.6 cm outer diameter and 1.9 cm in height, was quench cooled in liquid nitrogen, less than −60°C and placed in the cooling cell also filled with liquid nitrogen. The XRD structures of the quench cooled alkanes were reproducible and easily identified from the interplanar standard patterns [4].

The samples used in this study were gas chromatographic grade normal alkanes from Supleco, >99% purity [14]. A mixture of 90% hexadecane and 10% tetredecane was compared to a commercial mixture of nominally 90% hexadecane and 10% tetredecane [15]. The latter was analyzed by gas chromatography to determine the exact composition.

2.2. Case II – Space heater deformed by explosion or external source

A recovered *wool winter coat* was examined with a Seiko-Haake TGA and DTA. It was used to simulate the fire and exothermic conditions in the mobile bedroom to 900°C in air. The experimental protocol included the following: temperature program rate, 20°C/min; temperature range, 40–900°C; data collec-

Table 1
Melt and crystallization properties of *n*-alkanes by DSC

Normal alkanes		Temperature (°C)			Heat of transition (J/g)		
		T_m [b]	T_n [c]	T_m [a] (lit) [f]	ΔH_m [d]	ΔH_c [e]	ΔH_m [a d]
Octane	C_8H_{18}	−59	−59	−56	176	181	
Decane	$C_{10}H_{22}$	−32	−33	−32	177	177	
Dodecane	$C_{12}H_{26}$	−12	−13	−12,−10	182	188	
Tetradecane	$C_{14}H_{30}$	4.2	4.3	5.5	220	221	
Mixture	C_{14}/C_{16} (10/90) wt/wt	11	11	17 [a]	180	178	178 [a]
Hexadecane	$C_{16}H_{34}$	16	16	18, 16	174	172	
Octadecane	$C_{18}H_{38}$	27	27	28	177	175	
Eiocosane	$C_{20}H_{42}$	36	36	38	199	201	
Docosane	$C_{22}H_{46}$	42	43	43	196	197	

[a] Calculated value based on property additivity of $C_{14}H_{30}$ and $C_{16}H_{34}$.
[b] Melt temperature based on ASTM E794-97.
[c] Nucleation/crystallization temperature based on ASTM E794-97.
[d] Heat of fusion.
[e] Heat of crystallization.
[f] Literature values.

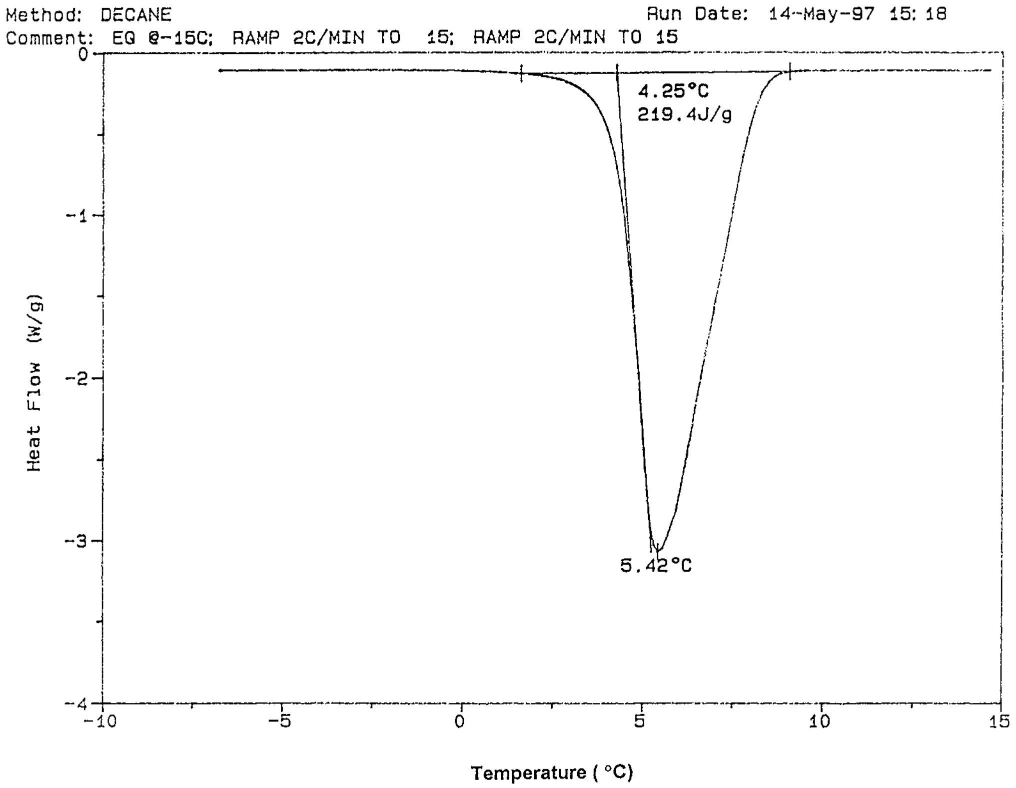

Fig. 3. DSC of tetradecane at 2°C/min.

tion, 0.5 s; sample mass, 1–15 mgs; and a DTA reference, an empty platinum pan. Selected samples recovered from the fire were examined with and without the fuel, kerosene, identified by FTIR spectroscopy.

