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University of Glasgow

Contextualising sooty soiling significance by fuel source for textile conservation

MPhil Dissertation

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Submitted in partial fulfilment of the requirements for the Degree of Master of Philosophy in Textile Conservation in the School of Culture and Creative Arts, University of Glasgow, 18th August 2016

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Abstract

Soot is a chemically complex compound which is not often studied in textile conservation. Whether to clean or not to clean depends on the social and historical evidence contained in soot against its harmful properties. This paper looks into the previous research carried out by textile conservators and their current treatment approaches. It investigates the significance of the source of soot on an object to a social historian. Finally, it collates published scientific research using various analytical techniques to identify the fuel source of the soot.

Most soot studies focus on car engines and atmospheric pollution. Valuable information pertinent to textiles can be gleaned from this data. Most of these being on diesel. Scientific analysis proved that pyrolysis products from lignin can be used to identify wood soot using GC/MS. DRIFTS has limited success in identifying the fuel source. The analysis identifies the presence of carboxylic groups in pure wood soot, but further studies on sooted textiles are needed.

Further study is needed investigating historically deposited soot. By using aged samples and looking at degradation of soot once deposited on a textile it would be possible to understand more fully the impact which soot has on a textile.

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LIST OF ABBREVIATIONS

Acronyms

AC	Aciniform Carbon
ATR	Attenuated Total Reflectance
BC	Black Carbon
СВ	Carbon Black
СТС	Centre for Textile Conservation
DEP	Diesel Exhaust Particulate
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EC	Elemental Carbon
FTIR	Fourier's Transformation Infer Red
GC/MS	Gas Chromatography/ Mass Spectroscopy
HPLC	High Performance Liquid Chromatography
HRGC	High Resolution Gas Chromatography
IRUG	Infrared and Raman User Group
NMR	Nuclear Magnetic Resonance
NO _x	Nitrogen Oxides
NPAH	Nitrated (Nitro) Polycyclic Aromatic Hydrocarbon
PCA	Principal Component Analysis
PCs	Principle Components
РАН	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter

RH Relative Humidity

- SEM Scanning Electron Microscope
- SOF Soluble Organic Fractions
- TCC Textile Conservation Centre
- TEM Transmission Election Microscope
- VOCs Volatile Organic Compounds

1 INTRODUCTION

Sooty soiling is a black grainy substance with a complex mixture of chemicals which readily deposits onto historical textiles see Figure 1. However, very little analysis has been carried out into the nature of historical soot. This is important to understand in order to help conservators decide whether the soot should be removed as harmful or retained as evidential.



Figure 1: Soot on textile:

Currently, the standard course of action for a sooty object is to clean it off with water or detergent, often noticing that the water from cleaning is acidic¹. That soot may hold key information regarding the significance and evidence of the social history of the object has not been substantially looked into. Some sources of soot may be more damaging to an object than others which may further aid decision making.

Soot deposited on an object from various sources such as coal, wood or peat fires could reveal relationships to the social class of the object's owner, the location or environment in which it was used and in the socio-economic uses of different fuels in different eras. This type of information, valuable to a social historian needs to be taken into consideration when making cleaning decisions.

¹ Ágnes Tímár-Balázsy and Dinah Eastop, *Chemical Principles for Textile Conservation* (Abingdon: Routledge, 2011). P158

Additionally to historical soot, soot from diesel (a fuel only used since 20th century) may indicate that modern air pollution is affecting our historic textiles; an issue for contemporary museum staff and the subject of many recent studies²³⁴.

The aim of the research presented here is to look into current knowledge about soot and sooty soiling within conservation and scientific fields. Using published articles and research sources to contextualise information useful to conservators as well as conservation scientists and social historians the paper will discuss whether different soot sources impacts on decisions regarding evidential soiling.

1.1 RESEARCH AIMS AND OBJECTIVES

This dissertation attempts to bring together material information about soot of potential relevance to textile conservation research of sooty soiling. Because soot is a complex material, the primary aim is to create a body of information as a basis for more in-depth future conservation research.

<u>Aims</u>

The four aims of the research are

- Identify the chemical compositions of different sources of soot for conservation research
- Propose theories for how soot chemicals may deposit onto textiles
- Evaluate how information regarding the combustion source of soot can inform social historians and museum staff
- Assess a method of chemical characterisation to detect surface deposits on textiles expected from sooty soiling

Objectives

The research was undertaken with the following objectives:

² Josep Grau-Bové et al., 'Simulation of Particulate Matter Ingress, Dispersion and Deposition in a Historical Building', *Journal of Cultural Heritage* 18 (March 2016): 199–208, doi:10.1016/j.culher.2015.08.006.

³ Helen Lloyd et al., 'The Effects of Visitor Activity on Dust in Historic Collections', in *Preventive Conservation in Museums*, ed. Chris Caple (Oxford: Routledge, 2011), 280–89.

⁴ Roman Kozłowski et al., 'Particle Sources and Deposition in the Indoor Environment of Historic Churches', in *1st International SEAHA Conference* (SEAHA, London: SEAHA, 2015).

- Literature review of current conservation understanding of sooty soiling sources
- Literature review of the social history of soot for an overview of sources
- Literature review of environmental science studies and related fields for chemical analysis and characterisation of soot.
- Spectroscopic analysis of model test samples of modern sooty soiling by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

When looking at the significance which can be gleaned from soot analysis, this research will demonstrate the history of various sources of soot. The social history focusses on British fuel sources. Because of regional fuel preferences, for example, France used much less coal in the home.

1.2 WHAT IS SOOT?

Soot is important to textile conservators as many historical items have some degree of sooty soiling and little is known about its chemistry. Soot can be hard to define and misidentification is possible. In one study, a church noticed an apparent increase in dust after insulation had been installed. The dust was actually soot which could no longer escape from incense and candles⁵. When people think of soot they normally think of a black grainy from of carbon. This is linked to a major component of soot light-absorbing carbonaceous aerosols known as Black Carbon.

1.3 WHAT IS MEANT BY SOOTY SOILING?

When soot is in contact with textile objects, it is not just Black Carbon particles that are deposited. Tars and oils from the combustion process are typically mixed in with the carbon and contribute up to 50% of the overall weight of sooty soiling⁶. These tar and oil compounds can be yellow, brown or black in colour⁷ and from a number of sources:

- Fuel droplets unchanged through the burning process,
- The condensation products of heavy hydrocarbons which have been formed

⁵ C.H. Huynh et al., 'Impact of Thermal Proofing of a Church on Its Indoor Air-Quality—the Combustion of Candles and Incense as a Source of Pollution', *Science of The Total Environment* 102 (1991): 241–51.

 ⁶ Joanne Hackett, 'Observations on Soot Removal from Textiles', in *Annual Meeting of the AIC (26)* (Textile Speciality Group Postprints, Washington D.C.: AIC. Textile Speciality Group, 1999). P63
 ⁷ B. S. Haynes and H. Gg. Wagner, 'Soot Formation', *Progress in Energy and Combustion Science* 7, no. 4 (1 January 1981): 229–73, doi:10.1016/0360-1285(81)90001-0. P230

• Soot particles which heavy hydrocarbons have condensed onto⁸.

In this dissertation, the mixture of carbonaceous compounds, tars and oils will be referred to as sooty soiling. As the research is aimed at informing conservators whether to clean the soot off a textile or not it is important to consider all the sooty soiling as one compound. One cannot clean the tars without the carbon and vice versa. To a conservator the choice to clean or not clean is taken for all the sooty soiling and not just part of it.

1.4 STUDIES CARRIED OUT BY CONSERVATORS

Research carried out by conservators regarding soot on historic objects has a main focus on cleaning textiles after fire or accidental damage⁹¹⁰¹¹. There have been numerous large fires in historic buildings over the last few decades upon which much of the research has focused.

There is a general theme in the conservation literature focusing on the oily nature of the soot rather than the carbonaceous which interests more scientific journals¹²¹³¹⁴. The oily nature of sooty soiling is a particular concern to conservators as it makes the soiling far harder to clean. A better understanding could lead to better cleaning techniques if removal is the chosen treatment for the soiling.

1.4.1 To clean or not to clean

Although cleaning removes potentially harmful soiling and improves the visual aspect significantly, the decision to clean or not to clean an object is often a difficult one to make. Unlike many conservation treatments, cleaning is irreversible so the decision to clean needs to be carefully considered¹⁵. In general, there are two situations when an object is not cleaned;

⁸ Ibid. P230

 ⁹ Sarah Spafford-Ricci and Fiona Graham, 'The Fire at the Royal Saskatchewan Museum, Part 2: Removal of Soot from Artifacts and Recovery of the Building', *Journal of the American Institute for Conservation* 39, no. 1 (1 January 2000): 37–56, doi:10.1179/019713600806113310.
 ¹⁰ Hackett, 'Observations on Soot Removal from Textiles'.

¹¹ Janice Grey Armstrong et al., 'A Furnace Puff-Back: The Unique Problem of Soot on Objects and Costume', in *Ninth Annual Meeting* (American Institute for Conservation of Historic and Artist Works, Philadelphia, Pennsylvania: AIC. Textile Speicality Group, 1981), 10–19.

¹² Spafford-Ricci and Graham, 'The Fire at the Royal Saskatchewan Museum, Part 2'.

¹³ Armstrong et al., 'A Furnace Puff-Back: The Unique Problem of Soot on Objects and Costume'.

¹⁴ Hackett, 'Observations on Soot Removal from Textiles'.

¹⁵ Dinah Eastop and Mary Brookes, 'To Clean or Not Clean: The Value of Soils and Creases', in *ICOM CC 11th Triennial Meeting 1-6 Sepember 1996 Preprint*, ed. Jane Bridgeland (Edinburgh: Lond: James and James Science Publishers Ltd, 1996). P687

- 1. If the object is too fragile to undergo a cleaning treatment,
- 2. If the soiling removed could be of evidential value¹⁶.

The decision for situation 1 is fairly straightforward and a trained conservator should be able to make a clear decision regarding the strength of the object, however, for situation 2 it is less clear. The concept of keeping soiling on an object as evidence is relatively new. In archaeology in particular, there has been a huge advancement of research through the analysis of the soiling on objects found as well as the object itself¹⁷.

One of the difficulties of deciding whether soiling is significant is predicting the future significance of soiling and improvements in analytical techniques. In some cases where the soiling is damaging to the object it is still not cleaned in order to preserve its 'true nature'¹⁸ meaning evidence of the object's origin, the original construction and materials and information on manufacture¹⁹.

Examples of this include retaining mud on a soldier's uniform from the battle of the Somme²⁰ or retaining the blood on a shirt from a commander for the UN Peacekeeping force in Cambodia²¹. In both instances the soiling is evidence of an event and plays a significant part in the object's history. By leaving the soiling in place there is also a possibility of future research being carried out.

It is interesting to note how different the opinions of conservators can be when it comes to the evidential value of soiling. In two journals, both with titles that begin with the question of 'to clean or not to clean' Eastop and Brookes' article looks in favour of retaining evidence even when this may be detrimental to the object²² whereas Windsor strongly

¹⁶ Ibid.

¹⁷ Vanessa Fell, 'Washing Away the Evidence', in *Archaeological Conservation and Its Consequences* (IIC Copenhagen Congress, Copenhagen: IIC, 1996), 48–51. P48

¹⁸ Eastop and Brookes, 'To Clean or Not Clean: The Value of Soils and Creases'. P689

¹⁹ Dinah Eastop, 'Conservation as Material Culture', in *Handbook of Material Culture*, ed. Chris Tilly et al. (London: Sage, 2006), 516–33. P517

²⁰ Ibid. P521

²¹ Sarah Clayton et al., 'Clear as Mud: How Cultural Significance Determines Preservation Choices', in *Tales in the Textile: The Conservation of Flags and Other Symbolic Textiles*, vol. 4 (North American Textile Conservation Conference, New York: North American Textile Conservation Conference, 2003), 23–30.

