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Title: Volatile organic compound analysis of accelerant detection canine distractor odours

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Abstract: Ignitable liquid detection dogs have been observed to falsely-respond to the pyrolysis products of common burned household items such as carpets and garden hoses, where ignitable liquids were not present. These responses from the canines are described as coming from distractor odours and decrease the reliability of detector dogs. The purpose of this research was to study the volatile organic compounds (VOCs) present in the odour profile of pyrolysed carpet and garden hose substrates, and determine whether a chemical similarity exists between these pyrolysis headspace profiles and target ignitable liquids, which may explain the false-positive behaviour of these detector dogs. Garden hose and carpet samples obtained from domestic settings were heated at a constant temperature for a specified time to produce pyrolysis products. A solid-phase microextraction (SPME) method was developed to extract the VOCs from burned substrates. The odours of the burned substrates were analysed by gas chromatography-mass spectrometry (GC/MS) and gas chromatography-tandem mass spectrometry (GC/MS/MS). A GC-MS/MS method was developed targeting the characteristic aromatic compounds in gasoline. Each pyrolysed substrate produced a complex and unresolved odour profile when analysed by GC-MS. GC-MS analysis failed to find any similarities between the odours of the burned substrates and ignitable liquids. GC-MS/MS analysis of pyrolysed garden hose and carpet substrate odours resolved and identified a wide range of aromatic target compounds - and these were present in high abundances in the hose samples. This indicates that there are significant chemical similarities between vapours of ignitable liquids and their distractor odours, which will have implications for the training of ignitable liquid detector dogs.

Volatile organic compound analysis of accelerant detection canine distractor odours

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We demonstrate a specific analysis for odors in burnt samples using a GC/MS/MS method

The pyrolysis products were shown to contain target compounds of gasoline

High concentrations and a wide variety of individual target components were produced

False-positive responses by ILR canines may be due to pyrolysis of household items

These pyrolysis products are produced under realistic fire conditions

Keywords: Ignitable liquid detection canines, distractor odours, volatile organic compounds, pyrolysis, GC/MS/MS

Abstract

Ignitable liquid detection dogs have been observed to falsely-respond to the pyrolysis products of common burned household items such as carpets and garden hoses, where ignitable liquids were not present. These responses from the canines are described as coming from distractor odours and decrease the reliability of detector dogs. The purpose of this research was to study the volatile organic compounds (VOCs) present in the odour profile of pyrolysed carpet and garden hose substrates, and determine whether a chemical similarity exists between these pyrolysis headspace profiles and target ignitable liquids, which may explain the false-positive behaviour of these detector dogs.

Garden hose and carpet samples obtained from domestic settings were heated at a constant temperature for a specified time to produce pyrolysis products. A solid-phase microextraction (SPME) method was developed to extract the VOCs from burned substrates. The odours of the burned substrates were analysed by gas chromatography-mass spectrometry (GC/MS) and gas chromatography-tandem mass spectrometry (GC/MS/MS).

A GC-MS/MS method was developed targeting the characteristic aromatic compounds in gasoline. Each pyrolysed substrate produced a complex and unresolved odour profile when analysed by GC-MS. GC-MS analysis failed to find any similarities between the odours of the burned substrates and ignitable liquids. GC-MS/MS analysis of pyrolysed garden hose and carpet substrate odours resolved and identified a wide range of aromatic target compounds – and these were present in high abundances in the hose samples. This indicates that there are significant chemical similarities between vapours of ignitable liquids and their distractor odours, which will have implications for the training of ignitable liquid detector dogs.

Introduction

Detector dogs used in law enforcement and forensic science are a screening tool for target chemicals. While they can indicate the presence of a target compound, confirmatory analysis is required to confirm their response [1]. Unlike other screening tests, detector dogs have been shown to be highly specific in a variety of different applications [2-4], as well as having superior sensitivity for target odours in many situations [5]. The dogs can be readily trained to alert on a wide variety of chemicals [6, 7]. However, false responses are an issue in the use of detector dogs for law enforcement, especially at the crime scene [8].

False responses occur when a dog responds to a non-target odour, known as a false positive response, or fails to respond in the presence of a target odour, known as a false negative response. False responses are undesirable as they decrease the reliability of detector dogs.

There is no definitive answer to the question of why trained detector dogs will respond to a non-target (distractor) odour. The breed and history of the dog plays a role, with selectivity shown to depend on the breed, while dogs that are re-trained for a new class of targets are less efficient than dogs trained for their entire career on one class of targets [8]. The training method, skill of the trainer, and the frequency of training sessions for the handler and their dog are all factors in false positive detection rates. Guidelines have been developed to provide uniform training processes in order to improve training for all classes of detector dogs [9]. At the scene, physical conditions such as temperature can also affect the performance of the dogs [10,11]. Furthermore, distractor odours may be chemically similar to a target odour, or may trigger the dog's olfactory system through chance.

Ignitable liquid detection canines are used at fire scenes to detect traces of ignitable liquids such as gasoline. The presence of ignitable liquids may indicate arson as the cause of a fire. Ignitable liquids are predominantly oil derivatives consisting of a complex mixture of hydrocarbons, and the various products have similar physical properties – high vapour pressures and flash points below 100 °C.

Distractor odours which may produce a false positive response by ignitable liquid detector dogs are thought to be volatile organic compounds (VOCs) which have a chemical similarity to these target odours. While the key VOCs may be present before the fire, it is hypothesised that the majority of distractor odours for these dogs are produced during the fire via pyrolysis of various fuels [12].

Previous studies have been conducted to identify and characterise background and pyrolysis compounds of common household items [12-14]. Lentini et al. analysed background VOCs of many common household items including clothing, shoes, building materials, and adhesives. Petroleum-derived products such as toluene and xylenes used in the manufacturing process of the materials (for example, adhesives in shoes) were detected in a passive headspace experiment [15]. Furton identified many pyrolysis compounds from common fire debris substrates such as straight-chain and branched alkanes, and aromatics such as toluene and naphthalenes, which are also components of many ignitable liquids and the major components of gasoline [12]. Further studies with carpet samples have agreed with these findings [13].

Some common household items are thought to be the source of distractor odours for ignitable liquid detector dogs. These items readily pyrolyse when subjected to fire conditions and are suspected to

be the cause of subsequent false-positive responses by the dogs in fire scenes. In particular, for domestic fire scenes handlers report that false positive results from fire debris have been associated with carpet and with garden hoses [16,17]. The mixture of VOCs produced by these materials under fire conditions is poorly understood at present.

Gas chromatography/mass spectrometry (GC/MS) is the technique of choice for ignitable liquid residue (ILR) analysis, with the method standardised in ASTM E1618-14 [18]. Over 90% of laboratories analysing fire debris utilise this technique, and many publications of ILR studies have been carried out using GC/MS [19-24]. While current GC/MS is sufficient for most fire debris samples encountered in a forensic laboratory, samples with highly weathered ILRs or in the presence of heavy interference products pose a significant challenge for GC/MS analysis and often result in inconclusive results [25]. In the analysis of VOC mixtures such as pyrolysis interference products in fire debris samples, complex mixtures are often unable to be determined due to the number of unresolved components [16]. For this reason, advanced GC/MS techniques such as gas chromatography/tandem mass spectrometry (GC/MS/MS) [26] have been employed which provide a higher separation capability, sensitivity, and specificity.