A yellow-orange liquid recovered by the police was identified as kerosene by FTIR spectroscopy. The FTIR 1600 FT Perkin–Elmer infrared spectrometer was utilized in this study.

The damaged space heater was photographed in various positions and at 1–3× magnification with a Minolta 6Xi and a 35–80 mm zoom/macro lense.

3. Results and discussion

3.1. Case I

The DSC melt and crystallization properties of the *n*-alkanes studied are summarized in Table 1. The ASTM melt temperature, Tm, the extrapolated onset temperature of the endotherm, and the crystallization temperature, T_n, the extrapolated onset temperature of the exotherm were in good agreement for each alkane (E794-97) [13]. There was also a good correlation between the observed T_m and published values.

The commercial and Supleco blended mixtures of $C_{14}H_{30}$ and $C_{16}H_{34}$, (10/90) wt/wt had the same physical properties, melt temperature and heat of fusion, T_m, 11°C and T_n, 10°C. The mixture had a predictable heat of fusion, ΔH_m (see Table 1 and Figs. 3 and 4). The melt temperature of the mixture was not predictable. It was observed at a lower melt temperature, 11°C, rather than the calculated value of 16–17°C. The DSC freezing and melt temperature of the mixtures were confirmed by thermal microscopy (Table 2). The defected hexadecane structure with tetradecane with have a depressed melting temperature. The alkane melt temperatures were

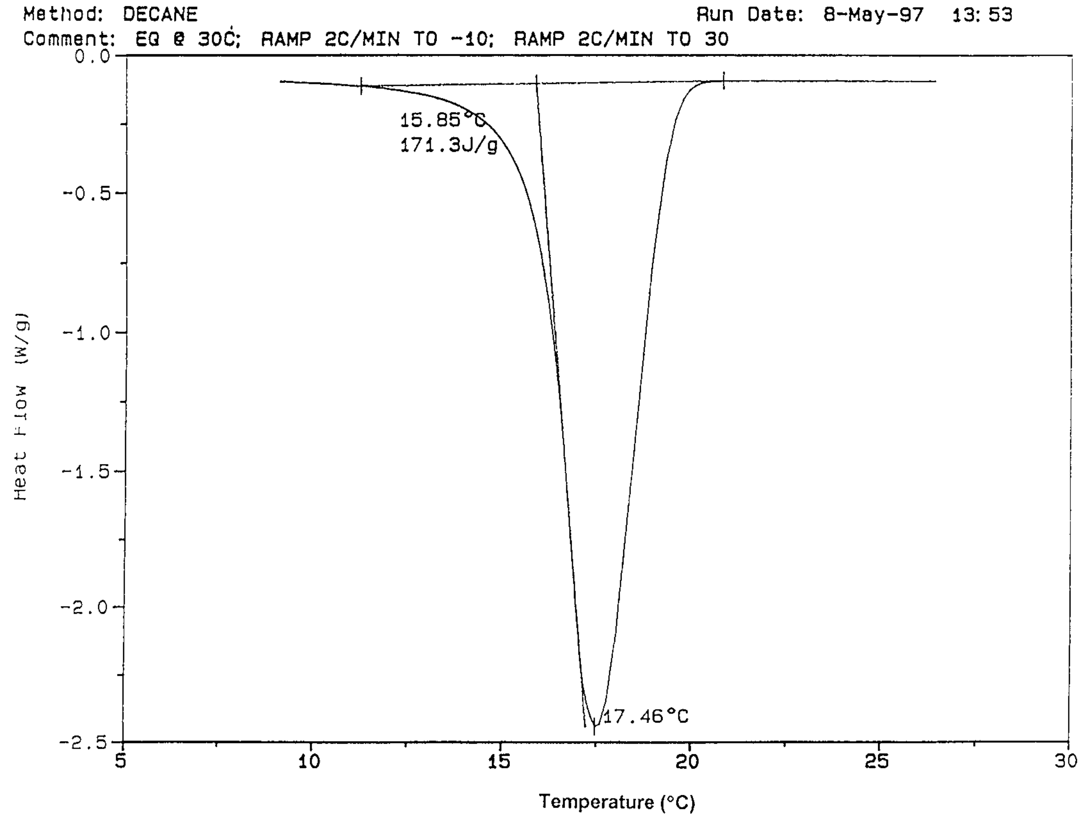

Fig. 4. DSC of hexadecane at 2°C/min.

Table 2
Thermal microscopy of mixture $C_{14}H_{30}/C_{16}H_{34}$, (10/90) wt/wt

Experimental	Time (min)	Temperature observations (°C)	100× magnification
Cooling cycle (partial record)	6.9	15.5	liquid
Cooling rate=1.2 °C/min	8.5	14.2	liquid
	9.6	12.1	solids forming
Crystallization temperature	10.4	11.1	rapid crystallization
	11.3	10.3	most solids formed
	12.2	9.5	white solids [a]
	13.1	8.7	white solids [a]
[a] Birefringent shards, aggregates, fiber-like particles and flakes	14.2	7.5	white solids [a]
	15.3	3.2	white solids [a]
	16.1	1.6	white solids [a]
Heating cycle (partial record)	40.8	2.3	white crystals [a]
Heating rate=0.84 °C/min	41.9	3.5	white crystals [a]
	43.1	4.4	white crystals [a]
	44.5	5.6	white crystals [a]
	45.8	6.7	white crystals [a]
	46.5	7.7	white crystals [a]
	47.9	8.9	white crystals [a]
T_1=onset melt	49.3	9.6	edges melting
	50.6	9.8	edges melting
	51.9	10.5	solids melting
T_1=melting temperature→	53.2	11.2	rapid liquefication
most solids liquefied 90–95%	54.3	11.4	rapid liquefication
	55.2	12.2	large shards noted
T_3=complete melt→ large shards→liquid	56.5	13.1	complete melt
	57.9	14.5	liquid
	59.2	15.9	liquid