²² Eastop and Brookes, 'To Clean or Not Clean: The Value of Soils and Creases'.

believes that the object should be protected at all costs regardless of evidence value²³. These are wildly differing views considering the subject matter is almost identical. As the journals were written only a year apart this is not a change in view over time but possibly a divide across the Atlantic where the UK has a smaller, more intimate heritage sector²⁴ and the views of different specialisms can be shared. This means the value of soiling may be better understood.

1.4.2 Cleaning sooty soiling

In the situation of soot on textiles the decision to clean is almost always taken. This is the case for two reasons, the acidity of the soiling and the association with accidental fires.

When a sooty textile is wet cleaned, it typically causes a pH drop in the bath, creating an acidic condition which has to be carefully managed during treatment, such as when the University of Glasgow graduation gown was cleaned²⁵. However, as the measurement of pH is generally taken in the presence of water, it is not fully understood whether the sooty soiling becomes acidic due to its interaction with water and/or whether it has an inherent low pH. Acidity on a textile is harmful as this can cause hydrolysis under wet conditions which breaks down the polymeric chains in both cellulosic and proteinaceous textile fibres leading to degradation and strength loss²⁶.

Many textile conservators refer to a book called Chemical Principles of Textile Conservation²⁷. In this book black carbon (i.e. soot) is stated to attract and absorb acid and alkali agents which can lead to hydrolytic breakdown of the textile fibres and oxidation or reduction reactions²⁸. Unfortunately, these statements are not referenced and it is unclear what scientific research backs the statements up

²³ Deidre Windsor, 'To Clean or Not to Clean? Decision Making Fir Textile Wet CleanIng', in American Institute for Conservation 23rd Annial Meeting St Paul Minnisota (Textile Speciality Group Postprints, Minnesota: AIC. Textile Speicality Group, 1995), 39–51.

²⁴ Phyllis Dillon, 'A Comparison of British and American Conservation Services - Textile History - Volume 13, Issue 2', *Textile History* 13, no. 2 (2013): 144–50.

²⁵ Karen Thompson, SallyAnne Coupar, and Julie Benner, "Most I Saw Were Very Dirty, Some Very Ragged and All of Very Coarse Cloth": The Conservation of the Nineteenth-Century Student Gown in the Hunterian, University of Glasgow', in *Transactions of the Burgon Society*, vol. 12 (Burgon Society, 2012), 36–45, http://eprints.gla.ac.uk/91974/. P44

 ²⁶ Tímár-Balázsy and Eastop, *Chemical Principles for Textile Conservation*. P31, 46,47
 ²⁷ Ibid.

²⁸ Ibid. P158

Sooty soiling is often formed on textiles after the event of a fire. In these cases the significance of the soot is not deemed high and the intent to restore the objects to their pre fire condition is the main focus of treatment. Historical soot, although encountered frequently by conservators, is rarely written about in published work.

Joanne Hackett focused on the methods of cleaning not only at the Higley family fire on which the article was based but also looked at the cleaning methods used after previous fires elsewhere²⁹. The results proved cleaning soot off cotton was easier than wool and synthetics whilst vulcanised rubber sponging and solvent cleaning worked well at cleaning soot³⁰.

1.4.3 Museum environments

Today air pollution inside a museum is far lower than even 50 years ago when curators were known to smoke in their office³¹ and the 1850s when gas lighting was noted to be causing the rotting of leather bindings and armchairs in the Athenaeum Club³². Despite this, the effect of modern air pollution, such as diesel soot, in the museum environment is still being analysed today by University Collage London (UCL) among others^{33,34}.

Observation of the black insoluble particulates that remained after aqueous wet-cleaning of a 19th Century University of Glasgow graduation gown at the Centre for Textile Conservation (CTC)³⁵ initiated thoughts with Dr Anita Quye, CTC lecturer in Conservation Science, about the environmental and social history evidential value of sooty soiling ³⁶. This resulted in 'Dirty Stories', a collaborative scientific investigation with Dr Johannes Keiffer, a chemical engineer at the University of Aberdeen, to evaluate different spectroscopic methods to identify the presence of soot soiling and distinguish it from other soiling

²⁹ Hackett, 'Observations on Soot Removal from Textiles'.

³⁰ Ibid. P66

³¹ 'Minneapolis Institute of Arts Probes 60-Year "Disappearance", *Star Tribune*, accessed 9 August 2016, http://www.startribune.com/minneapolis-institute-of-arts-probes-60-year-disappearance/206801621/.

 ³² Norbert S. Baer and Paul N. Banks, 'Indoor Air Pollution: Effects on Cultural and Historic Materials', *International Journal of Museum Management and Curatorship* 4, no. 1 (1 March 1985): 9–20, doi:10.1016/0260-4779(85)90049-4. P9

³³ Ibid.

³⁴ Nigel Blades, Declan Kruppa, and May Cassar, 'Development of A Web-Based Software Tool for Predicting the Occurrence and Effect of Air Pollutants Inside Museum Buildings', UCL Discovery, 2002, 9–14.

³⁵ Thompson, Coupar, and Benner, "Most I Saw Were Very Dirty, Some Very Ragged and All of Very Coarse Cloth". P22

³⁶ Ibid.

sources, which was followed up in the MPhil dissertation project by CTC textile conservation student Nora Mellor in 2013³⁷.

1.4.4 Characterisation of soot on textiles

There are very few papers which have come out of the conservation field where the chemical composition and characterisation of soot has been analysed on textiles. To date the main body of work comes from 'Dirty Stories' and Nora Meller's dissertation research where she used multiple methods of analysis to characterise soot³⁸. Taking samples from historic textiles is not always possible, so the dissertation focussed on non-invasive analytical research. One of the findings which Nora found was that using simple methods of examination, using visual and tactile examination, stereomicroscopy and infrared photography could indicate of the presence of sooty soiling³⁹, although saying it was specifically soot was not straightforward. One hindrance was the lack of analytical references for known materials to compare unknown historic samples⁴⁰.

1.4.5 Soot deposition on historic objects

It is important to bear in mind that not all sooty soiling on historical textiles is historically significant of the original sources, and that 'contamination' from other soot sources is a high possibility. A case in point is the situation faced by the Museum of Stony Brook after the malfunction of a heat exchanger. The museum's conservators recorded how much soot deposited on all textile and packaging. Although reduced, the level of soot inside the wardrobes, boxes, and shelves still visible blackened the textile⁴¹. The article also noted that the position of the costumes had an effect on the amount and type of soot noting that larger agglomerates were deposited nearer the air vents⁴².

1.4.6 Analytical research on sooty soiling

Analytical research has been carried out by conservators however this is uncommon. When analytical research has been carried out, reasons for analysis and the success of the research have been variable. None of the existing research has looked into the historical importance of the soot as the focus is on fire damage. The source of soot was analysed at Royal Saskatchewan Museum in Regina, Canada after a fire in 1990. The purpose of this

³⁷ Nora Meller, 'A Preliminary Investigation into the Characterisation of Sooty Soilings on Historic Textiles' (University of Glasgow, 2013).

³⁸ Ibid.

³⁹ Ibid. P107

⁴⁰ Ibid. P107

 ⁴¹ Armstrong et al., 'A Furnace Puff-Back: The Unique Problem of Soot on Objects and Costume'. P15
 ⁴² Ibid.

analytical research was to determine the best method of cleaning the sooty soiling. FTIR analysis of soot samples found similar spectra for an oily substance in the soiling. These were identified as polyester from fiberglass resin and polyurethane from insulation foam⁴³, and both were combustion contamination.

The Museum of Stony Brook also traced the source of the sooty soiling but for a very different reason. As soot can be dispersed by airborne means, it embedded inside cupboards and boxes, and the museum faced challenges with the insurance company refusing to pay for the cleaning of packaged items. The research intended to prove that all the soot came from the same source. Analysis of the soot carried out was using transmitted light microscopy to identify visually the granular nature of soot. Gas Chromatography was applied to identify the fuel source but this could not be concluded⁴⁴.

1.5 OTHER RESEARCH ON SOOTY SOILING

Most conservation research of soot does not use analytical tools. Lachelin wrote her dissertation thesis at the Textile Conservation Centre (TCC) regarding the cleaning of fire damaged textiles⁴⁵. The research did not look into the source of the fire or the ethics of cleaning. Methods of cleaning researched were wide ranging from the more standard methods of surface, solvent and wet cleaning to the more advanced methods of ultrasonic, foam and laser cleaning⁴⁶.

In many cases of fire damaged textiles soot is not the only issue but also loss from heat damage. In the case of the fire at the Freemasons Centre in Clarkenwell, the affected banners were remade instead of conserved due to the amount of damaged caused⁴⁷.

1.6 The effect of soot of textiles

The effect of soot in the air and discolouration of textiles was noted by Robert Boyle in the early 19th Century who theorised that the presence of 'nitrous or salino-sulphureous

⁴³ Spafford-Ricci and Graham, 'The Fire at the Royal Saskatchewan Museum, Part 2'. P45

 ⁴⁴ Armstrong et al., 'A Furnace Puff-Back: The Unique Problem of Soot on Objects and Costume'. P16
 ⁴⁵ Christine Lachelin, 'Preliminary Investigation into the Problems of Removing Soot and Smoke
 Odour from Historic Textiles: Considerations for Conservation' (Courtauld Institute of Art, University of Art, London, 1996).

⁴⁶ Ibid. p22-25

⁴⁷ Ray Konyn, 'The Recovery of 130 Fire and Water Damaged Banners from the Freemasons Centre Clarkenwell: Part 1', in *Coping with Emergencies* (Post Prints of the Forum held at Victoria and Abert Museum, London: United Kingdom Institute for Conservation, 1995), 19–20. P20

spirits' were causing this fading and measuring the fading could be used to detect the presence of such atmospheric pollutants⁴⁸.

1.7 SOOT RESEARCH IN OTHER CONSERVATION FIELDS

Due to the higher value of paintings compared to other materials in need of conservation, the effect and cleaning methods of soot on paintings has been explored relatively more closely than other conservation fields.

In the past, preventive conservation treatments were applied to lime- based wall paintings to prevent soot settlement. This treatment involved covering the most significant parts of the painting with a water resistant wash so that the painting could be cleaned with a wet cloth. In the long run, the damp cloth solubilised the soot which was then attached to the water resistant wash leading to an even dirtier effect. This failure limited the amount to intrusive treatments carried out today⁴⁹.

Cleaning works of art can be expensive to carry out and in some cases not possible⁵⁰. For this reason, the effect the soot has visually on the image is an important factor in the decision to clean as well as the safety of the object. Research has been carried out into what level of soot is acceptable to viewers on a piece of art in order to determine if and when action is needed⁵¹

Stone is most susceptible to soot deposition, therefore many methods of cleaning soot, such as laser cleaning⁵², come from this field of conservation.

1.8 SUMMARY

There is a small body of researching which exists in conservation regarding characterising soot, however the main focus is on cleaning the soiling and preventing the deposition while in a museum's care rather than gaining evidence. Although sooty soiling is thought to

⁴⁸ Peter Brimblecombe, *The Big Smoke: A History of Air Pollution in London Since Medieval Times* (Abingdon: Routledge, 2011). P76

⁴⁹ Isabelle Brajer, 'Taking the Wrong Path: Learning from Oversights, Misconceptions, Failures and Mistakes in Conservation.', *CeROArt. Conservation, Exposition, Restauration d'Objets d'Art*, no. 3 (21 April 2009), http://ceroart.revues.org/1127?lang=en.