An ideal ignitable liquid analysis technique should equal or at least approach the sensitivity provided by detector dogs at a fire scene. A less sensitive technique may result in a failure to identify ILRs present on a sample which the dog has correctly identified. The capabilities of both GC/MS and GC/MS/MS have been compared to the sensitivity of a detector dog in detecting heavily weathered ignitable liquids in burnt substrates [27]. GC/MS failed to confirm ILRs in several instances whereas GC/MS/MS confirmed the detector dog alerts. The study showed that GC/MS/MS more closely resembled the sensitivity and specificity of detector dogs than GC/MS, but does not exceed the capability of the canines [27,28].

This study aimed to produce pyrolysis headspace volatile organic compounds from objects known to be ignitable liquid detection canine distractors. A controllable and reproducible pyrolysis method was developed and used to collect pyrolysis headspace VOCs from these materials under specified conditions. The analysis was carried out using GC/MS/MS, in an attempt to selectively detect target compounds and exclude background interferences.

Materials and Methods

Samples

Ignitable liquid samples

The ignitable liquid used in this study was gasoline. Unweathered unleaded gasoline standards were purchased from Restek Chromatography. The standards were prepared as 5000 µg/mL solutions in methanol. An ignitable liquids standard containing 50 ppm of common target compounds for ILR analysis was used for peak identification (listed in Table 1).

Table 1: List of compounds included in the ignitable liquid standard.

Carpet samples

Three carpet cut-outs were obtained from domestic households. Carpet typically consists of the carpet fibres and two backing layers. The composition of each carpet sample was identified by Fourier transform infrared (FTIR) spectroscopy. The carpet samples were analysed as:

- Polypropylene carpet; polypropylene fibres with cotton and polyester backing layers
- Nylon carpet; nylon 6,6 fibres with polypropylene and polyester backing layers
- Wool carpet; wool fibres with cotton and calcium carbonate backing layers

Hose samples

Samples from two used garden hoses were obtained from domestic households. The two hose samples were different in appearance; however examination by FTIR spectroscopy showed that both samples contained a polyvinyl chloride (PVC) polymer heavily modified with diethylhexyl phthalate plasticiser.

Sample Preparation

Ignitable liquid standards for headspace studies were prepared by pipetting 2 μL of the ignitable liquid standard onto a piece of filter paper, placing the filter paper into a clean metal can and sealing the can.

Carpet samples were cut into 2 cm squares and hoses were cut into 2 cm lengths. Each sample was placed into a clean metal can. Carpet and hose samples were subjected to heating to produce pyrolysis products.

A Bosch PHG 630 DCE heat gun fixed above the can was directed at the sample and the temperature of the sample measured using a thermocouple. During method optimisation, samples were pyrolysed by being heated at various temperatures for 5 minutes, and the pyrolysis temperature which produced the greatest abundance and widest range of VOC pyrolysis products was selected for sample analysis.

Optimal temperatures were: nylon carpet 300 °C, polypropylene carpet 350 °C, wool carpet 400 °C, garden hose 300 °C. Samples were allowed to cool to room temperature before the metal can was sealed. A hole was made in the middle of the lid using a nail for subsequent VOC collection. Clear adhesive tape was placed over the hole in the lid to allow the headspace to accumulate.

Solid-phase microextraction

A solid-phase microextraction (SPME) method was developed for the collection of VOCs from gasoline standards and the pyrolysis samples. All of the pyrolysis samples and standards were analysed using the optimised SPME method. The SPME fibre was conditioned for 30 minutes at 270 °C in the GC injection inlet prior to first use, and for 10 minutes at 270 °C at the beginning of daily analysis. Blank fibre tests were performed after conditioning and periodically throughout an analysis sequence to check for possible carry-over between sampling.

For VOC extraction, the can containing the ignitable liquid standard or pyrolysis sample was heated in a sand bath using an Accuplate temperature-controlled hotplate (Labnet International Inc., Edison, New Jersey) and equilibrated at 60 °C for 20 minutes. A DVB/CAR/PDMS-coated SPME fibre was inserted into the can by piercing the adhesive tape covering the hole in the lid with the SPME needle, exposing the fibre, and extracting within the headspace at 60 °C for 10 minutes.

Instrumental method

Immediately after extraction of the sample headspace, the SPME fibre was manually injected into a Thermo Fisher Scientific Trace 1310 Gas Chromatograph coupled to a TSQ 8000 triple quadrupole mass spectrometer, and thermally desorbed for 10 minutes. A 30 m HP – 5MS 0.25 μm /0.25 mm GC column was used for all experiments with 1 mL/min helium as carrier gas. The GC injection port was heated to 275 °C with a 10:1 split ratio. The column temperature program was 45 °C held for 0 min, then 5 °Cmin⁻¹ to 75 °C, held for 2.5 min, then 8 °Cmin⁻¹ to 115 °C, held for 0 min, then 15 °C min⁻¹ to 250 °C, held for 4 min for a total run time of 26.5 min.

Product ion scans targeting prominent aromatic compounds in ignitable liquids were selected. The aromatic compounds targeted in this study are important diagnostic components of gasoline [18]. The target compounds, parent ion analysis times, and collision energies are detailed in Table 2.

Table 2: MS/MS conditions

All chromatograms and mass spectra were acquired and processed using the Chromeleon 7 software (Thermo Fisher Scientific, Sydney Australia). The 2014 National Institute of Standards and Technology (NIST) mass spectral library was used for compound identification. The Chromeleon 7 AutoSRM software was used in the optimisation of MS/MS conditions. To ensure that VOCs originating from the background and sample cans did not contribute to the results, a metal can blank was analysed at the beginning of an analysis sequence and its spectrum subtracted from the substrate spectra.

Results and Discussion

Reproducibility of the pyrolysis products

Previous pyrolysis studies of fire debris samples generated pyrolysis products by either igniting the sample and allowing it to burn freely or by analysis using Pyrolysis-GC-MS [12,16]. It was difficult to control the extent of pyrolysis product generation or the temperature in a freely-burning sample, with two burns of the same sample producing inconsistent relative amounts of pyrolysis products. Analysis by Pyrolysis-GC-MS is unable to adequately analyse impure or inhomogenous samples [12]. The current work aimed to produce pyrolysis products from realistic samples in a reproducible manner by heating at a constant temperature using a heat gun.

To evaluate the reproducibility of pyrolysis product creation, samples were heated in duplicate for each temperature. Duplicate SPME injections of each duplicate were analysed, leading to four recorded chromatograms for each sample. The chromatograms for the green hose at the chosen pyrolysis temperature of 300 °C are shown in Figures 1a–1d. Figure 1a and Figure 1b, and Figure 1c and Figure 1d are duplicate SPME injections of a pyrolysis headspace. This method showed excellent reproducibility regarding the presence of the same peaks, indicating that the same pyrolysis products were being produced. Intensities of peaks in the chromatogram were observed to be comparable for duplicate injections of the same sample, but showed differences when comparing duplicate pyrolysis experiments. The relative ratios of peaks remained consistent when comparing the four chromatograms of the same sample, a result which was unable to be obtained in free-burning experiments [12].

Figure 1: VOC profile of four replicate green hose samples heated at 300 °C, analysed in GC/MS full scan mode

Pyrolysis headspace of distractor items

There was a trace level of ethylbenzene present in the wool carpet prior to pyrolysis. There were no other target aromatic compounds present in the wool carpet before the pyrolysis experiments. All of the other samples were negative for all of the target aromatic compounds before the pyrolysis experiments.

Figure 2 shows the pyrolysis headspace of the polypropylene carpet analysed by a) GC/MS and b) GC/MS/MS product ion.