[a] Birefringent shards, aggregates, fiber-like particles and flakes.

proportional to the number of carbon atoms in the chemical, Fig. 5.

All of the alkanes characterized by XRD were of the triclinic crystal system. The solid-state structure of the alkanes revealed a specific crystallographic orientation was related to the melt temperature. The (001) orientation was directly proportional to the observed DSC melt temperature with a correlation coefficient of

Table 3
X-ray diffraction structure properties of *n*-alkanes

n-Alkanes	Formula	DSC temperature (°C)	XRD Interplanar distances (Å) (*hkl*)			
		T_m=melt temp	(001)	(002)	(010)	(011)
Octane	C_8H_{18}	−59	10.9	5.45	4.6	4.47
Decane	$C_{10}H_{22}$	−32	13.3	6.65	4.58	4.46
Dodecane	$C_{12}H_{26}$	−12	15.7	7.91	4.61	4.47
Tetredecane	$C_{14}H_{30}$	−4.5	18.1	9.08	4.56	4.44
Mixture	$C_{14}H_{30}$ 10 wt% $C_{16}H_{34}$ 90 wt%	11	20.4	10.24	4.57	4.44
Hexadecane	$C_{16}H_{34}$	16	20.4	10.24	4.56	4.43
Octadecane	$C_{18}H_{38}$	27	21.9	10.9	4.59	4.47
Eiocosane	$C_{20}H_{42}$	36	24.5	12.2	4.57	4.46
Docosane	$C_{22}H_{46}$	42	27.4 (calculated)	13.7	4.53	4.44

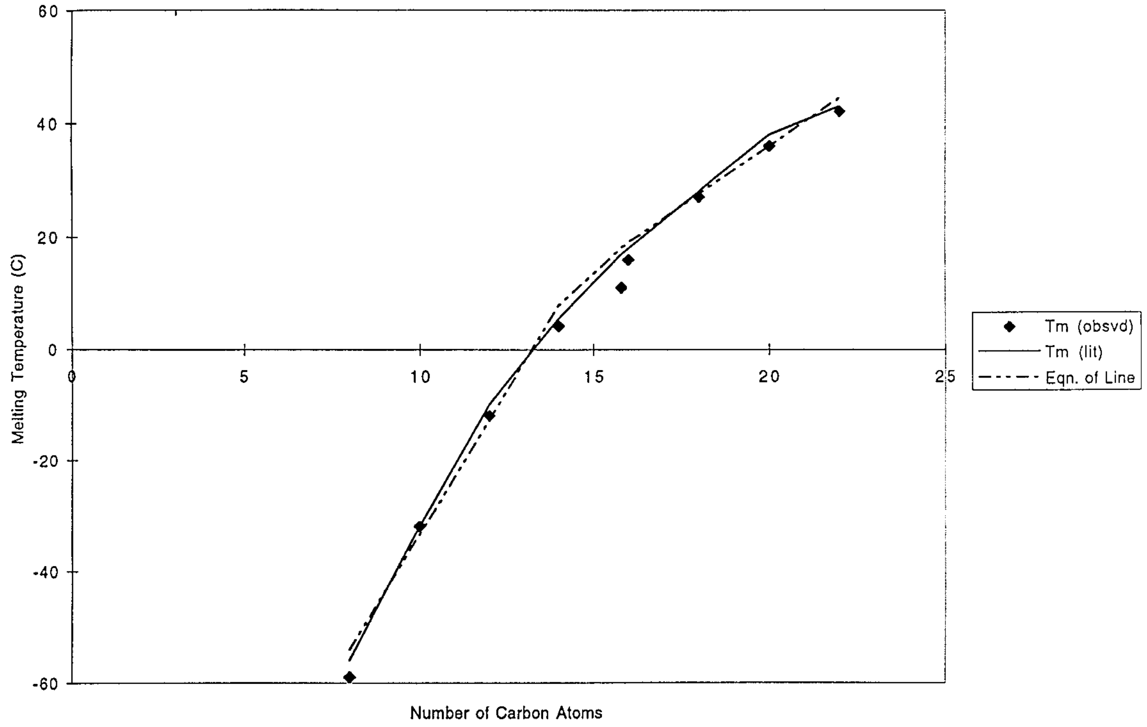

Fig. 5. Number of carbon atoms vs. melt temperature for even n-alkanes.