⁵⁰ Leon M. Bellan, Lynn G. Salmon, and Glen R. Cass, 'A Study on the Human Ability To Detect Soot Deposition onto Works of Art', *Environmental Science & Technology* 34, no. 10 (1 May 2000): 1946–52, doi:10.1021/es990769f. P1947

⁵¹ Ibid.

⁵² J.M Teule et al., 'Controlled Laser Cleaning of Fire-Damaged Paintings', in *13th Triennial Meeting Rio de Janeiro*, vol. 2 (ICOM Committee for Conservation, Rio de Janeiro: ICOM, 2002), 252–60.P252

be acidic in nature, if soiling can be used as a form of evidence of an event or how the object was used then this is may change the debate between to clean or not to clean. This decision cannot be made without scientific assessment and understanding of the significance it can bring to a social historian.

2 STUDIES CARRIED OUT BY SOCIAL HISTORIANS

2.1 HOW SOCIAL HISTORY RESEARCH IS CARRIED OUT

In order to get a well-rounded piece of research, social historians go beyond the written evidence as many of the voices are of the middle classes. The working class voices can be found though popular songs, poetry, cartoons and postcards⁵³⁵⁴⁵⁵

2.2 SOURCES OF HEAT

Before central heating, the home was a very sooty place, with coal fires in the 19th Century leading to high level of atmospheric pollution and leading to sooty deposits on decorations and soft furnishing in the home⁵⁶. Fuels were used not just for warming the home but also to cook. Since the fourteenth century, country house kitchens had large open fireplaces known to produce large amounts of smoke and soot when cooking meat⁵⁷ making the kitchen a very sooty environment.

The popularity of different sources of fuel has changed over the years making the significance of the fuel source vary depending on the object. In the 1500s, although sea coal⁵⁸ was imported into the UK, wood was still the most popular fuel source in the home. It was only when a shortage of wood occurred that coal became widely used. Coal was brought into the home in Scotland before England due the high wood fuel costs⁵⁹ and it was when James VI of Scotland or James I of England started using coal in his English Palaces that coal became fully accepted in England⁶⁰.

⁵³ Shelley Trower, *Place, Writing, and Voice in Oral History* (New York: Palgrave Macmillan, 2011). P1-17

 ⁵⁴ R. J. Shafer, A Guide to Historical Method (Homewood, Illinois: The Dorsey Press, 1974). p77-84
 ⁵⁵ Stephen Mosley, 'Common Ground: Integrating Social and Environmental History', Journal of Social History 39, no. 3 (2006): 915–933, doi:10.1353/jsh.2006.0007. P922

⁵⁶ Judith Miller, *Period Fireplaces: A Practical Guide to Period-Style Decorating* (Hong Kong: Reed International Books, 1995). P9-10

⁵⁷ Mark Girourd, *Life in the English Country House* (London: Yale University, 1978). P37

 ⁵⁸ James G. Speight, *Handbook of Coal Analysis*, Second Edition (Hoboken, New Jersey: Wiley, 2015).
 P3

⁵⁹ Brimblecombe, *The Big Smoke: A History of Air Pollution in London Since Medieval Times*. P22 ⁶⁰ Ibid. P30

By the Victorian era coal was the most popular source in the home and also used in the kitchen range for cooking⁶¹. Some sources suggest that the soot produced from coal had become synonymous with a warm, affluent and welcoming home⁶² while other sources suggest 'belching out smoke soon made the owner unpopular'⁶³.

2.2.1 Peat fires

In rural areas such as the Scottish highlands and Islands, peat was used as a source of heat where wood was scarce⁶⁴.

In the traditional black houses of the Isle of Lewis, an open peat fire was in the centre of the home, with the smoke having to escape through the cracks in the thatched roof leaving a very soot environment⁶⁵⁶⁶. This practice continued on islands such as Lewis until the early 20th Century⁶⁷.

2.3 SOURCES OF LIGHT

The use of combustion sources for light has existed since ancient times. In ancient Greece castor oil and salt was used⁶⁸ and the use of a candle with a fibre wick was used in Egypt and Crete 3,000 BC.⁶⁹ The type of lighting used has often been seen as a status symbol⁷⁰.

2.3.1 Candle light

From the candle's invention to the early 19th Century, it was the most common form of artificial light^{71,72}. Good wax candles were expensive and therefore only used by the rich⁷³, with beeswax producing the least smoke or smell and providing the brightest light⁷⁴.

⁶¹ Miller, Period Fireplaces: A Practical Guide to Period-Style Decorating. P67

 ⁶² Brimblecombe, *The Big Smoke: A History of Air Pollution in London Since Medieval Times*. P92
 ⁶³ Lorna Hepburn, *The Tenement House*, ed. Helen MacDougall (Scotland: The National Trust for Scotland, 2015). P10

⁶⁴ Kenneth Macdonald, *Peat Fire Memories: Life in Lewis in the Early Twentieth Century* (East Lothian: The National Museums of Scotland, 2003). P1-2

⁶⁵ Calum Smith, Around the Peat Fire (Edinburgh: Birlinn, 2010). P1-3

⁶⁶ Macdonald, Peat Fire Memories: Life in Lewis in the Early Twentieth Century. P6

⁶⁷ Smith, Around the Peat Fire. Pxi

 ⁶⁸ Jonathan Bourne and Vanessa Brett, Lighting in the Domestic Interior (London: Sotheby's, 1991).
 P12

⁶⁹ Ibid. P16

⁷⁰ Country House Lighting (Leeds: Leeds City Art Galleries, 1992). P5

⁷¹ Bourne and Brett, *Lighting in the Domestic Interior*. P16

⁷² Joakim Pagels et al., 'Chemical Composition and Mass Emission Factors of Candle Smoke Particles', *Aerosol Science* 40 (2009),

http://www.sciencedirect.com/science/article/pii/S0021850208001894. P320

⁷³ Bourne and Brett, Lighting in the Domestic Interior. P8

⁷⁴ Ibid. P16

Alternatives such as oil lamps, tallow candles and rushlights were known to be smoky and smelly⁷⁵.

As both wax and tallows candles were expensive there was a desire to produce a cheaper material. In the 18th century the answer was Spermaceti, made of the recovered oil from the head cavities of a sperm whale. This was only marginally cheaper and in the 19th century paraffin wax which is formed from the distillation of petroleum⁷⁶ was introduced and became popular⁷⁷.

As we know the dates when these forms of candles were introduced, the identification of soot could be used to date an object.

Tallow could be made out of different animal fats which had different burning properties. Mutton was known to be the cleanest burning, with pig fat only being occasionally burnt due to the black smoke produced⁷⁸. As tallow burned at half the temperature of beeswax, the candles were known to burn quickly, sometimes faster than the cotton wick⁷⁹

The amount and type of candle apparatus in paintings gives us a good indication of the social standing of the painted subject⁸⁰. Nitrous Oxide pollution from candle soot is noted to be a problem in churches⁸¹ and the black soot is known to stain walls, paintings and sculptures and tapestries^{82,83,84,85}.

2.3.2 Rushlights

Rushlights were produced using a rush stalk and excess fat from cooking and in the middle ages were used by all walks of man⁸⁶. They were used where rushes were commonly

⁷⁵ Ibid. P8

⁷⁶ John. S. Mills and Raymond White, *The Organic Chemistry of Museum Objects*, 3rd Edition (Abingdon: Routledge, 2011). P42

⁷⁷ Country House Lighting. P5

⁷⁸ Bourne and Brett, *Lighting in the Domestic Interior*. P8

⁷⁹ Country House Lighting.P5

⁸⁰ Bourne and Brett, *Lighting in the Domestic Interior*. pP8

⁸¹ Velichka Kontozova et al., 'X-Ray Spectroscopy for Preventive Conservation of Cultural Heritage', *ISEAC* 35, no. 50 (2008): 43–44. P44

 ⁸² Pagels et al., 'Chemical Composition and Mass Emission Factors of Candle Smoke Particles'. p193
 ⁸³ H. G. M. Edwards and C.J. Broke, 'Raman Spectroscopic Study of Post-Medieval Wall Paint in Need of Conservation', *Bioanalytical Chemistry* 383 (2005): 312–321.P320

⁸⁴ C.H. Huynh et al., 'Impact of Thermal Proofing of a Church on Its Indoor Air-Quality—the Combustion of Candles and Incense as a Source of Pollution', *Science of The Total Environment* 102 (1991): 241–251. P245

 ⁸⁵ Rull F. Perez, H. G. M. Edwards, and L. Dummond, 'Fourier Transform Raman Spectroscopic Characterization of Pigments in the Mediaeval Frescoes at Convento de L Peregrina, Sahagun, Leon, Spain. Part 1', *Journal of Raman Spectroscopy* 30, no. 4 (1999): 301–305. P303
 ⁸⁶ John Caspall, *Ma*

found, for instance in Ockley in Surrey and parts of Wales⁸⁷in working class homes and occasionally in country houses during the 18th Century⁸⁸. This means that identification of Rushlight soot could narrow down where an object came from. Although the homemade approach to rushlights made them a working class staple, when the poor could not afford meat, there was not enough fat for candles. This meant during times of extreme poverty more expensive candles had to be bought⁸⁹.

2.3.3 Oil light

In the UK, oil was mainly burnt using cruise lamps. They were used mainly in cottages rather than country houses and often burnt fish oil⁹⁰

king Fire and Light in the Home Pre-1820, 3rd ed (Suffolk: Antique Collectors Club /ltd, 1995). P171 ⁸⁷ Bourne and Brett, Lighting in the Domestic Interior. P18

⁸⁸ Country House Lighting. P5

⁸⁹ Bourne and Brett, *Lighting in the Domestic Interior*.

⁹⁰ Caspall, Making Fire and Light in the Home Pre-1820. P207

Type of fuel	Advantage	Disadvantage	
Beeswax candle	Bright light, little smoke or	Cost three time as much as	
	smell	tallow in 18 th century	
Paraffin	Cheap alternative to wax or	Not invented until 19 th	
	tallow, bright light	century	
Spermaceti	Cheaper than wax candles	Not much cheaper then	
		tallow	
Mutton tallow	Best performing form of	Tallow burns quickly and	
	tallow	smells	
Beef tallow	Cheaper than mutton	Tallow burns quickly and	
		smells	
Pig tallow	Cheapest form of tallow	Created smelly black	
		smoke, burns quickly	
Rushlight	Cheap, possible to home	Feeble light produced	
	make		

Table 1: Comparison of lighting fuel types⁹¹⁹²

2.3.4 Introduction of gas light

Natural Gas is made from coal and was originally considered a waste product manufactured in the gas works⁹³. Gas lights were first installed into the home by William Murdoch in 1792⁹⁴. Until this point, the fireplace had been the strongest source of light⁹⁵. Gas lighting became popular globally, with a writer noting in 1872 'there is not a city of any size in the civilised world which does not have gas light'⁹⁶. In Victorian Scotland the tenements were lit using gas lights, often from pendant lamps^{97,98}, with newer houses in the 1920s also being fitted with gas lighting⁹⁹.

⁹¹ Bourne and Brett, Lighting in the Domestic Interior. P16

⁹² Country House Lighting.

⁹³ Raphael Meldola, *Coal and What We Get from It; A Romance of Applied Science* (London: Society for Promoting Christian Kowledge, 1891). P38

⁹⁴ 'History of Gas Light in Brief.', *The London Reader : Of Literature, Science, Art and General Information* 19, no. 475 (8 June 1872): 143–143.