Figure 2: a) GC/MS TIC b) GC/MS/MS product ions of polypropylene carpet sample

Target compounds identified in the polypropylene carpet sample included: 1 Toluene, 2 1,3,5-trimethylbenzene, 3 naphthalene. The abundance of the target compounds in the pyrolysis headspace of the polypropylene carpet was 6 – 10 times the limit of detection for the method.

Figure 3 shows the pyrolysis headspace of the nylon carpet analysed by a) GC/MS and b) GC/MS/MS product ion.

Figure 3: a) GC/MS TIC b) GC/MS/MS product ions of nylon carpet sample

Target compounds identified in the nylon carpet sample included: 1 Toluene, 2 ethylbenzene, 3 (1-methylethyl)benzene, 4 propylbenzene, 5 1,3,5-trimethylbenzene, 6 naphthalene. The abundance of the target compounds in the pyrolysis headspace of the nylon carpet was 3 – 7 times the limit of detection for the method, except for naphthalene (abundance approximately 15 times the detection limit).

Figure 4 shows the pyrolysis headspace of the wool carpet analysed by a) GC/MS and b) GC/MS/MS product ion.

Figure 4: a) GC/MS TIC b) GC/MS/MS product ions of wool carpet sample

Target compounds identified in the wool carpet sample included: 1 Toluene, 2 ethylbenzene, 3 m/p-xylene, 4 (1-methylethyl)benzene, 5 propylbenzene, 6 1,3,5-trimethylbenzene, 7 naphthalene, 8 2-methylnaphthalene. The abundance of 1,3,5-trimethylbenzene in the pyrolysis headspace of the wool carpet was approximately 100 times the detection limit for the method. Toluene and naphthalene were present in the pyrolysis headspace at an abundance approximately 30 times the detection limit. The other compounds were present in the pyrolysis headspace at an abundance of 4 – 16 times the detection limit.

The two hoses produced similar results to each other. Figure 5 shows the pyrolysis headspace of the green hose analysed by a) GC/MS and b) GC/MS/MS product ion.

Figure 5: a) GC/MS TIC b) GC/MS/MS product ions of green hose sample

A comparison of the product ion chromatograms for the gasoline standard and the two hose samples is shown in Figure 6.

Figure 6: Product ion chromatograms of a) Gasoline standard, b) Green hose, c) Brown hose

The target aromatic compounds detected in the pyrolysis headspace of the garden hoses are listed in Table 3. The abundance of toluene, indane and naphthalene in the pyrolysis headspace of the hose samples was higher than in the gasoline standard, and beyond the linear range of the instrument. The other target compounds were present in abundances ranging from 10 – 50 times the detection limit for the method.

Table 3: Target compounds present in the pyrolysis headspace of the hose samples

Discussion

It is necessary to identify possible sources of the target aromatic compounds in these pyrolysis experiments. It is a well-understood possibility for linear polymers to cyclize and aromatize under pyrolysis conditions. However, the pyrolysis headspace of the polypropylene carpet produced a low abundance of only a limited number of target compounds. The pyrolysis headspace of the nylon carpet was similarly low in abundance and showed a diversity of target compounds. The wool carpet produced a higher abundance and wider range of target compounds than the other carpet samples. Wool is a peptide polymer containing a high abundance of the amino acids tyrosine and phenylalanine; the side chains of these amino acid residues may be capable of pyrolysing into the target aromatic compounds. Alternatively, the linear chain of the peptide may cyclise after side-group scission in pyrolysis conditions.

The garden hoses produced a high abundance of target aromatic compounds. These ranged in volatility from toluene through to 2-methylnaphthalene, virtually the entire range of aromatic compounds present in gasoline. Alkyl benzenes were present in the pyrolysis headspace in high abundance and in a diverse range of structures. Indane and naphthalene were present in the headspace in particularly high abundance. Methylnaphthalenes were present in the headspace in high abundance.

These results could be due to either the pyrolysis of PVC polymer or of di-ethylhexyl phthalate plasticisers, present in the hoses in high concentration. PVC is well-established as a source of aromatic hydrocarbons during pyrolysis, including alkylbenzenes and indane. Phthalates are aromatic compounds with flexible side chains and are capable of rearranging under pyrolysis conditions into aromatic hydrocarbons detected in these experiments, including toluene, naphthalene and methylnaphthalene [29, 30].

Conclusion

Controlling the pyrolysis conditions in a VOC experiment allows a better insight into the pyrolysis process than free-burning experiments can provide. In these experiments, the widest variety and highest abundance of target compounds were produced with steady heating of the substrate at 300 °C. It is unlikely that an experiment which burns the substrate could reproduce this result. On the other hand, radiation effects on a substrate in a real fire may produce a similar heating profile and generate a high abundance of target compounds.

The GC/MS/MS instrument is designed to target known compounds in a complex mixture. It is suited to detection and analysis of a well-understood product such as gasoline. In addition, there are selective product ions that can be chosen for the analysis of aromatic compounds within gasoline. The use of GC/MS/MS in these experiments allowed the sensitive and selective targeting of

aromatic compounds of interest. This was a significant improvement on experiments relying on GC/MS.

The presence of phthalate plasticiser in the garden hoses may explain the very high abundance of target compounds in the pyrolysis headspace of these items. Phthalates are present in many consumer items, albeit in lower concentrations than those present in flexible PVC hoses. This leads to the possibility of canine false positive results arising from consumer goods subject to fire conditions, due to pyrolysis of phthalates. Additional controlled pyrolysis experiments could be carried out on pure samples of phthalate compounds to test this hypothesis. Further work could be conducted on the controlled pyrolysis of other consumer items containing phthalate plasticisers.

The detailed product-ion chromatogram of the headspace from the hoses could not be mistaken for gasoline by an analyst. However, most of the target aromatic compounds from gasoline are present, including a range of different classes of aromatic compounds (alkyl benzenes, naphthalenes, methylnaphthalenes, indane). This result confirms the hypothesis that the VOCs constituting a distractor odour for ignitable liquid detector dogs can be similar to those in the target odour. Attempting to train ignitable liquid detector dogs to ignore this VOC mixture would be problematic and would likely lead to false negative results from gasoline residues.