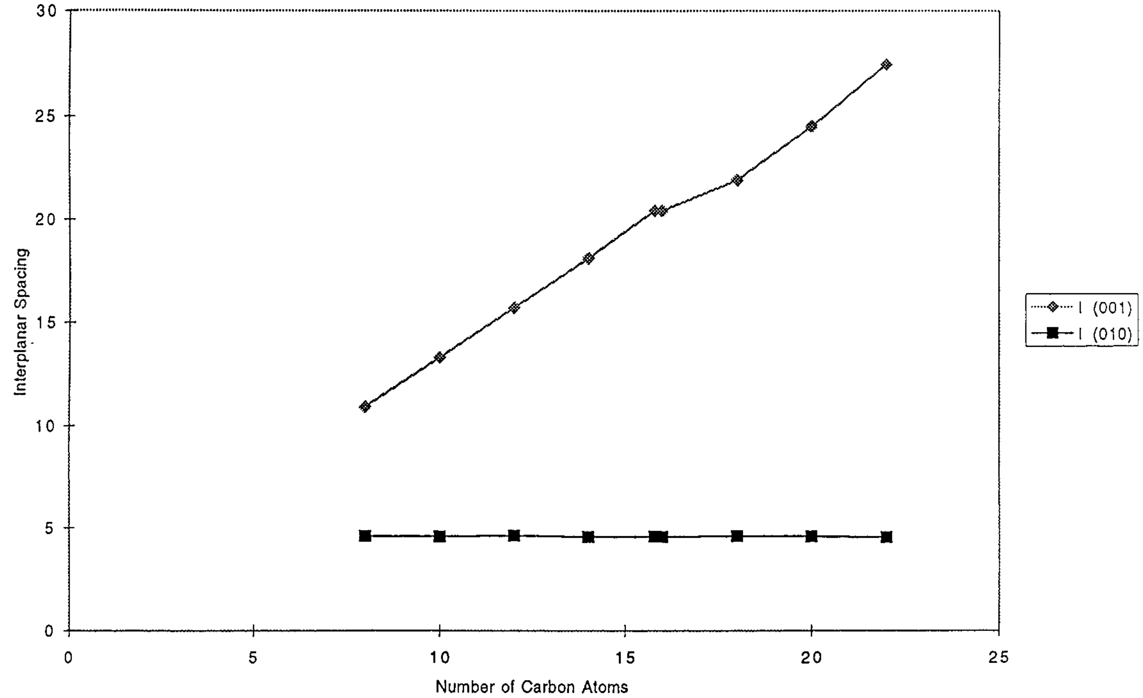

Fig. 6. Number of carbon atoms vs. XRD interplanar spacing for even n-alkanes for the crystallographic orientations of (001) and (010).

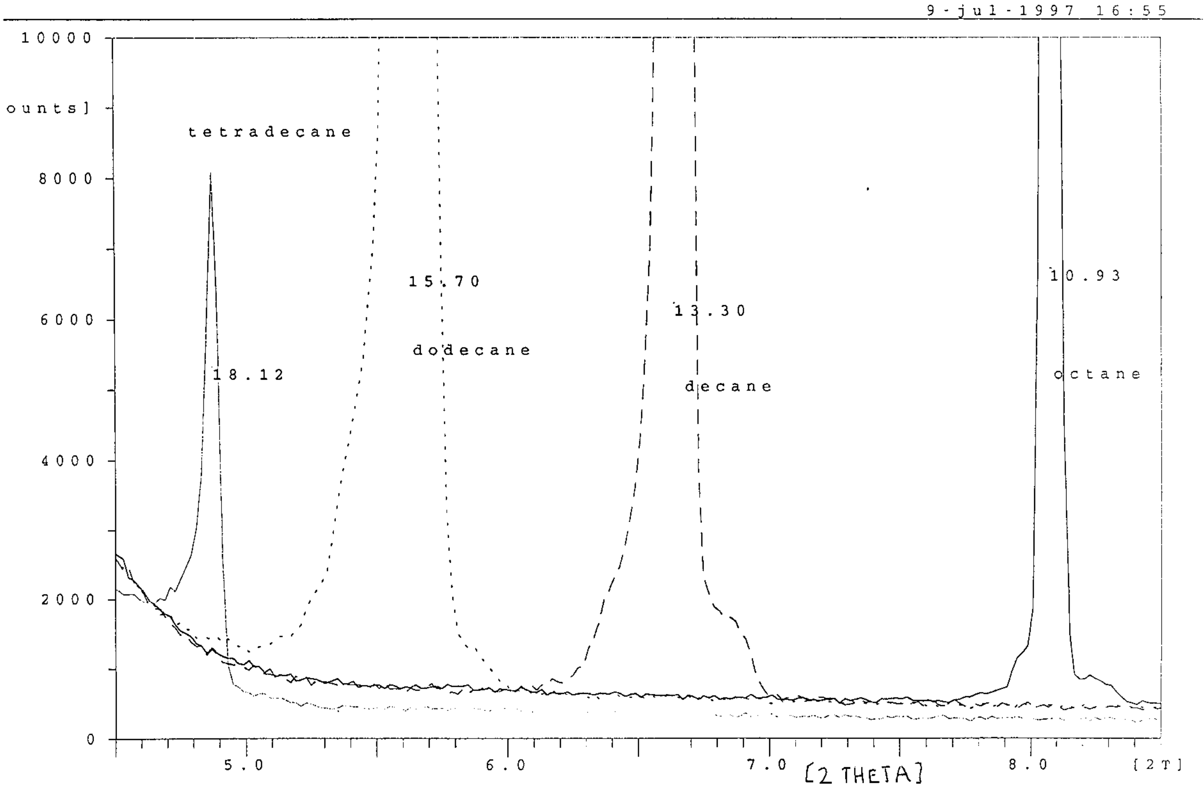

Fig. 7. XRD of octane to tetradecane: (001) crystallographic orientation: C_{14}=18.1 Å, C_{12}=15.7 Å, C_{10}=13.3 Å and C_8=10.9 Å.