⁹⁵ Bourne and Brett, Lighting in the Domestic Interior. P8

⁹⁶ 'History of Gas Light in Brief.'

⁹⁷ Frank Worsdall, The Tenement: A Way of Life (Edinburgh: W & R Chambers, 1979). P39

⁹⁸ Hepburn, *The Tenement House*.

⁹⁹ Worsdall, The Tenement: A Way of Life. P131

Gas was also used for cooking, which is where the saying 'now we are cooking on gas' meaning being efficient comes from¹⁰⁰. It was invented in the 19th century and become popular in the 20th century with the invention of town gas¹⁰¹.

Gas light was found to be a highly polluting form of light, producing sulphuric acid, sulphurous acid, and carbonic acid¹⁰². For this reason, gas lighting was never installed at the National Gallery in London¹⁰³.

2.3.5 The use of artificial lights

Due to the cost of candles in the 18th and 19th century, when a family in a country home was alone very few candles were burnt¹⁰⁴, this meant that little candle soot would deposit on their everyday clothes and non-entertaining rooms. The opposite was true when these families had guests¹⁰⁵. This suggests that the ball rooms and fancy clothes are far more likely to have candle soot present on them.

2.4 SOURCES OF ENERGY

The invention of the car led to a new source of soot in the atmosphere which plagues many museums to this day.

From here there are two main types of diesel soot, engine soot which never travels beyond the engine and exhaust soot which is expelled from the engine¹⁰⁶. Diesel fuel is also often used in the formation of Carbon Black, however, due to the differences in burning in a vehicle engine and a highly controlled manufacturing furnace the chemical composition of the soot is different¹⁰⁷. Petroleum, from here on to be referred to as petrol, is another form of fuel for car engines.

¹⁰⁰ 'Cooking with Gas - Wiktionary', accessed 9 August 2016,

https://en.wiktionary.org/wiki/cooking_with_gas.

¹⁰¹ Miller, Period Fireplaces: A Practical Guide to Period-Style Decorating. P67

¹⁰² David Saunders, 'Pollution and the National Gallery', *National Gallery Technical Bulletin* 21 (2000): 1–19.

¹⁰³ Ibid.

¹⁰⁴ Country House Lighting. P6

¹⁰⁵ Ibid.

 ¹⁰⁶ A. D. H Clague et al., 'A Comparison of Diesel Engine Soot with Carbon black', *Carbon* 37, no. 10 (1999): 1553–1565, doi:10.1016/S0008-6223(99)00035-4. P1553

¹⁰⁷ Ibid. P1564

2.5 How social history affects conservation

As previously discussed, the 'true nature' of an object is an important part of the conservator's decision on how it is treated¹⁰⁸. Much of the true nature is to do with the value of the object to a social historian. The interaction in the decision making between scientists, social historians and conservators is shown in Figure 2.



Figure 2: Decision making process for cleaning soiling

Deciding what is significant on an object can differ depending on the institution to which it belongs¹⁰⁹. In a social history museum, evidence of use can be deemed important whereas a design focused museum requires objects to look as new wherever possible. This demonstrates the true importance of the social historian in the collaboration with a conservator.

The carcinogenic effect of PAHs was only discovered through the observation that Chimney sweeps had a high rate of lung, bladder, skin and scrotum cancer than the general population¹¹⁰.

¹⁰⁸ Dinah Eastop, 'Decision Making on Conservation: Determining the Role of Artefacts (1998)', in *Changing Views of Textile Conservation*, ed. Mary Brookes and Dinah Eastop (Los Angeles: Getty Conservation Institute, 2011), 277–83. P277

¹⁰⁹ Ibid. p280

¹¹⁰ B.J. Alloway and D.C. Ayres, *Chemical Principles of Environmental Pollution* (Glasgow: Blackie Academic and Professional, 1993). P207

2.6 NON CHEMICAL RESEARCH INTO SOOT

It is not just the chemical nature of the soot which can inform a social historian. The placement of furniture in a room relative to a fireplace is something which has changed over time and with social standing. This position would change the level and location of the soot deposition. From the early 19th century, English country houses started to place their furniture by the fire instead of push up against the wall¹¹¹. This would have led to more soot deposition on the upholstery.

2.7 SUMMARY

Multidisciplinary research is not new and has been used successfully in many cases. There is cultural significance in the types of fuels people used, particularly in the type of candle light used. This of interest to a social historian and the possibility for scientists to uncover this information could greatly inform others regarding the history of an object.

As the role of a conservator is to negotiate with historians and curators to ensure that evidential soiling is retained as part of the object's history, the significance to a social historian is directly linked to the conservator's design to clean or not to clean.

¹¹¹ Freya Gabbutt, 'In What Ways Did the Decoration and Furnishing of Early Nineteenth Century Country Homes Respond to Changes in Social Conventions.' (University of St Andrew, 2010). P2

3 SCIENTIFIC STUDIES OF SOOT

The focus on analysing soot tends to be linked with looking into the health implications of the soot in the atmosphere or the effect soot particles have on climate change¹¹². For this reason, there is a focus on taking air samples rather than samples from objects where soot has deposited. When environmental scientists are researching soot sources in terms of climate change, the research has a focus on how much light the soot particles absorb and what changes this level¹¹³

Soot particles, in their most basic form, are made up of Organic Carbon (OC), elemental Carbon (EC) and Carbonate (see Appendix 1: Glossary for more detail) but EC particles are the only ones which appear black in colour¹¹⁴. BC is considered to be generally inert, however the combustion process from which it is formed in soot means organic matter such as Poly Aromatic Hydrocarbons (PAH) are particle bound¹¹⁵

BC is often confused with Carbon Black (CB) and compared in Table 2. Unlike soot, Carbon Black has industrial uses in inks, paints and tyres¹¹⁶ consisting almost entirely of Elemental Carbon (EC) with an Aciniform Carbon (AC) morphology. Soot is made up of a varying

¹¹² Eric J. Jensen and Owen. B. Toon, 'The Potential Impact of Soot Particles from Aircraft Exhaust on Cirrus Clouds', *Geophysical Research Letters* 24, no. 3 (1 February 1997): 249–52, doi:10.1029/96GL03235.

 ¹¹³ E. Weingartner et al., 'Absorption of Light by Soot Particles: Determination of the Absorption
 Coefficient by Means of Aethalometers', *Journal of Aerosol Science*, Intercomparison of Soot
 Measurement Techniques, 34, no. 10 (October 2003): 1445–63, doi:10.1016/S0021-8502(03)00359 8.

¹¹⁴ E. Weingartner et al., 'Absorption of Light by Soot Particles: Determination of the Absorption Coefficient by Means of Aethalometers', *Journal of Aerosol Science*, Intercomparison of Soot Measurement Techniques, 34, no. 10 (October 2003): 1445–1463, doi:10.1016/S0021-8502(03)00359-8. P1445

¹¹⁵ Laura E. LaRosa, Timothy J. Buckley, and Lance A. Wallace, 'Real-Time Indoor and Outdoor Measurements of Black Carbon in an Occupied House: An Examination of Sources', *Journal of the Air* & Waste Management Association 52, no. 1 (1 January 2002): 41–49, doi:10.1080/10473289.2002.10470758. P41

¹¹⁶ Christopher M. Long, Marc A. Nascarella, and Peter A. Valberg, 'Carbon Black vs. Black Carbon and Other Airborne Materials Containing Elemental Carbon: Physical and Chemical Distinctions', *Environmental Pollution* 181 (October 2013): 271–86, doi:10.1016/j.envpol.2013.06.009.

degree of Aciniform Carbon and the fuel source is thought to make a difference to the quantity¹¹⁷¹¹⁸.

Carbon type	Elemental Carbon	Source material	Production method
Carbon black	>97%	Acetylene, natural	Commercially
		gas,	manufactured for
		coal-tar residues,	tyres, paints and
		petroleum oil	inks
Soot from air sample	<50%	Fuel oil, gasoline	Incomplete
containing black		fuel, diesel	combustion
carbon		fuel, coal, coal-tar	
		pitch, wood, paper	

Table 2: Types of carbon particles and their characteristics¹¹⁹

It is important to understand the difference between BC and CB as they are often confused with each other, however the chemistry of the two is very different. The research will only look into BC as the focus of the research is the uncontrolled formation of soot.

3.1.1 Formation of soot

Soot only appears black at room temperature. At high heat soot particles appear yellow, without soot, the flames are generally blue in colour instead of yellow¹²⁰. Although the chemical composition of soot can differ depending on many variables the temperature in which soot luminance appears is always the same at ~1600K¹²¹. In car engines the internal combustion engine creates soot through fuel and compression.

Units of soot particles are spherical with a diameter of 200-300Å which will be referred to as elementary soot particles¹²². Elementary soot particles aggregate to form straight and branched chains which are visible under an electron microscope¹²³ as seen in Figure 3. The

¹¹⁷ Ibid. P271

¹¹⁸ Avrom I. Medalia, Donald Rivin, and Daniel R. Sanders, 'A Comparison of Carbon Black with Soot', *Science of The Total Environment* 31, no. 1 (1 October 1983): 1–22, doi:10.1016/0048-9697(83)90053-0.P2

¹¹⁹ Long, Nascarella, and Valberg, 'Carbon Black vs. Black Carbon and Other Airborne Materials Containing Elemental Carbon'.

¹²⁰ Christopher. R. Shaddix and Timothy C. Williams, 'Soot:Glver and Taker of Light', *American Science* 95 (2007): 232–239. P232

¹²¹ Mark S. Solum et al., '13C NMR Analysis of Soot Produced from Model Compounds and a Coal', *Energy & Fuels* 15, no. 4 (1 July 2001): 961–971, doi:10.1021/ef0100294. P963
¹²² Haynes and Wagner, 'Soot Formation'. P230

agglomerated soot particles are a defining feature of identifying soot which can be used in identification under electron magnification.



Agglomerated soot particles

Primary Soot Particle

Figure 3: Example of primary soot particle

The exact chemical composition of the soot which is formed is dependent on many variables including the fuel source of the incomplete combustion, however, reading literature from the 1980s it is clear that this has not always been known¹²⁴.

3.1.2 Health effects of soot

Polycyclic Aromatic Hydrocarbons (PAHs) are made up of carbon and hydrogen molecules which are not generally damaging to objects, however there are many links to PAHs being carcinogenetic and or mutagenic in humans when inhaled¹²⁵. For conservators, the soot particles could become suspended in the air when agitated through any cleaning process and breathed in.

When the focus is on health, the size of the particulate matter is important as it determines how far into the lungs the particles deposit. This has led many health based journals to document the size and shape of soot particles using electron microscopic

 ¹²⁴ M. M. Hirschler, 'Soot From Fires: I. Properties and Methods of Investigation', *Journal of Fire Sciences* 3, no. 5 (9 January 1985): 1, doi:10.1177/073490418500300505. P343
 ¹²⁵ Daekyun Kim et al., 'Environmental Aging of Polycyclic Aromatic Hydrocarbons on Soot and Its Effect on Source Identification', *Chemosphere* 76, no. 8 (August 2009): 1075–81, doi:10.1016/j.chemosphere.2009.04.031.
techniques such as SEM and TEM. If the size of the particles is different depending on the fuel source then this could be used as an identification tool.

3.1.3 Polycyclic Aromatic Hydrocarbons

Research has been carried out to determine the type of PAHs in soot. Health scientists are interested in studying the effects of PAHs and how they degrade due to their carcinogenic and mutagenic effects when inhaled. For conservation the health implications affect the personal protection equipment needed for the conservator when cleaning sooty soiling but does not in itself lead to damage on the textile objects.