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Figure 1
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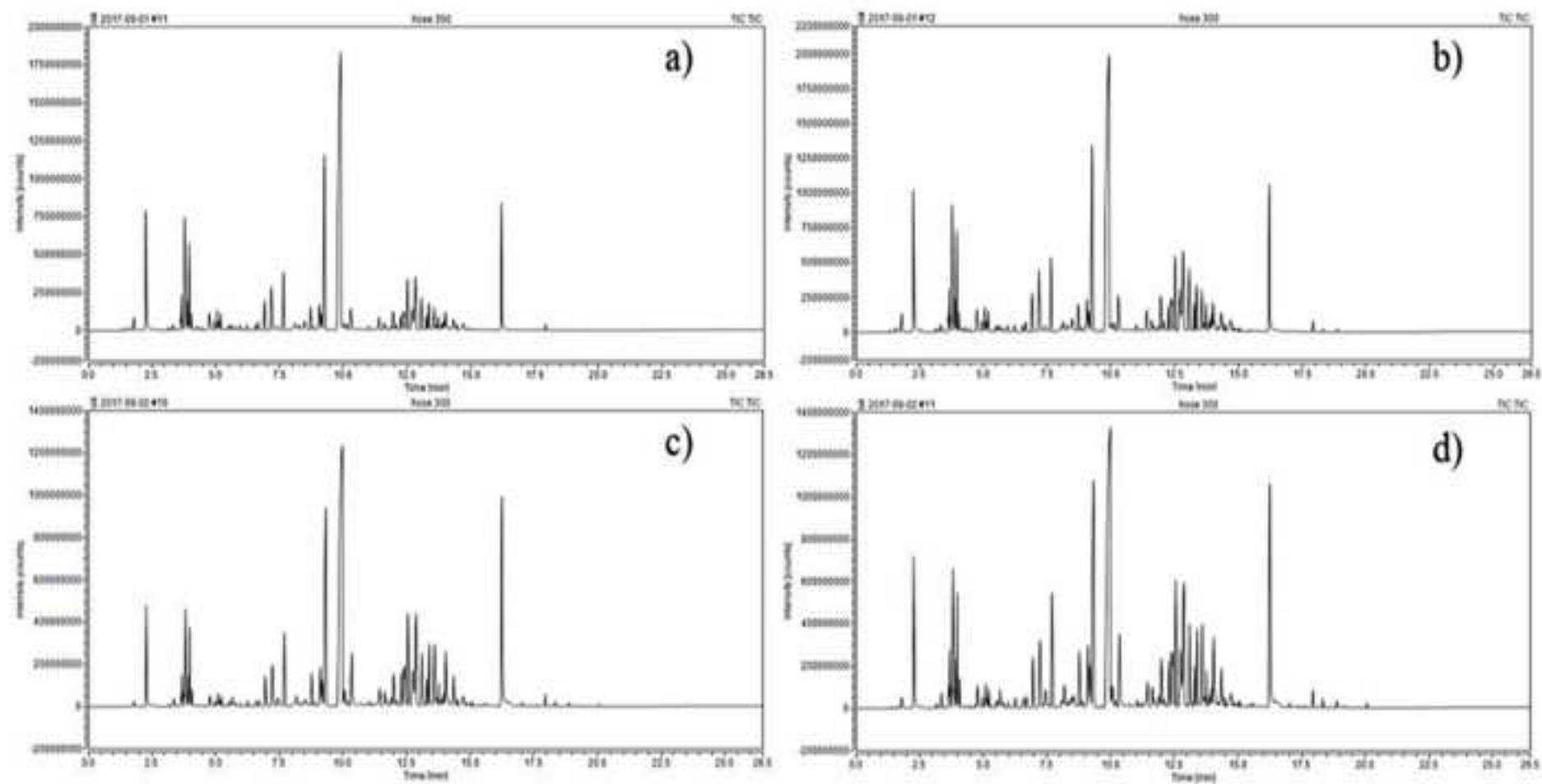


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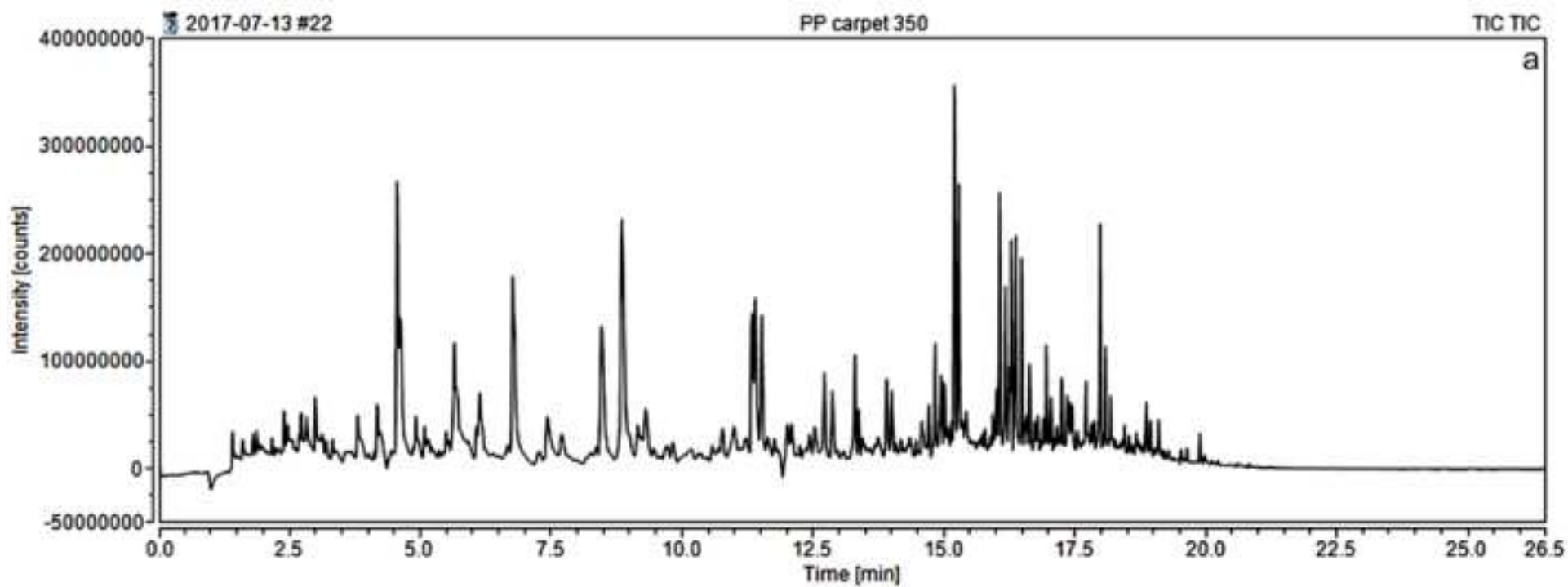


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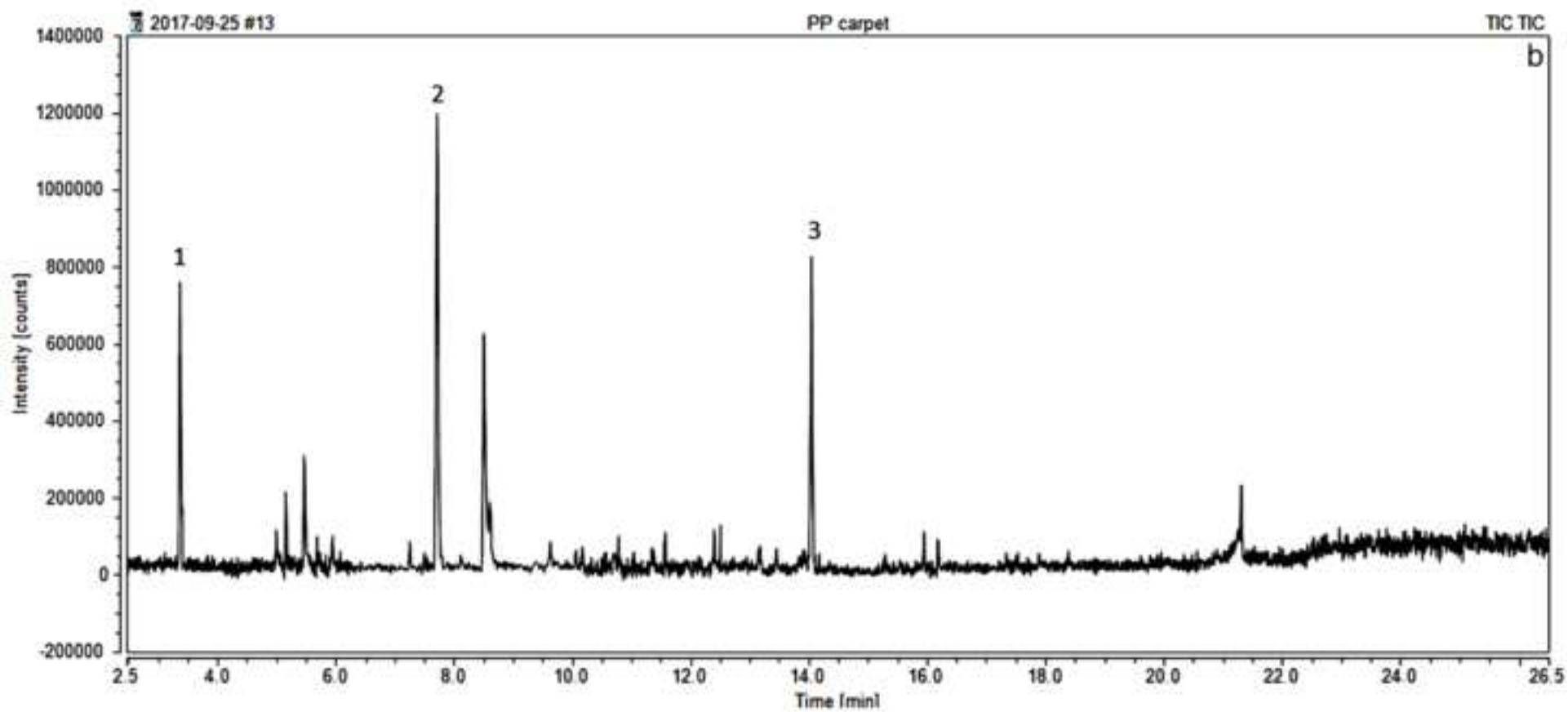