0.98 (see Table 3 and Figs. 5 and 6–9). However, other key interplanar orientations, the (010) and (011), were not related to the melt temperature.

Both mixtures of tetradecane, $C_{14}H_{30}$ and hexadecane, $C_{16}H_{34}$, (10/90) wt/wt had diffraction properties identical to hexadecane, see Table 3 and Fig. 6 for the Supleco blend. However, the melt temperature, though related to the (001) orientation in the pure alkanes, was *not* proportional to the *c*-axis dimension of the mixture. An explanation of this inconsistency is that the mixture is an orientational solid solution of 10 wt% $C_{14}H_{30}$ in the $C_{16}H_{34}$ structure.

3.2. Case II

A review of the physical condition of the space heater from the burnt mobile home was undertaken and documented photographically. The space heater consisted of a forged sheet metal base or fuel reservoir, a lower cylindrical body, or canister and an upper combustion heater assembly enclosed in glass. A protective metal cage is fitted over the combustion heater assembly. Deformation and laminar flow of the glass cover is indicative of external high temperatures. It is clear by observation that the space heater did not explode, the glass flowed, it did not shatter.

The yellow-orange liquid was identified as kerosene based on the FTIR spectra. This was accomplished utilizing direct comparison of the recovered liquid to a commercial kerosene and gasoline. This comparison was performed in accordance with an established protocol utilizing the Aldrich IR Library of Spectra, ASTM E 334 and ASTM E204.

A number of recovered materials were examined by TGA/DTA, with and without added kerosene. An example of the modeling was the DTA/TGA of the unburnt *wool winter coat*, where it exothermically degraded at 244 and 449°C (major) exothermic-DTA, with a 3.3 wt% residue (Fig. 10). The *orange-yellow fluid* identified by FTIR as *kerosene*