In general there is Naphthalene, acenaphthylene, acenaphthene, pyrene and fluorene¹²⁶.

Figure 4: Chemical structure of Fluorene

PAHs degradation has been a focus of numerous studies about the health implications of breathing in soot to determine if aged soot is less carcinogenic/mutagenic. Studies have found that the molecules are broken down through interactions with UV¹²⁷. Whilst this is good for human health, the resulting compounds may or may not be more damaging to a textile. This should be looked at in future investigations for textile conservation.

3.1.4 Nitrated polycyclic aromatic hydrocarbons

Some PAHS have Nitrogen groups attached to the structure and are known as nitrated polycyclic aromatic hydrocarbons (NPAH). The majority of which are insoluble in water but are soluble in solvents, with non-polar solvents leading to faster degradation of itself¹²⁸. This suggests unless the NPAH has already degraded to release the NO₂ nitric acid will not be formed with water.

¹²⁶ Ibid. P1075

 ¹²⁷ F. Valerio and A. Lazzarotto, 'Photochemical Degradation of Polycyclic Aromatic Hydrocarbons (PAH) in Real and Laboratory Conditions', *International Journal of Environmental Analytical Chemistry* 23, no. 1–2 (1 November 1985): 135–51, doi:10.1080/03067318508076440.
 ¹²⁸ Gernerique Stewart et al., 'Photochemical Reaction of Nitro-Polycyclic Aromatic Hydrocarbons: Effect by Solvent and Structure', *Environmental Chemistry Letters* 8, no. 4 (22 April 2009): 301–6, doi:10.1007/s10311-009-0221-2. P304

Photolysis is a major degradation pathway for the nitrofluoranthenes and nitropyrenes¹²⁹. The result of the degradation includes the creation of NO₂ which is known to degrade PAHs so this may be a chain reaction¹³⁰. The exact chemicals which result from degradation of the PAH and NPAH is often not stated in scientific journals, presumably because the carcinogenic and mutagenic risk is low. But for research of soot on historic objects the chemistry of degraded PAH is significant. As both NPAHs and PAHs can break down over time the chemical components on historic objects may not be the same as originating source, which current research is based on.

3.1.5 Heavy metals

Unlike organic compounds in soot, heavy metals such as zinc, iron and copper in soot from London smog¹³¹ and diesel soot¹³² will remain intact for hundreds of years¹³³. Heavy metals are often catalysts for photo-oxidation which leads to degradation of textiles fibres¹³⁴ and warrants further study of sooty soiling.

3.1.6 Morphology

Scientific research does not just focus on the chemical composition of soot, but also the size and shape of the primary soot particles¹³⁵. The temperature of the flame the soot is derived from determines the shape in which the soot forms¹³⁶. As shown in Figure 5 and Figure 6. This is interesting to textile conservation as it may determine the fuel source by microscopy.

 ¹²⁹ Anders Feilberg and Torben Neilsen, 'Effect of Aerosol Chemical Composition on the Photodegradation of Nitro-Polycyclic Aromatic Hydrocarbons - Environmental Science & Technology (ACS Publications)', *Environmental Science & Technology* 34, no. 5 (2000): 789–97. P789
 ¹³⁰ 'Factors Which Influence Polycyclic Aromatic Hydrocarbon Decomposition on Wood Smoke Particles', accessed 12 July 2016,

http://www.sciencedirect.com/science/article/pii/0160412085900066.

¹³¹ Andy Whittaker et al., 'Killer Smog of London, 50 Years on: Particle Properties and Oxidative Capacity', *Science of The Total Environment*, Highway and Urban Pollution, 334–335 (1 December 2004): 435–45, doi:10.1016/j.scitotenv.2004.047. P443

¹³² Clague et al., 'A Comparison of Diesel Engine Soot with Carbon Black'. P1555

¹³³ Alloway and Ayres, *Chemical Principles of Environmental Pollution*. P153

 ¹³⁴ Tímár-Balázsy and Eastop, Chemical Principles for Textile Conservation. P89
 ¹³⁵ Artur Braun et al., 'Size-Range Analysis of Diesel Soot with Ultra-Small Angle X-Ray Scattering',

Combustion and Flame 137, no. 1–2 (April 2004): 63–72, doi:10.1016/j.combustflame.2004.01.003. ¹³⁶ Solum et al., '13C NMR Analysis of Soot Produced from Model Compounds and a Coal'. P271



Figure 5: Diesel Soot under SEM ©MacCrone Atlas¹³⁷ Figure 6: Oil Soot under SEM ©MacCrone Atlas¹³⁸

For example research has shown that Diesel Exhaust Particulate (DEP) is known for having Aciniform aggregates of carbon black which other types of soot do not¹³⁹. This is important in identifying diesel soot. As diesel soot is a modern fuel the significance of its presence is low and therefore should be cleaned. The presence of diesel soot also suggests the object has been, or is being, subjected to air pollution and the storage or display solution may need rethinking to protect the object.

There is research into the effect of temperature on the chemical structure of soot particularly focusing on when aromatic hydrocarbon convert to PAH¹⁴⁰. Although the reasons for the scientific research are broad ranging and different from conservation factors, the data that is created and information researched is of high value to conservation in providing reference material.

Investigations that have looked into the amount and type of carbon in carbon black and different soot samples from various sources¹⁴¹¹⁴² show a clear difference in terms of elemental carbon versus organic carbon. However, between types of soot the results are

¹³⁷ 'McCrone Atlas of Microscopic Particles', accessed 28 July 2016,

http://www.mccroneatlas.com/viewer/index.asp?MODE=PA2&TECHNIQUE_ID=16&PARTICLE_ID=1 051&F_IS_BIREFRINGENT=%5F&F_KEYWORD=diesel&F_PARTICLE_NUMBER=&F_IS_HIGH_INDEX=% 5F&F_SAMPLE_NAME=%20&F_TYPE_ID=&F_BINARY_CODE1=%3F%3F&F_BINARY_CODE2=%3F%3F %3F%3F%3F%3F&F_SHAPE=&F_IS_OPAQUE=%5F&F_IS_COLORED=%5F&F_IS_FLAT=%5F&F_IS_ELO NGATED=%5F&F_SEARCH=Search.

¹³⁸ Ibid.

¹³⁹ Long, Nascarella, and Valberg, 'Carbon Black vs. Black Carbon and Other Airborne Materials Containing Elemental Carbon'. P271

 ¹⁴⁰ Solum et al., '13C NMR Analysis of Soot Produced from Model Compounds and a Coal'.
 ¹⁴¹ Long, Nascarella, and Valberg, 'Carbon Black vs. Black Carbon and Other Airborne Materials Containing Elemental Carbon'.

¹⁴² Medalia, Rivin, and Sanders, 'A Comparison of Carbon Black with Soot'.

too similar to be able to determine the source from this data alone. The size and shape is a more likely source of recognising the fuel source with biomass soot showing to be significantly larger in particle size, which could be most useful to textile conservation research.

3.1.7 Carbon porosity

One form of carbon in soot is in an activated state. Activated carbon is used as a filter in many applications such as removing heavy metals and dyes from waste water¹⁴³ as well as drinking water and air purification^{144,145,146}. In the case of activated carbons and graphite the absorption of other chemicals is through the porosity of the carbon¹⁴⁷. The porosity is created through voids or pores in the carbon structure as seen in Figure 7.



Figure 7: Activated carbon particle¹⁴⁸

¹⁴³ K Kadirvelu et al., 'Utilization of Various Agricultural Wastes for Activated Carbon Preparation and Application for the Removal of Dyes and Metal Ions from Aqueous Solutions', *Bioresource Technology* 87, no. 1 (March 2003): 129–32, doi:10.1016/S0960-8524(02)00201-8.

¹⁴⁴ T. Otowa, Y. Nojima, and T. Miyazaki, 'Development of KOH Activated High Surface Area Carbon and Its Application to Drinking Water Purification', *Carbon* 35, no. 9 (1 January 1997): 1315–19, doi:10.1016/S0008-6223(97)00076-6.

¹⁴⁵ B. Tryba, A. W. Morawski, and M. Inagaki, 'Application of TiO2-Mounted Activated Carbon to the Removal of Phenol from Water', *Applied Catalysis B: Environmental* 41, no. 4 (31 March 2003): 427–33, doi:10.1016/S0926-3373(02)00173-X.

 ¹⁴⁶ C. Brasquet and P. Le Cloirec, 'Adsorption onto Activated Carbon Fibres: Application to Water and Air Treatments', *Carbon* 35, no. 9 (1 January 1997): 1307–13, doi:10.1016/S0008-6223(97)00079-1.
 ¹⁴⁷ Brian McEnaney and Timothy J. Mays, 'Porosity in Carbons and Graphite's', in *Introduction to Carbon Science*, by Harry Marsh (London: Butterworths, 1989). P154

¹⁴⁸ Bruch Dvorak and Sharon Skipton, 'Drinking Water Treatment: Activated Carbon Filtration', Nebraska Extension, accessed 13 August 2016,

http://extensionpublications.unl.edu/assets/html/g1489/build/g1489.htm.

Soot has a relatively low level of elemental carbon, leading many researchers to deem soot is not porous¹⁴⁹, but very little is actually known about the surface area of soot. Studies are now investigating the porosity of soot which leads to other chemicals being absorbed into the soot^{150 151}. This is important to look into as the porosity could potentially lead to the absorption of polychlorinated biphenyls, and other VOCs such as chlorinated compounds¹⁵². The potential damaging effects on historic objects including textiles has yet to be examined but it is possible that acidic compounds could be absorbed and lead to acid hydrolysis with the textile.

It is not known whether the porous carbon attracts chemicals during the burning process or if other chemicals are attracted to the soot after deposition onto an object. If the carbon is porous whilst still on a textile then information could potentially be obtained regarding historic air pollution regardless of heat.

As there are a large number of variables with soot, further study would be needed in order to determine how porous the soot which deposits on historical textiles are and the pollutants which are absorbed. The absorbed pollutants may be a useful piece of evidence for the history of the object. If there turns out to be large quantities of these contained in the soot, then cleaning would be the best course of action for a sooty textile.

High temperatures can lead to soot particles being more ordered and the morphology more closely resembling graphite. Although the ordering process is not deemed reversible, it is understood that aged soot is more crystalline¹⁵³ and has less hydrogen because the carbon changes from an organic to an elemental state¹⁵⁴. The implication for historic objects is that the soot could be more crystalline in nature and not correlate with newer reference samples. If soot is analysed to have very little order it could suggest that the soot is a new addition which could be of interest to the object's history.

¹⁴⁹ Angelo W. Kandas et al., 'Soot Surface Area Evolution during Air Oxidation as Evaluated by Small Angle X-Ray Scattering and CO2 Adsorption', *Carbon* 43, no. 2 (2005): 241–51, doi:10.1016/j.carbon.2004.08.028. P242

¹⁵⁰ Ibid.

¹⁵¹ Karl J Rockne, Gary L Taghon, and David S Kosson, 'Pore Structure of Soot Deposits from Several Combustion Sources', *Chemosphere* 41, no. 8 (October 2000): 1125–35, doi:10.1016/S0045-6535(00)00040-0.

¹⁵² Ibid. 1133

¹⁵³ Haynes and Wagner, 'Soot Formation'. P232

¹⁵⁴ Ibid.

3.2 LIMITATIONS OF RESEARCH

3.2.1 Soot distribution

Once soot is formed in the atmosphere the direction and distance travelled is determined by many factors. There is also a different composition of soot depending on the distance the soot is collected or deposited from the fuel source as some constituents of the soot will not travel as far. For this reason, the results of the chemical composition may be affected depending on the location of the object in relation to the where the soot was generated.