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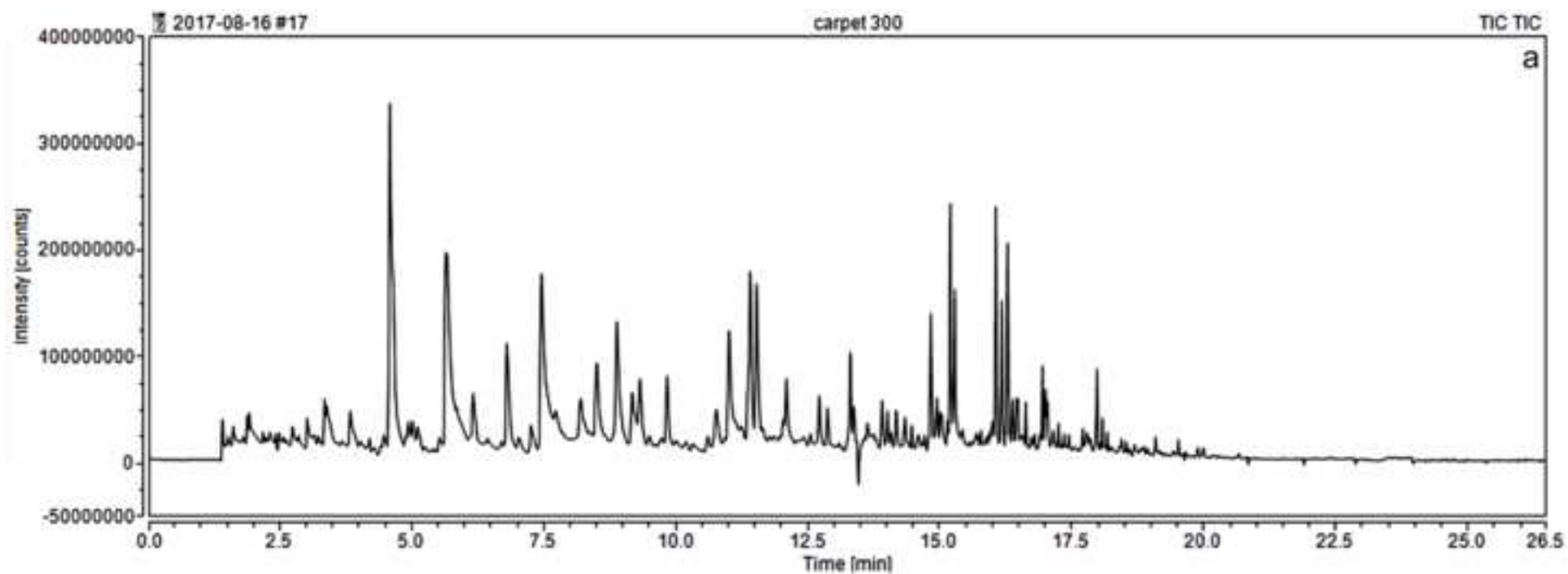


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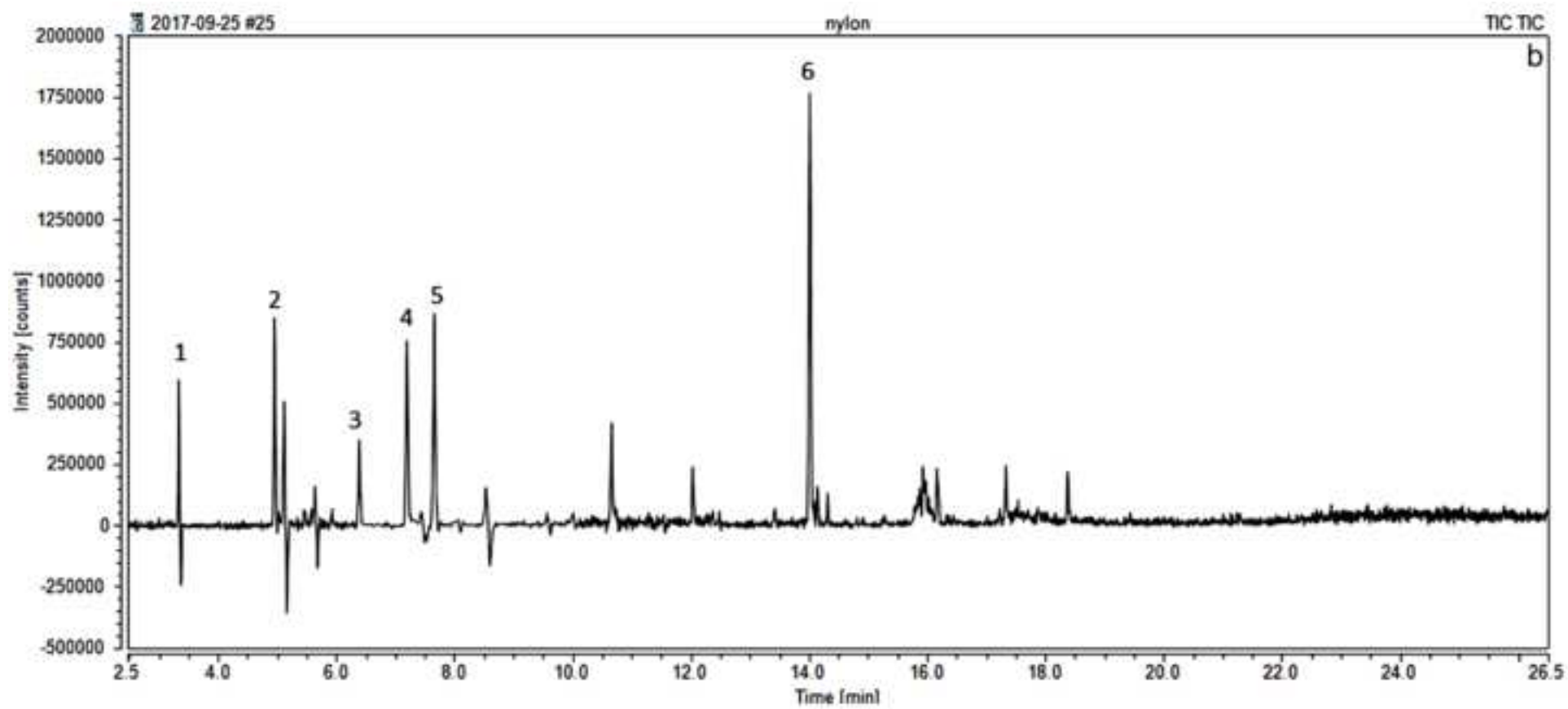