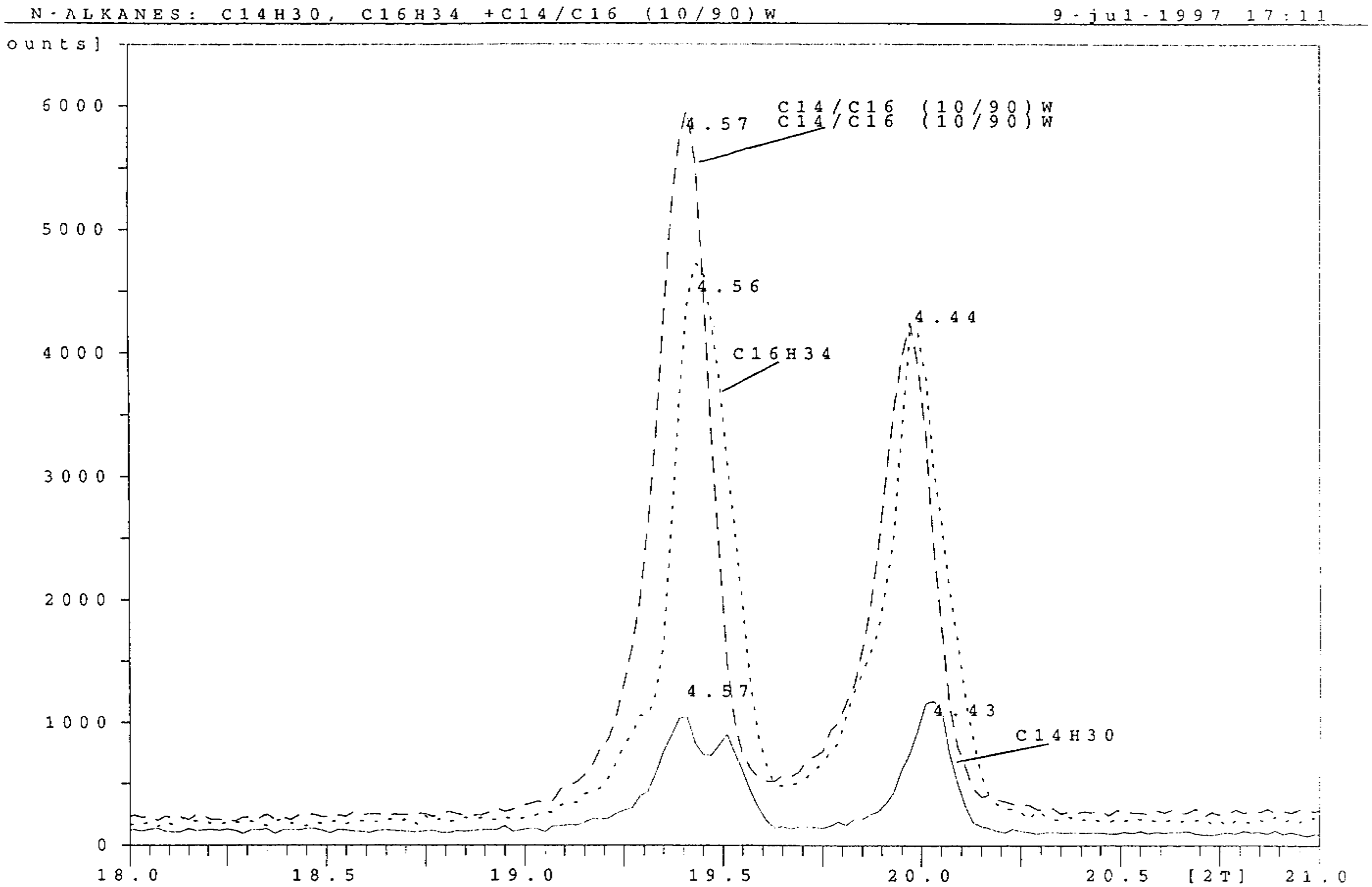

Fig. 8. XRD of hexadecane, tetradecane and ‘mixture’: (010) and (011) crystallographic orientations: C_{14}=4.57 and 4.43 Å, C_{16}=4.56 and 4.44 Å and $C_{14/16}$=4.57 and 4.44 Å.

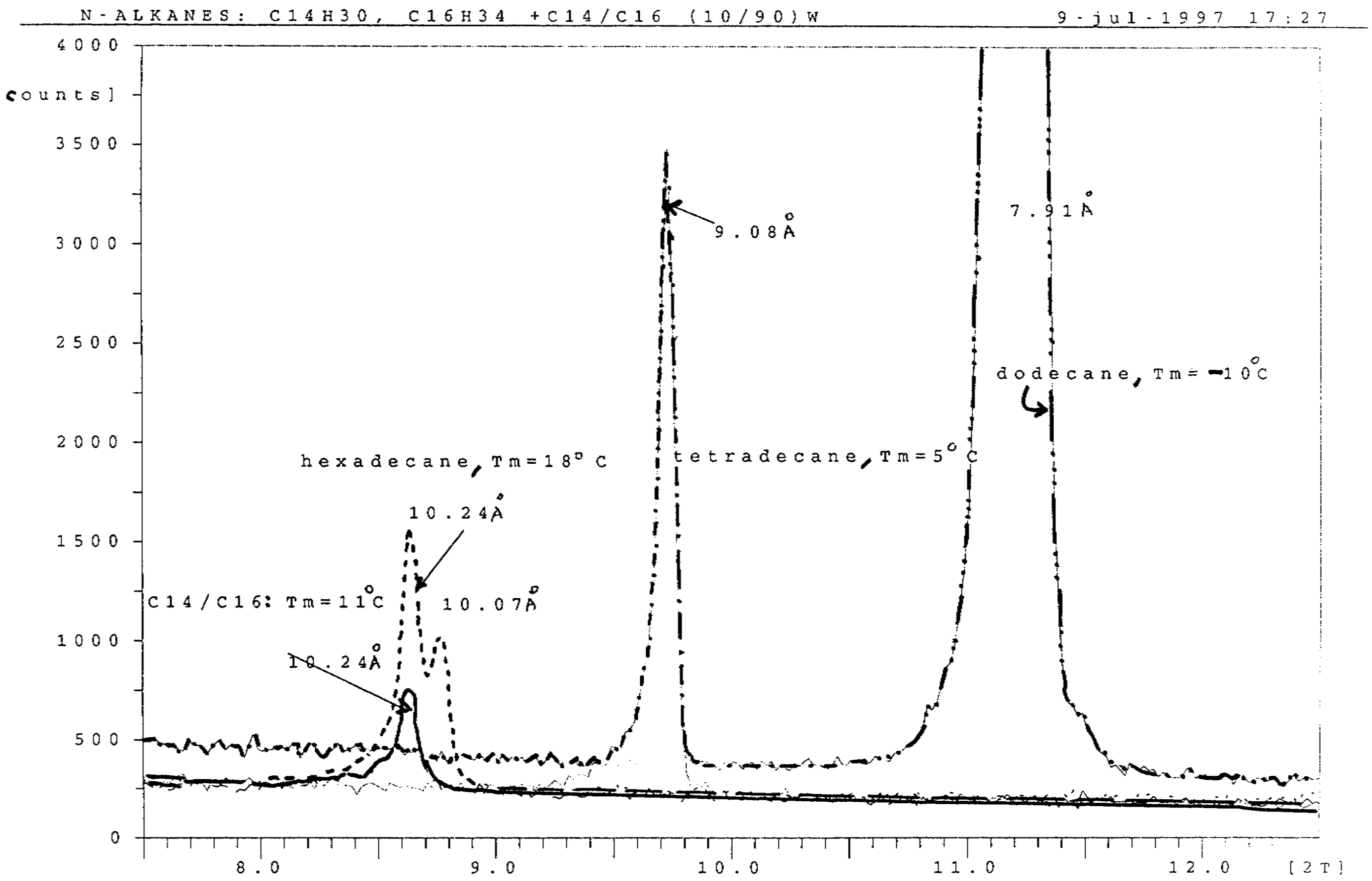

Fig. 9. XRD of hexadecane, tetradecane, dodecane and mixture $C_{14/16}$ (10/90) wt/wt: (001) crystallographic orientation: C_{12}=7.91 Å, C_{14}=9.08 Å, C_{16}=10.24 Å, and $C_{14/16}$= 10.24 Å.