For example, the chemical composition of diesel soot in the engine and the exhaust pipe. The soot that has travelled to the exhaust pipe is lower in Carbon content and higher in sulphur, phosphorus, iron, calcium and zinc¹⁵⁵.

3.3.1 Historical environments

Black sulphurous-smelling rain was recorded repeatedly in the 19th century in areas of low local fuel consumption¹⁵⁶. The cause was hundreds of kilometres away, with airstreams transporting soot from industrial areas¹⁵⁷. Terms such as 'moorgrime' were used in Yorkshire and Lancashire where soot coated the sheep on the moors¹⁵⁸. These show how soot affected everyone in the past and its source may not always be obvious. Thus analytical research for textile conservation may be able to identify the chemical composition of a sooty soiling, but pinpointing the source may prove too difficult because of the number of variables.

3.3 SUMMARY

Although the reason for the scientific research is broad ranging and different from conservation factors, the data that is created and information researched is of value to conservation in providing reference material, although only selectively.

Soot has some level of porosity to it which could absorb pollutants either evidential or damaging. Further research is needed to determine whether to clean or not to clean. As

¹⁵⁵ Clague et al., 'A Comparison of Diesel Engine Soot with Carbon black'. P1654
¹⁵⁶ Peter Brimblecombe, Trevor Davies, and Martyn Tranter, 'Nineteenth Century Black Scottish Showers', *Atmospheric Environment (1967)* 20, no. 5 (1 January 1986): 1053–57, doi:10.1016/0004-6981(86)90292-1. P1053
¹⁵⁷ Ibid.
¹⁵⁸ Ibid. P1057

the size of the particles is different depending on the fuel source this could be used as an identification tool however more research is needed.

Soot research is generally not carried out in historical samples. NPAHs and PAHs can break down over time meaning the chemical components on historic objects may not be the same as originating source. Heavy metals are often catalysts for photo-oxidation which leads to degradation of textiles fibres¹⁵⁹ and warrants further study for sooty soiling.

The implication for historic objects is that the soot could be more crystalline in nature and not correlate with newer reference samples. If soot is analysed to have very little order it could suggested that the soot is a new addition which could be of interest to the object's history. To see if there are any indicators to identify the fuel source in the long term, the chemical composition must be researched in more detail.

¹⁵⁹ Tímár-Balázsy and Eastop, Chemical Principles for Textile Conservation. P89

4 CHEMICAL COMPOSITIONS OF SOOT

4.1 DIFFERENT SOURCES OF SOOT

Category	Fuel	Chemical composition				
Source of	Coal	Mainly- carbon				
heat		Small proportions- silicon dioxide, calcium oxide and				
		magnesium oxide, sulphates ¹⁶⁰				
	wood	Mainly- lignin, cellulose, hemicellulose				
		Small proportion- resins, fatty acids, alcohols, phenols ¹⁶¹				
	Peat	Mainly- carboxyl and phenolic hydroxyl groups				
		Small proportions- fatty acids waxes, carbohydrates, terpene				
		and nitrogen ¹⁶²				
Sources	Beeswax	Mainly- alkanes, alkenes, free fatty acids, monoesters, diesters				
of light		and hydroxymonoesters				
		Small proportions- fatty alcohols and hydroxydiesters ¹⁶³				
	Tallow	Fatty acids, triglycerides				
	Spermaceti	Mainly- cetyl palmitate				
		Small proportion- esters of other fatty acids, including lauric,				
		myristic and stearic ¹⁶⁴				
	Paraffin	Saturated hydrocarbons ranging from $C_{21}H_{44-}C_{57}H_{116}^{165}$. Very				
		pure.				
	Natural gas	Methane, ethane, propane ¹⁶⁶				

¹⁶⁰ Stanislav V. Vassilev, Kunihiro Kitano, and Christina G. Vassileva, 'Some Relationships between Coal Rank and Chemical and Mineral Composition', *Fuel* 75, no. 13 (1 October 1996): 1537–42, doi:10.1016/0016-2361(96)00116-0. P1538

 ¹⁶¹ B. L. Browning, *Methods of Wood Chemistry* (New York: Interscience Publishers, 1967). P9
 ¹⁶² Mall Orru, Monika Übner, and Hans Orru, 'Chemical Properties of Peat in Three Peatlands with Balneological Potential in Estonia', *Estonian Journal of Earth Sciences* 60, no. 1 (2011): 43–49. P46-7

¹⁶³ H.R. Hepburn, C.W.W. Pirk, and O. Duangphakdee, *Honeybee Nests: Composition, Structure, Function* (London: Springer Berlin Heidelberg, 2014). P12

¹⁶⁴ M. Wellendorf, 'Composition of Spermaceti', *Nature* 198, no. 4885 (15 June 1963): 1086–87, doi:10.1038/1981086b0.

¹⁶⁵ George L. Clark and Howard A. Smit, 'X-Ray Diffraction Study of Fractionated Paraffin Waxes', *Industrial & Engineering Chemistry* 23, no. 6 (1 June 1931): 697–701, doi:10.1021/ie50258a025. P701

¹⁶⁶ J. D. Naber et al., 'Effects of Natural Gas Composition on Ignition Delay under Diesel Conditions', *Combustion and Flame* 99, no. 2 (1 November 1994): 192–200, doi:10.1016/0010-2180(94)90122-8. P192

Category	Fuel	Chemical composition
Source of	Diesel	Aliphatic hydrocarbons $C_{10}H_{22} - C_{19}H_{40}$ (paraffin), aromatic
energy		hydrocarbons, polycyclic aromatic hydrocarbons, alkanoic
		acids, olefins, sulphur, nitrogen ¹⁶⁷
	Petrol	Aliphatic hydrocarbons (paraffin), aromatic hydrocarbons,
		polycyclic aromatic hydrocarbons, olefins, sulphur ¹⁶⁸

Table 3: Chemical composition of different fuel sources

4.1.1 Sources of heat

Coal is a sedimentary rock made up mainly of carbon, hydrogen, sulphur, nitrogen and oxygen in varying ratios along with some mineral matter^{169,170}. It is made from ancient plant and woody matter which has decomposed under pressure and heat to form coal seams, which are layers in sedimentary rock that can be between a few centimetres to hundreds of meters thick¹⁷¹. When coal is burnt it has a heat value of between 5,000 and 15,000 BTU/lb.

The composition of coal varies considerably. There are 4 broad categories of the fuel. Each category is formed from the last. The process is called coalification¹⁷².

- 1. Lignite,
- 2. Sub-bituminous coal,
- 3. Bituminous coal, and
- 4. Anthracite¹⁷³.

¹⁶⁹ Bruce G. Miller, 'The Chemical and Physical Characteristics of Coal', in *Clean Coal Engineering Technology* (Boston: Butterworth-Heinemann, 2011), 53–68,

¹⁶⁷ Fuyan Liang et al., 'The Organic Composition of Diesel Particulate Matter, Diesel Fuel and Engine Oil of a Non-Road Diesel Generator', *Journal of Environmental Monitoring* 7, no. 10 (2005): 983–88. P985

¹⁶⁸ James G. Speight, *The Chemistry and Technology of Petroleum* (New York: Marcel Dekker, 1980). P425

http://www.sciencedirect.com/science/article/pii/B9781856177108000029. P53

¹⁷⁰ Speight, Handbook of Coal Analysis. P1

¹⁷¹ Ibid. P1-2

¹⁷² Miller, 'The Chemical and Physical Characteristics of Coal'. P56

¹⁷³ Speight, Handbook of Coal Analysis. P2

Peat is found in swamps, fens, bogs and moors¹⁷⁴. Different types of wetlands produce different types of peat¹⁷⁵. To some, peat is considered as a precursor to coal¹⁷⁶. Similar to coal, it is formed in stagnant water with microbial action breaking down organic plant matter. However, no pressure is applied making a more soil like substance which new plant matter can grow through^{177,178}. The relationship between peat and coal can be defined in far more complex terms which can be found in literature such as Moore and Shearer¹⁷⁹.

Although wood, peat and coal have the same origin, they have different relative carbon content as seen in Table 4.

Fuel	Carbon %	Hydrogen %	Oxygen %	Nitrogen %
Wood	50	6.25	42.75	1
Peat	57	5.15	36.85	1
Lignite	65	4	30	1
Sub-bituminous coal	79	5.45	14	1.55
Bituminous coal	91	4.5	2.2	1.6
Anthracite	97	0.6	1.8	0.6

Table 4: Chemical changes during coalification¹⁸⁰

Wood is made up of lignin which is a polymer primarily made up of units of coniferyl alcohol shown in Figure 8¹⁸¹. In peat and coal this structure is broken down.

¹⁷⁴ Fredrick J. Rich, 'Peat; Its Origins, Characteristics and Transformations', in *Coal and Peat Fires: A Global Perspective*, ed. Glenn B. Stracher, Anupma Prakash, and Guillermo Rein (Amsterdam: Elsevier, 2015), 14–39. p14-15

¹⁷⁵ Ibid.

¹⁷⁶ Speight, Handbook of Coal Analysis. P3

¹⁷⁷ Miller, 'The Chemical and Physical Characteristics of Coal'. P53

¹⁷⁸ Rich, 'Peat; Its Origins, Characteristics and Transformations'. P14

¹⁷⁹ T. A. Moore and J. C. Shearer, 'Peat/coal Type and Depositional Environment—are They Related?', *International Journal of Coal Geology* 56, no. 3–4 (December 2003): 233–52,

doi:10.1016/S0166-5162(03)00114-9.

¹⁸⁰ Wilfred Francis, *Coal : Its Formation and Composition*, 2nd Edition (London: Edward Arnold, 1961). P441

¹⁸¹ Mills and White, The Organic Chemistry of Museum Objects. P69

Figure 8: Chemical structure of coniferyl alcohol

Tars from wood can be identified by the presences of methyldehydroabietate, norabietatrienes, 1,2,3,4-tetrahydroretene and retene¹⁸².

4.1.2 Sources of light

A candle burns from a fat or wax which is taken up on a wick. Waxes are generally made up of long chain hydrocarbons and alcohols¹⁸³. Waxes are generally very chemically stable as the majority of components are fully saturated¹⁸⁴.

Beeswax is found to have very little chemical variation, with the same hydrocarbons, free acids and esters making identification relatively simple¹⁸⁵.

Animal fats (tallow) are chemically a type of lipid made up of fatty acids and triglycerides¹⁸⁶. As there are double bonds in many of the fatty acids the boiling point is lower in tallow candles compared to wax¹⁸⁷. The fatty acid composition is different for each type of fatty acid which can be determined using gas chromatography¹⁸⁸.

The yellow light from candles is formed from soot oxidation. All soot formed can be oxidised, but this is not always the case and is dependent on many factors such as the flame flickering¹⁸⁹.

Candle soot is found to be low in PAH and VOC compared to other combustion sources¹⁹⁰.

¹⁸² Ibid. P54

¹⁸³ Ibid. P41

¹⁸⁴ Ibid. P41

¹⁸⁵ Ibid.P41

¹⁸⁶ Ibid. P26

¹⁸⁷ Ibid. P28

¹⁸⁸ Ibid. P28

¹⁸⁹ Pagels et al., 'Chemical Composition and Mass Emission Factors of Candle Smoke Particles'.P321

¹⁹⁰ Ibid. P321

4.1.3 Sources of energy

The amount of sulphur present in diesel soot has dramatically decreased over the years to produce a cleaner fuel¹⁹¹. In diesel, pentane, toluene and xylene are known to survive unreacted through the car engine and ending up in the sooty soiling mix¹⁹². More journals, however, focus on these solvents due to the health implication of breathing in the vapour whilst in the atmosphere.