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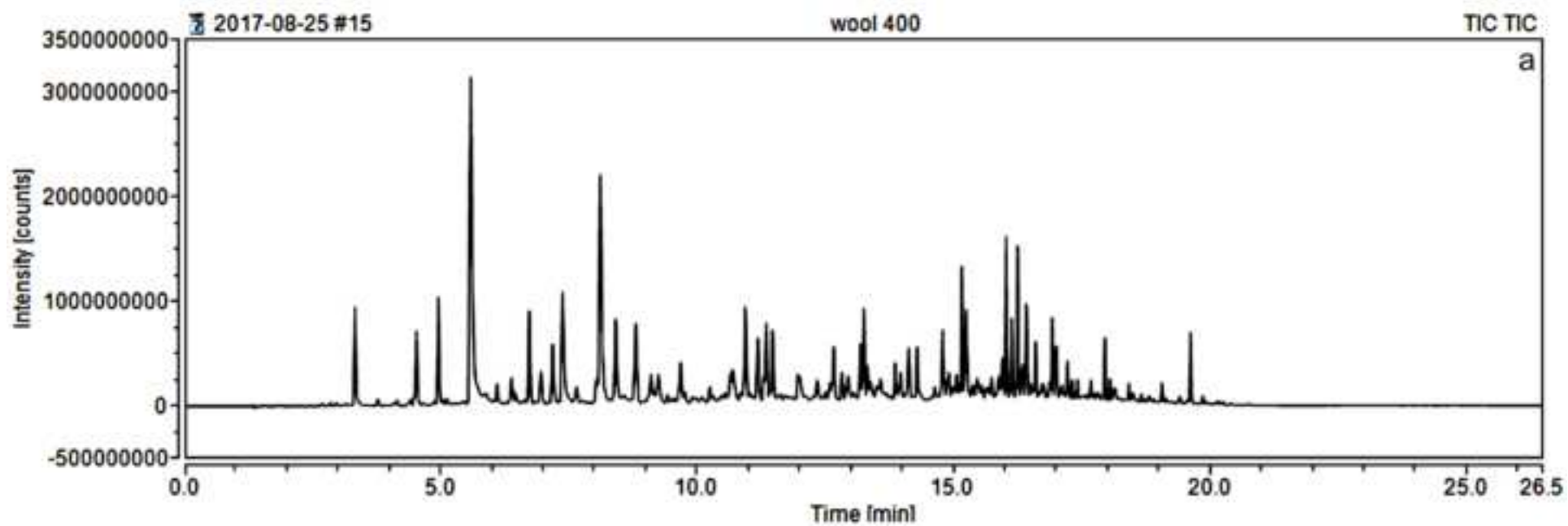


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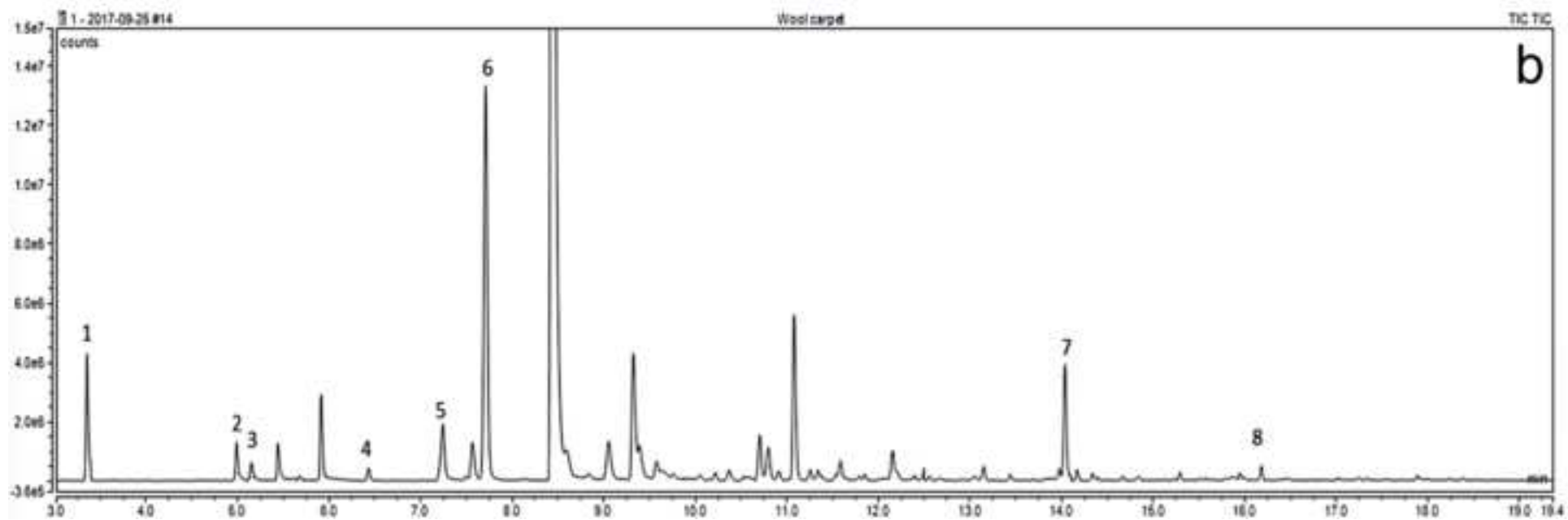