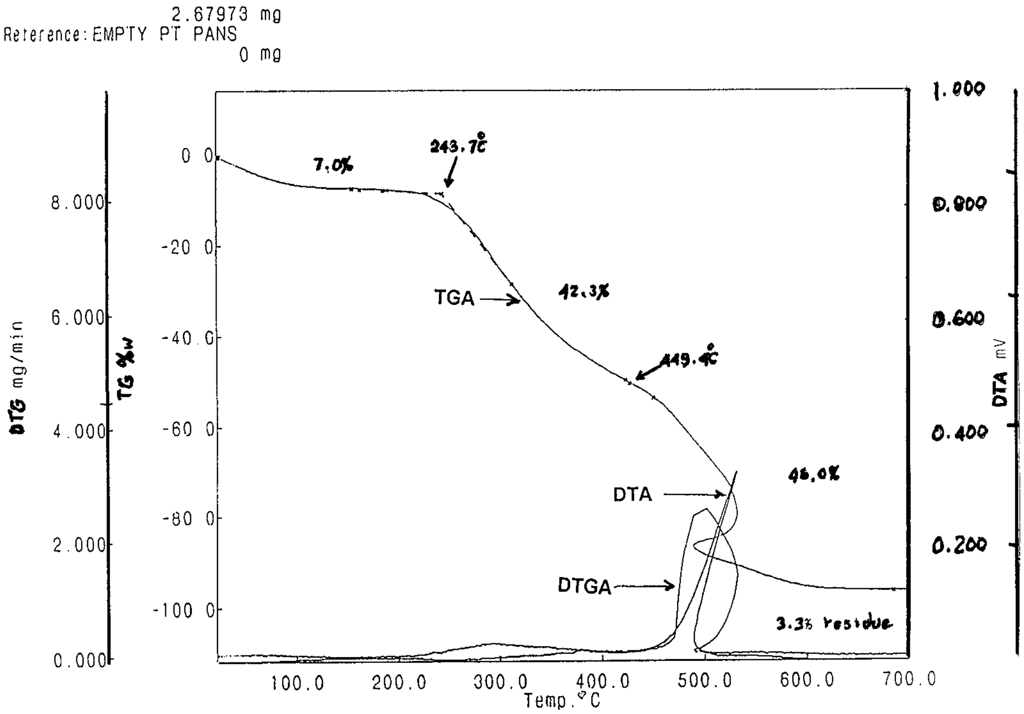

Fig. 10. TGA/DTA in air of winter wool coat.

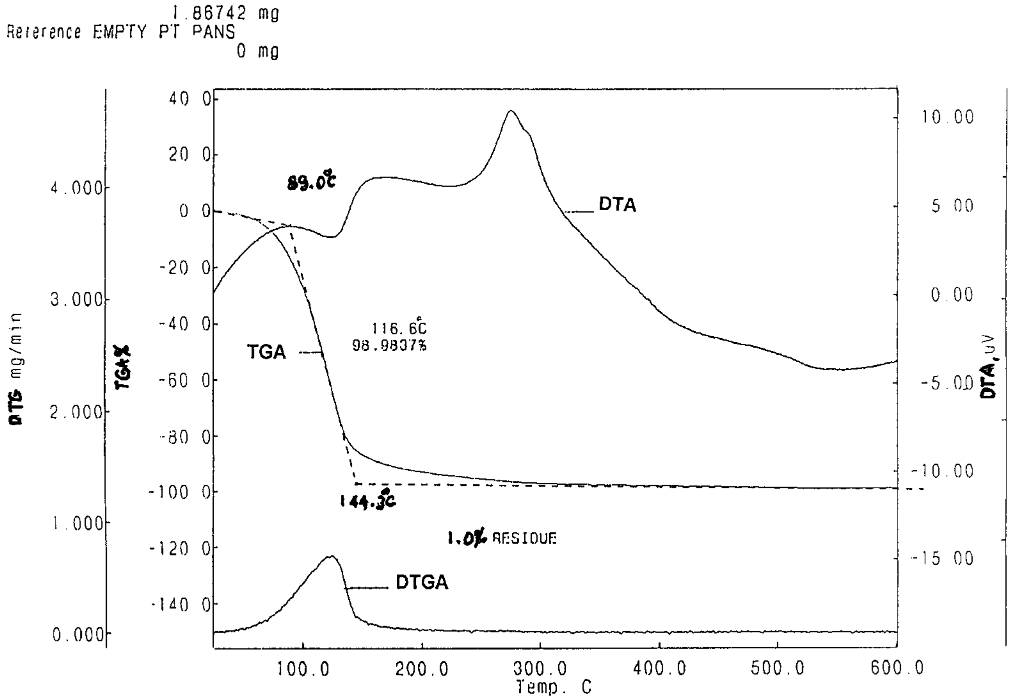

Fig. 11. TGA/DTA in air of kerosene identified by FTIR.