4.2 METHODOLOGIES FOR ANALYSING SOOT

There are many different types of analysis which have been carried out on soot each with their different specialisms. These can be broadly broken down into the following

- Carbon Hydrogen Nitrogen (CHN) analysis
- Infrared Spectroscopy
- Chromatography with Mass Spectrometry

4.2.1 CHN analysis

CHN Analysers can be used to determine the quantity of carbon, hydrogen and nitrogen in a substance. The equipment has been used to look into the amount of elemental carbon in different types of soot, but indistinguishable results make CHN inappropriate for analysing the source of soot as seen in Table 5.

 ¹⁹¹ Teh C. Ho, 'Deep HDS of Diesel Fuel: Chemistry and Catalysis', *Catalysis Today*, International Symposium on Advances in Hydroprocessing of Oil Fractions (ISAHOF 2004), 98, no. 1–2 (24 November 2004): 3–18, doi:10.1016/j.cattod.2004.07.048. P3
 ¹⁹² Peter Brimblecombe, *Air Composition and Chemistry* (Cambridge: Cambridge University Press, 1986). P95

	Carbon	Diesel	Gasoline	Biomass	Woodstove
	Black				
Total	97-99	50-90	63%	50-70	28-62
Carbon (%)					
Elemental	>97	33-90	25-42	8-10	1-79
Carbon					
Organic	1-2	7-49	44-76	40-71	10-59
Carbon					
H/C ratio	<1	1-5	3-5	<10	<6

Table 5: Results of Carbon, Hydrogen and Nitrogen analysis¹⁹³

Although the results are different depending on the soot source the results could overlap making the elemental carbon result an inappropriate method for analysing the source of soot.

4.2.2 Chromatography with Mass spectrometry

With soot being a complex chemical mixture, it is common for analytical studies to involve chromatography to separate out the different compounds, typically with gas chromatography¹⁹⁴. Mass spectrometry is often used to detect and identify the molecular composition of the separated compounds, especially for PAHs and NPAHs as seen in Table 6 and Table 7. The disadvantage of chromatography with mass spectrometry for analysing historic objects is that it is a destructive process with a sample needing to be removed from the object, this may not always be possible due to the position of the soiling. However, for the detailed chemical information that cannot be gained by non-invasive methods, this kind of destructive analysis is essential. For example, soot from two types of wood – hardwood and pine – contains a range of pyrogallol compounds, with syringol being common to both, but the woods can be distinguished by the significantly higher levels in pine wood of the aromatic compound guaiacol derived from wood creosote ^{182 183}. As syingol and guaiacol are both pyrolysis products from lignin in wood, their presence in historical soot would be a good indicator of this source for soot.

¹⁹³ Long, Nascarella, and Valberg, 'Carbon Black vs. Black Carbon and Other Airborne Materials Containing Elemental Carbon'. P276

¹⁹⁴ 'Bristol University - Gas Chromatography Mass Spectrometry (GC/MS)', accessed 10 August 2016, http://www.bris.ac.uk/nerclsmsf/techniques/gcms.html.

Analysis	GC/MS
Material	Coal soot
Pyrene	1
Phenanthrene, tetramethyl-	0.62
Chrysene, monomethyl-	0.54
Naphthalene, 2-phenyl-	0.51
Anthracene/phenanthrene, monomethyl-	0.5

Table 6: GC/MS peak intensity for PAHs in coal soot¹⁹⁵

soot sample	Diesel soot
PYR	140 (pg m⁻₃)
PHE	66 (pg m⁻₃)
PAH (5,5)	<4.6 (µg g⁻¹)
РАН (3,6)	282 (μg g ⁻¹)
PAH (3,4)	282 (μg g ⁻¹)
Nitro-PAH (3,4)	432 (pg m⁻₃)
Nirto-PAH (3,6)	455 (pg m⁻₃)

Table 7: HPLC results for Diesel cars¹⁹⁶

¹⁹⁵ Shaokai Gao et al., 'A Comparison between the Vacuum Ultraviolet Photoionization Time-of-Flight Mass Spectra and the GC/MS Total Ion Chromatograms of Polycyclic Aromatic Hydrocarbons Contained in Coal Soot and Multi-Component PAH Particles', *International Journal of Mass Spectrometry* 274, no. 1–3 (15 July 2008): 64–69, doi:10.1016/j.ijms.2008.05.003. P67

¹⁹⁶ Christian Schauer, Reinhard Niessner, and Ulrich Pöschl, 'Analysis of Nitrated Polycyclic Aromatic Hydrocarbons by Liquid Chromatography with Fluorescence and Mass Spectrometry Detection: Air Particulate Matter, Soot, and Reaction Product Studies', *Analytical and Bioanalytical Chemistry* 378, no. 3 (24 December 2003): 725–36, doi:10.1007/s00216-003-2449-1.

Although Mass spectrometry is a detailed analytical tool, results from different studies of the same sample can be difficult to compare if the research questions are different, as exemplified by studies of diesel car soot^{197,198}. There is currently little research into the different sources of soot to compare like with like. The different forms of chromatography and the bias towards the study of diesel soot means there is not a sufficient conclusion to make from existing data for the questions asked about historical textiles.

4.2.3 Infra-red spectroscopy

Before combustion, many infra-red spectra for different types of candles are very similar¹⁹⁹. This would make it hard, without further analysis, to determine which type of candle was being identified. Unfortunately, the spectra for tallow was not available. If there is any unburnt material deposited onto a textile to form a greasy layer the peaks in Table 8 should be visible.

Material	Spectral peaks					
Beeswax	2917	2850	1742	1468	1178	727
Spermaceti	2914	2846	1731	1461		
Paraffin	2913	2844	1460	729		

Table 8: Spectra peak of different candle waxes²⁰⁰

The peaks around 2900 cm⁻¹ are Alkane C-H₂ Stretching while the peaks around 1730-1740 cm⁻¹ are Ketone C=O Stretching. As Paraffin is a purer fuel the ketone is not present.

Material	Spectral peaks (cm ⁻¹)					
Wood tar	Wave No.	2972	2912	1690	1455	
Coal Tar	Wave No.	2920	1595	1454	811	749

Table 9: Infrared spectra of tar resins²⁰¹

In Table 9 the peaks at 1455 and 1454 are unsaturated C=C bonds.

database?spectra_front_form_filter%5Bkeyword%5D%5Btext%5D=&spectra_front_form_filter%5B data_type%5D=infrared&spectra_front_form_filter%5Bmaterial_class%5D=.

¹⁹⁷ Ibid.

¹⁹⁸ Gao et al., 'A Comparison between the Vacuum Ultraviolet Photoionization Time-of-Flight Mass Spectra and the GC/MS Total Ion Chromatograms of Polycyclic Aromatic Hydrocarbons Contained in Coal Soot and Multi-Component PAH Particles'.

¹⁹⁹ 'Search IRUG Spectral Database | IRUG', accessed 18 July 2016, http://www.irug.org/search-spectral-

²⁰⁰ Ibid.

²⁰¹ Ibid.

Environmental studies with IR focus on gases²⁰²²⁰³ and these gaseous molecules may not be deposited on textiles, thus limiting the use of published data for textile conservation research. When Nora Meller analysed historic sooty soiling using ATR FTIR she found that the results when analysed on a smoke sponge were not clear but were more useful when analysing the soiling collected after solvent cleaning with IDA²⁰⁴.

4.2.3.1 Reasons to apply DIRFTS

Currently DRIFTS analysis has been not been carried out on sooty textiles. However there are a number of reasons that indicate it could be a useful technique to employ.

Infrared spectroscopy is a non-destructive technique which can be used on a historic object without damaging the object by taking a sample. This is a unique concern to conservation which does not apply to the majority of soot studies which have been carried out.

4.1 SUMMARY

Although many studies have been previously carried out in soot regarding the chemical composition and it is widely understood that the source of the soot affects the chemistry of the end product, very little research has come out of the conservation field. In the environmental science field, much of the soot samples are ambient air, and mixtures of different soot sources as well as gases which would not deposit onto a textile. This is the same for health-based studies. Much research has been made of car fuel emissions, so the analytical techniques target diesel or gasoline derived soot. This means it is not possible to compare the results which other fuel sources, particularly in the case of PAHs and NPAHs. As Diesel is a more polluting fuel than gasoline there has been more research which looks into diesel soot than gasoline soot. Because the aim of such is to improve the combustion or filtration of the fuel to ensure the amount of inorganic compounds is limited, it is not comparing the results and therefore many comparisons do not exist.

In the case of all the main research fields, how the soot changes over time, through the presence of light and humidity is not looked at. For a historic item with historic soot the

²⁰² Lei Tian et al., 'Nanosized Carbon Particles from Natural Gas Soot', *Chemistry of Materials* 21, no.
13 (2009.): 2803–9.

²⁰³ E. M. Fitzpatrick et al., 'Emission of Oxygenated Species from the Combustion of Pine Wood and Its Relation to Soot Formation', *Process Safety and Environmental Protection* 85, no. 5 (2007): 430–40, doi:10.1205/psep07020.

²⁰⁴ Meller, 'A Preliminary Investigation into the Characterisation of Sooty Soilings on Historic Textiles'. P76

chemical composition of soot may have changed considerably over time. UV for instance can peak down PAHs and NPAHs to an unknown degree and the results may not match the new samples created.

5 DRIFTS

5.1 WHAT IS DRIFTS?

Since Meller's investigation using a range of non-invasive spectroscopic analytical techniques to historical soot, there has been an FTIR advancement with DRIFTS (also known as Diffuse FTIR) including the use of DRIFTS to detect residues on historical textiles²⁰⁵ and pigments of dye²⁰⁶.

In this scenario DRIFTS was applied to and evaluated for a select number of unaged soot from selected known sources to see if source-specific components based on Chapter 4 could be detected or not. The outcome was evaluated in the context of informing its viability in future textile conservation studies.

FTIR is commonly used for analysing cultural heritage in situ due to the versatility of the technique²⁰⁷. Advances in recent years have resulted in attenuated total reflectance FTIR spectroscopy which allows in-situ surface analysis and which has been widely applied by many heritage scientists^{208,209}.

Different energies of radiation cause atomic and molecular effects in materials. This is useful for chemical analysis. One form of radiation is infrared (IR), with wavelengths of 4000cm⁻¹-400cm⁻¹210. The energy of this radiation causes bonds between atoms to move, through vibration, stretching and rotation, this phenomenon is applied in material analysis

²⁰⁵ Moe Sato, 'An Experimental Evaluation of Non-Ionic Surfactant Dehypon LS54' (University of Glasgow, 2014).

²⁰⁶ Julie Wertz, 'Unravelling 19th Century Turkey Red Textiles: Approaches for Heritage Science Through Historical Re-Creation and Chemical Analysis', in *2nd International Conference on Science and Engineering in Arts, Heritage and Archaeology* (SEAHA, Oxford: SEAHA, 2016).

²⁰⁷ Iker Arrizabalago et al., 'Applicability of a Diffuse Reflectance Infrared Fourier Transform Handheld Spectrometer to Perform in Situ Analyses on Cultural Heritage Materials', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, no. 129 (2014): 259–67. P260

²⁰⁸ Iker Arrizabalaga et al., 'Determination of the Pigments Present in a Wallpaper of the Middle Nineteenth Century: The Combination of Mid-Diffuse Reflectance and Far Infrared Spectroscopies', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 124 (24 April 2014): 308–14, doi:10.1016/j.saa.2014.01.017.