Figure 5a
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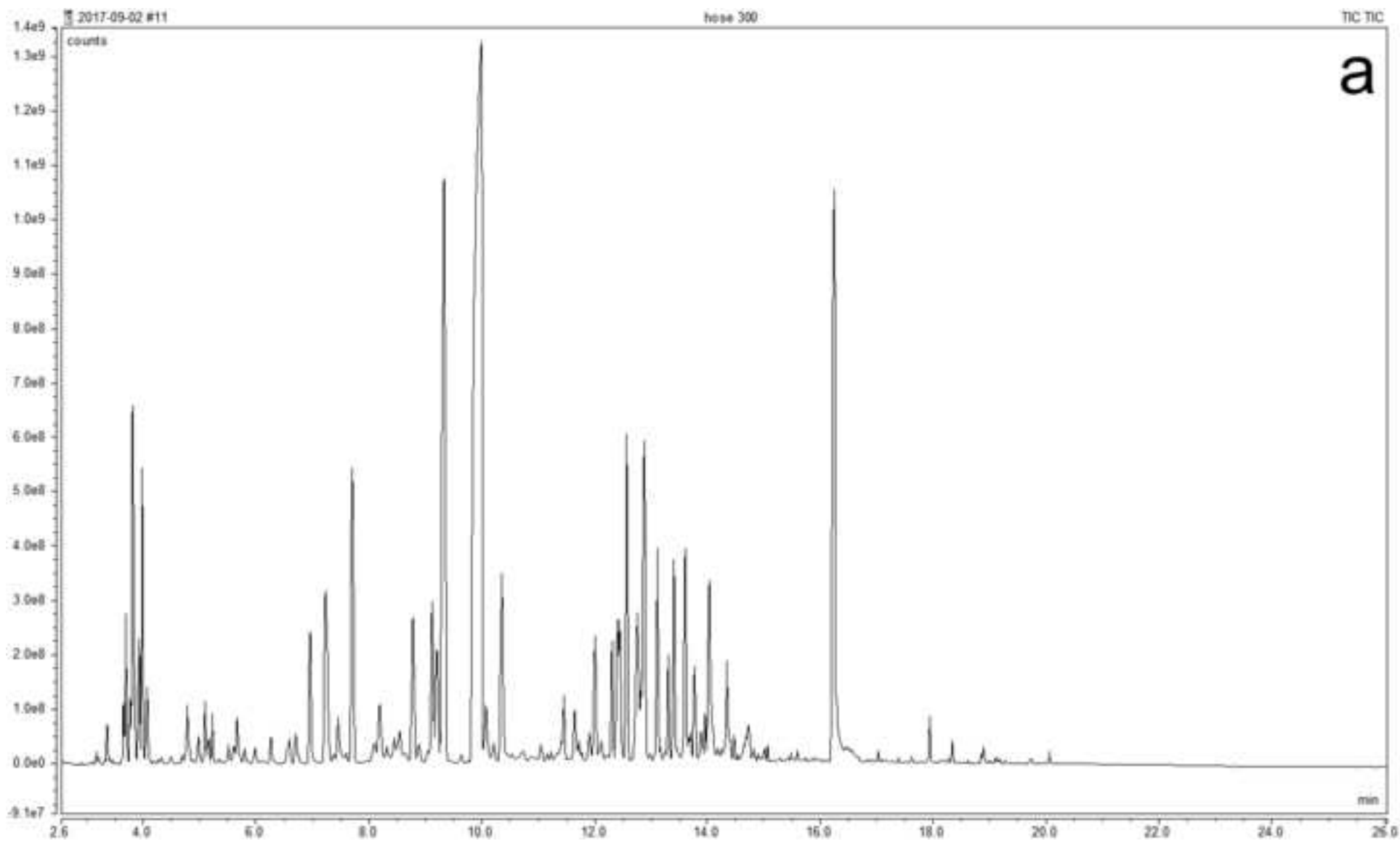


Figure 5b
[Click here to download high resolution image](#)

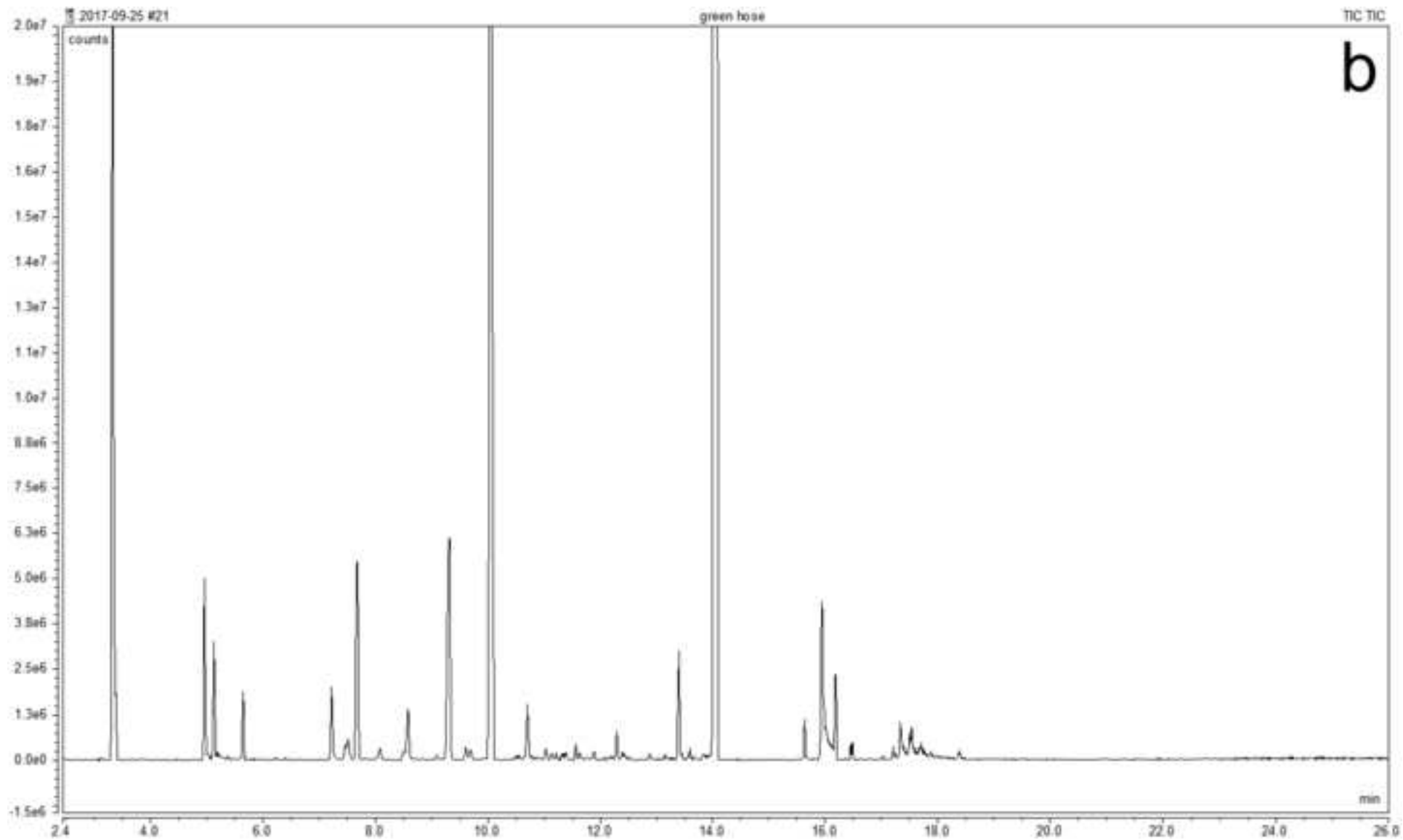


Figure 6
[Click here to download high resolution image](#)