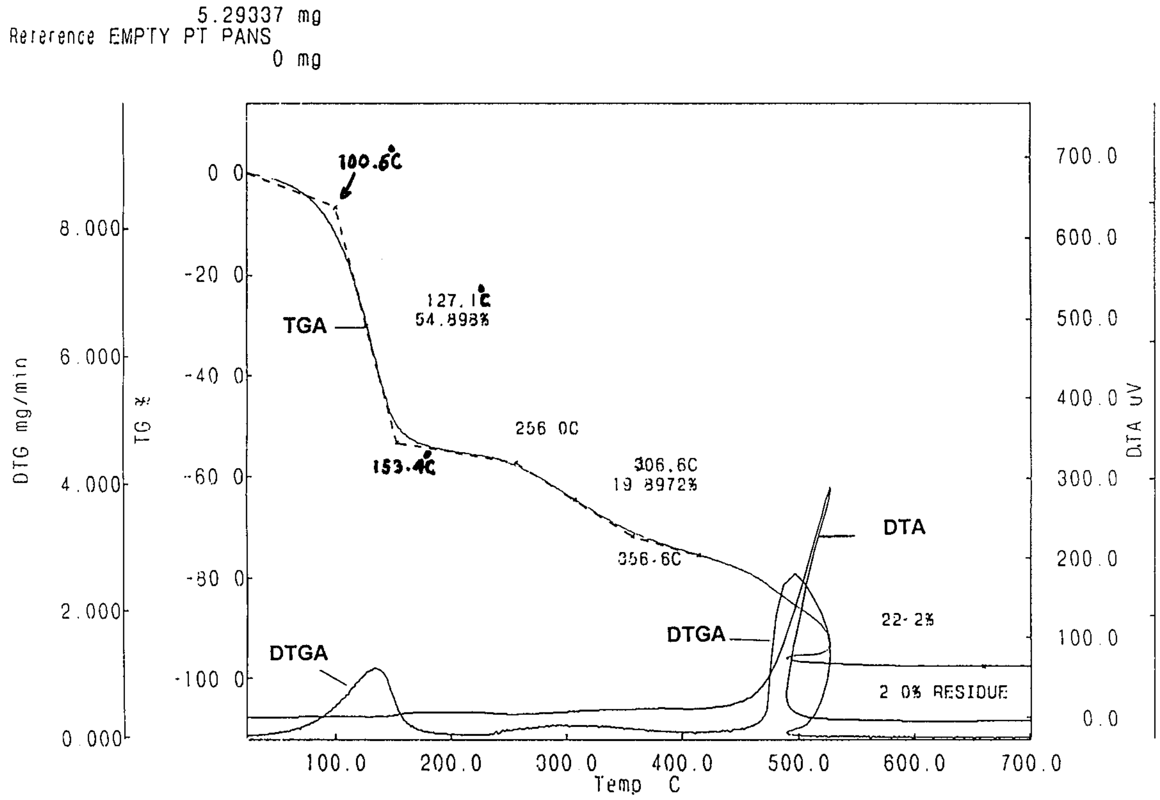

Fig. 12. TGA/DTA in air of winter wool coat+kerosene.

had a major volatilization from 89 to 144°C, with 99 wt% mass loss and a residue of <1 wt% (Fig. 11).

The TGA/DTA modeling study continued by adding a piece of the *wool winter coat* and the *kerosene* and then heating the composite to high temperatures, Fig. 12. There was a volatilization from 100° to 153°C, a boiling elevation due to the coat material. The exothermic degradation of the winter coat occurred at 256°C, and between 357 and 450°C. The *kerosene* sample raised the exothermic onset temperature of the winter coat.

4. Conclusions

4.1. Case I

The *major* XRD structural features of the alkanes, pure or the mixtures, were the same. The mixture of hexadecane and tetradecane had *attributes of a pure alkane*. Therefore, the ASTM definition of melt temperature (melting point) of pure chemicals, the extrapolated onset temperature, is also applicable to this chemical mixture. The alkane blend's crystal structure is identical to the hexadecane XRD structure, but a statistically lower melt temperature was observed for the blend. The mixture is probably an unique orientational solid solution. There was a trial ruling that if the melting temperature of the mixture in question was less than 15–16°C, and it was 10–11°C, then the jury ruled that the defendant won the law suit.

4.2. Case II

Kerosene did not exothermically alter the materials recovered by the State Police from the mobile home. The TGA/DTA fire/exothermic modeling corroborated the physical review that external heating, not an explosion, was the cause of the space heater's deformation.

Within a reasonable degree of scientific certainty: the liquid recovered by the police at the fire scene and identified as gasoline was in fact kerosene. No explosion took place at the mobile home structure; the cause of this mobile home structure fire was the failure to provide clearance between the kerosene space heater and the surrounding combustible fuel sources, such as the bedding, clothing, pillows and beds.

Thermal analysis was an aid to identifying the mixed alkane melt temperature and the space heater deformation by an external source, not an explosion.

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