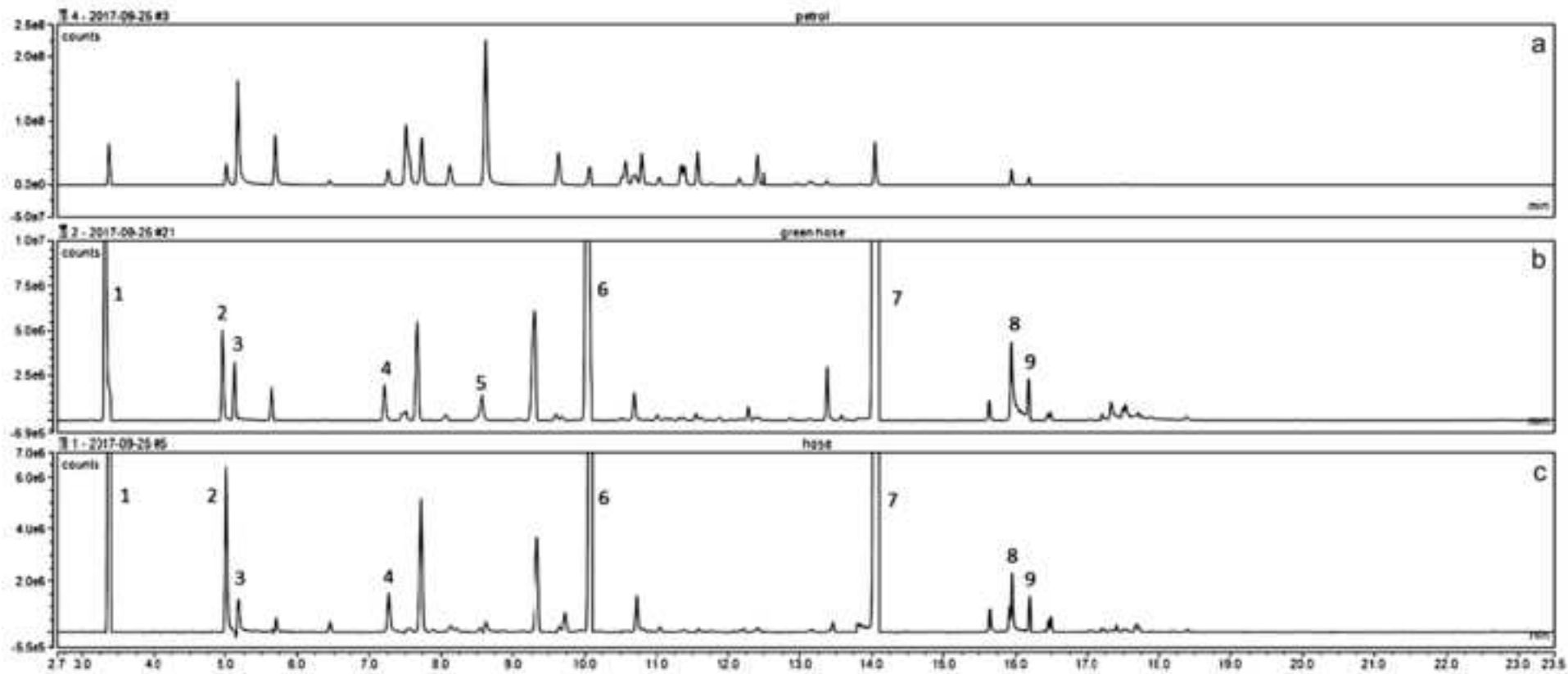


Table 1

Compound	Formula	Molecular weight	Compound	Formula	Molecular weight
<i>Alkanes</i>			<i>Aromatics</i>		
Octane	C ₈ H ₁₈	114	Toluene	C ₇ H ₈	92
Decane	C ₁₀ H ₂₂	142	o-Xylene	C ₈ H ₁₀	106
Dodecane	C ₁₂ H ₂₆	170	m-Xylene	C ₈ H ₁₀	106
Tetradecane	C ₁₄ H ₃₀	198	p-Xylene	C ₈ H ₁₀	106
Hexadecane	C ₁₆ H ₃₄	226	1-Ethyl-3-methylbenzene	C ₉ H ₁₂	120
Octadecane	C ₁₈ H ₃₈	254	1-Ethyl-4-methylbenzene	C ₉ H ₁₂	120
Eicosane	C ₂₀ H ₄₂	282	1-Ethyl-2-methylbenzene	C ₉ H ₁₂	120
			1,3,5-Trimethylbenzene	C ₉ H ₁₂	120
			1,2,4-Trimethylbenzene	C ₉ H ₁₂	120
			Naphthalene	C ₁₀ H ₈	128
			2-Methylnaphthalene	C ₁₁ H ₁₀	142

Table 2

Time (min)	Target compounds	Parent ion (m/z)	Collision energy (eV)	Product ions (m/z)
2.46	Toluene	91	30	30-200
3.4	C2-Benzenes	106	20	30-200
6.32	C3-Benzenes	120	20	30-200
9.88	Indane	117	30	30-200
10.1	C4-Benzenes	134	20	30-200
12.5	C5-benzenes	148	30	30-200
13.2	C6-Benzenes	162	10	30-200
13.79	Naphthalenes	128	20	30-200
14.1	C1-Naphthalenes	142	30	30-200
16.2	C2-Naphthalenes	156	30	30-200

Table 3

No.	Compound	RT (min)
1	Toluene	3.34
2	Ethylbenzene	5.01
3	m/p-Xylene	5.18
4	Propylbenzene	7.26
5	1,2,4-Trimethylbenzene	8.63
6	Indane	10.07
7	Naphthalene	14.02
8	1-Methylnaphthalene	15.95
9	2-Methylnaphthalene	16.18

Response to reviewer comments:

1) *When canine detection was first introduced to the world of fire investigation in 1982, the dogs were unfortunately called "accelerant detection canines." They are still called accelerant detection canines, but there has been a movement away from that terminology. The 2017 edition of NFPA 921 at 17.5.4.7 refers to "ignitable liquid detection canine/handler teams." It would be useful to encourage the more modern and less prejudicial name by at least inserting "(also known as ignitable liquid detection canines)".*

Change made to the text: 'accelerant detection' replaced with 'ignitable liquid detection' throughout.

2) *In the introduction, reference is made to the "inefficiency" resulting from false positives, to wit, "false responses are undesirable as they decrease the reliability of detector dogs, and in the case of false positive decrease efficiency and increase the cost of an investigation by requiring a confirmatory test." This leaves open the possibility that at some point we can just rely on the dog if we can only get them reliable enough. So far, including the results of this study, there is no evidence that a canine alert without a confirmatory test constitutes reliable evidence. The sentence should simply read "False responses are undesirable as they decrease reliability of detector dogs."*

Change made in the introduction as suggested.

3) *To suggest, as the authors do at page 4, that there is "no definitive answer to the question of why trained detector dogs will respond to a non-target (distractor) odour," overstates the complexity of the problem. The answer is almost certainly that the pyrolysis of some substances not associated with ignitable liquids produce exactly the same compounds that are found in ignitable liquids. This is why it will always be necessary to have a human interpret the significance of a finding the ILR components that triggered the alert by the canine.*

We disagree with "almost certainly". This is the hypothesis we were testing in this project, and there were alternative hypotheses available, as illustrated in this part of the introduction.

4) *In the Discussion on page 15, the authors advance the hypothesis that the high concentration of phthalates in PVC garden hoses may be responsible for the high concentration of aromatics in the pyrolyzate. It is actually well known that PVC itself through a process of side group scission results in the production of numerous aromatics including all of the aromatics identified in the garden hose sample. (See Stauffer, E, (2003) Concept of pyrolysis for fire debris analysts, Science and Justice, volume 43 number 1, 29-40.) In this reviewer's opinion, phthalates likely have nothing to do with the observation of the aromatics from the garden hose. Any PVC fuel, with or without phthalates, will produce those same aromatics. Stauffer's work on pyrolysis is a necessary reference in any discussion of pyrolysis products.*

We agree that PVC is a source of aromatic compounds from pyrolysis and have added the Stauffer reference to this part of the Discussion. However, there are publications which show that phthalates pyrolyse to produce these compounds, and we have also added a phthalate reference to this part of the discussion. The paragraph is re-worded to acknowledge both possibilities.

5) *A very minor point: The description of equipment suppliers was slightly jarring. Labnet International is in Edison, New Jersey, not in "New Jersey America." Likewise, Thermo Fisher Scientific has offices all over Australia. A little more specificity would be an improvement.*

Changes made in the Materials and Methods section to clarify equipment suppliers.

Authorship Statement

Douglas Leung: Methodology, Investigation, Validation

Shari Forbes: Conceptualization, Supervision, Writing – Review & editing

Philip Maynard: Methodology, Supervision, Writing – Original draft, Data curation