²⁰⁹ Grazia Accardo et al., 'Diffuse Reflectance Infrared Fourier Transform Spectroscopy for the Determination of Asbestos Species in Bulk Building Materials', *Materials* 7, no. 1 (16 January 2014): 457–70, doi:10.3390/ma7010457.

²¹⁰ Brian Smith, *Infrared Spectral Interpretation: A Systematic Approach* (New York: CRC Press, 1999). P6

as the technique called Fourier transform infrared spectroscopy (FTIR). In surface analysis applications of FTIR, IR radiation that interacts with the material is absorbed, reflected or scattered. Due to this, there are different types of FTIR, as shown in Figure 9;

- total reflectance
- Attenuated Total Reflectance (ATR) (Internal Reflectance)
- Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy, is often referred to a Diffuse FTIR²¹¹ (external reflectance)

Reflectance can be sub divided into internal and external reflectance measurements²¹².

Figure 9: Types of FTIR

The results of DRIFTS provide similar spectra to ATR FTIR, which is relatively common in heritage science laboratories. However there is more detail, particularly in the lower frequency end of the spectra²¹³. The reason for this is the increased depth of penetration which leads to more clear information regarding the nature of the compounds²¹⁴. Diffuse reflectance penetrates 7µm compared to 2µm for ATR, and is known to be particularly accurate with sampling powders and fibres²¹⁵.

DRIFTS has previously been used at the Centre for Textile Conservation (CTC) by Moe Sato in order to compare the chemical and physical properties of cotton and wool fibres before

²¹¹ Arrizabalaga et al., 'Determination of the Pigments Present in a Wallpaper of the Middle Nineteenth Century'. P309

²¹² Barbara Stuart, *Infrared Spectroscopy: Fundamentals and Applications* (New York: Wiley, 2004).P33

 ²¹³ Arrizabalago et al., 'Applicability of a Diffuse Reflectance Infrared Fourier Transform Handheld
 Spectrometer to Perform in Situ Analyses on Cultural Heritage Materials'.
 ²¹⁴ Ibid.

²¹⁵ Stuart, Infrared Spectroscopy: Fundamentals and Applications. P176

and after wet cleaning²¹⁶. Results showed surfactant residues were detected on surfaces of both cotton and wool after a wet cleaning treatment²¹⁷.

5.1.1 Limitations of DRIFTS

Although DRIFTS has an advantage of being able to detect highly absorbing chemicals the resulting spectra can only narrow down the results to the types of bonds present. Gas Chromatography/Mass Spectroscopy (GC/MS) is one of the most comprehensive tools to analyse organic materials which gives the size of the molecule and not just the functional groups²¹⁸.

The results only show an analysis of the surface of the object. If the soot granules are too large the analysis will not look inside the agglomerate.

Correlation of spectra between ATR-FTIR and DRIFTS is difficult because the ATR will have a bias towards the higher wavelengths and will therefore not show as much detail in the lower wavelengths compared to DRIFTS, as seen in Figure 10. As the depth of penetration is different this also affects the results. With DRIFTS, if the surface being analysed is less that 7µm thick then the layer below will also be analysed, which would not happen in ATR. However, on the thicker surfaces DRIFTS can provide stronger signals.

²¹⁶ Moe Sato, 'An Experiemental Evaluation of Non-Ionic Surfactant Dehypon LS54' (University of Glasgow, 2014). P53

²¹⁷ Ibid. P80

²¹⁸ Mills and White, The Organic Chemistry of Museum Objects. P21



Figure 10: Cotton spectra with ATR and DIFFUSE FTIR

5.1 SOOTY SAMPLES ANALYSED BY DRIFTS

Samples of soot from seven different sources were kindly supplied by colleagues and friends (Table 10). These seven soot sources were then used individually to soil separate pieces of cotton fabric to provide soiled samples of known source for this trial of DRIFTS. The cotton material used was fine unscored bleached cotton with a thread count of 24 X24 per cm. further details can found in Table 10.

Sample	Collection method	File name- DRIFTS/ATR
Control- no soot	N/A	01 Cotton no soot
Coal	Coal burning fire place	02 Cotton Coal soot
Mixed wood	Log burning fire place	03 Cotton Mixed wood soot
Diesel	Car exhaust	04 Cotton Diesel soot
Petrol	Car exhaust	05 Cotton Petrol soot
Pine wood	Log burning flume	06 Cotton Pine wood soot
Mixed wood	Log burning fire place	07 Mixed wood soot
Pine wood	Log burning flume	08 Pine wood soot

Table 10: Soot source against sample number

5.2 HISTORIC OBJECT

One historical sooty textile was chosen from the CTC reference collection for DRIFTS analysis. This was a fragment of cotton upholstery as seen in Figure 11 and Figure 12. The sample was chosen due to the large scale of soot covering the object



Figure 11: Full image of historic sample



Figure 12: Close up view of soot on historic sample

5.3 METHODOLOGY

Two models of DRIFTS instrumentation plus an ATR FTIR spectrometer (all Agilent Technologies) were used, all kindly supplied by Dr Leung Pik Tang, Agilent Technologies and based at the University of Strathclyde. Instrument details are given in Table 11.

Machine	Agilent 4100	Agilent 4300	Agilent 0147
Type of Signal	Diffuse	Diffuse	ATR
Configuration	Michelson	Michelson	Michelson
	interferometer	interferometer	interferometer
No. samples per	128	128	128
spectrum			
Apodisation	Happ-Genzel	Happ-Genzel	Happ-Genzel
Width of sample	4cm	4cm	4cm
Zero filling	No zero fill	No zero fill	No zero fill
Time between	8min	8min	10min
calibration			

Table 11: Detail of equipment and methods used from samples

Each sample was taken on the 4100 Diffuse machine with the lens facing up. The samples were then placed on top, face down. The samples were moved between each spectrum with 5–7 repeats of each sample taken depending on how many could be achieved in between calibration times.



Figure 13: 4100 Exoscan Diffuse FTIR in use

When using 4300 DRIFTS the handheld element was used due to the lighter weight of the machine. The sample was face up and the machine could be placed more accurately on top. As the method was the same as with 4100 the same samples were taken.



Figure 14: 4300 Exoscan FTIR in use

For ATR sampling on 0147 model the samples were placed over the lens face down with a folded piece of plastic film used between the sample and wedge to increase the contact with the diamond in the lens. Between samples on the ATR ethanol was used to clean the lens.



Figure 15: ATR FTIR in use



Figure 16: ATR FTIR analysing pure soot sample

5.3.1 Mathematical modelling using principal component analysis

Once the spectra had been created the data was used for Principal Component Analysis (PCA) to look for patterns which may not be visible by the naked eye. PCA is a multi-variant mathematical tool which looks for the most meaningful way to re-express the data into new variables known as Principal Components (PCs)^{219,220}.

To do this, Panorama PCA was set up and the data for Diffuse 4100 and Diffuse 4300 were uploaded separately and the repeats for each sample were grouped into different classes. A minimal processing option was chosen with only a weighted baseline and mean centre applied. For Diffuse 4300 PC3 was applied as the recommended value to use as seen in Figure 17 and in DIFFUSE 4100 PC4 was used as seen in Figure 18.

View:	SS	Q Table				
Number	PCs: 3	Auto Select				
	Percent Variance Captured by PCA Model (* = suggested)					
	Eigenvalue of Cov(X)	% Variance This PC	% Variance Cumulative	RMSEC	RMSECV	
1	8.66e+000	88.32	88.32	0.02225	0.03098	
2	8.18e-001	8.35	96.67	0.01188	0.01675	
3	1.15e-001	1.17	97.84	0.009569	0.01305	current*
4	2.12e-002	0.22	98.05	0.009078	0.01272	
5	1.64e-002	0.17	98.22	0.008678	0.01274	
6	1.52e-002	0.16	98.38	0.00829	0.01276	

Figure 17: PC recommendation for DIFFUSE 4300

	Eigenvalue of Cov(X)	% Variance This PC	% Variance Cumulative	RMSEC	RMSECV	
1	4.31e+001	83.95	83.95	0.05762	0.06534	
2	6.13e+000	11.92	95.88	0.0292	0.03697	
3	1.09e+000	2.13	98.01	0.02031	0.02837	
4	4.81e-001	0.94	98.94	0.0148	0.02251	current*
5	1.59e-001	0.31	99.25	0.01245	0.02029	
6	9.28e-002	0.18	99.43	0.01085	0.01899	

Figure 18: PC recommendation for DIFFUSE 4100

5.4 DRIFT RESULTS

Once the data had been collected, EssentialFTIR software was applied for interpretation.

To compare results the many duplicates created for each sample were normalised and

averaged out. As the spectra for the sooty soiling showed predominately the peaks for the

²¹⁹ Jonathon Shlens, 'A Tutorial on Principal Component Analysis', arXiv:1404.1100 [Cs, Stat], 3 April 2014, http://arxiv.org/abs/1404.1100. P2

²²⁰ Hervé Abdi and Lynne J. Williams, 'Principal Component Analysis', *Wiley Interdisciplinary Reviews: Computational Statistics* 2, no. 4 (1 July 2010): 433–59, doi:10.1002/wics.101. P433

cellulosic fibres beneath the cotton control was overlaid and the subtract toll was applied to ensure the cotton spectra was not present. Full results can be seen in Appendix 4. The results showed DRIFTS produced far more detailed results than ATR. On many of the ATR samples there was too little detection of any wavelengths to produce a spectrum. This was not an issue with DRIFTS.

The spectra for soot were mainly showing the functional groups of the cotton rather than the soot. This is the case for a number of reasons

- From analysing samples of pure soot, it is clear that there is very little absorbance observed. This suggests that the carbon black is absorbing the wavelengths of the soot. This is a known problem for IR analysis because black materials are highly effective at absorbing IR radiation
- The concentration of soot is not high enough and therefore the infrared is not positioned in front of a soot particle.
- Organic chemical components are absorbed into the porous soot particles rather than adsorbed on their surfaces and thus undetectable.



Figure 19: Mixed and pine wood ATR spectrum with cotton spectrum subtracted



Figure 20: Mixed and pine wood Diffuse 4100 with cotton subtracted



Figure 21: Mixed and pine wood Diffuse 4300 with cotton subtracted

When the cotton was subtracted from the spectra for all three devices the size of the peaks was dramatically reduced, suggesting that very little soot was detected. There were few defining features available, with the exception of the mixed and the pine wood soot in each of the examples. The ATR shown in Figure 19 shows two clear peaks at 2926 cm⁻¹ and 2860 cm⁻¹ which correspond to alkane C-H₂ and C-H₃. When comparing with Diffuse methods in Figure 20 and Figure 21 these peaks do not appear. In Figure 20 the Diffuse 4100 model shows peaks as 184 cm⁻¹ and 1194 cm⁻¹ and in Figure 21 there are no discernible peaks. This suggests that the low detection made the subtraction tool an inappropriate method. For this reason pure wood soot was analysed.



Figure 22: ATR spectra of pure soot and cotton showing presence carboxylic acid in the soot



Figure 23: Pure soot and the historic object using DIFFUSE 4100

There were no solid soot samples taken on the 4300 Diffuse equipment as the gain could not be increased enough to take the sample. However, when pure soot was analysed the results were informative. Figure 16 shows that the mixed and pine wood soot both exhibit carboxylic acid from the very broad peaks at wave number of 3000 cm⁻¹ and the –OH groups which form the Carboxylic acid at 1700 cm⁻¹. The presence of carboxylic acid shows the soot is acidic. However, the solubility of the carboxylic acid is not known because that is determined by the length of chain to which the carboxyl groups are attached and is unknown. Also, the acidic groups are only acids in the presence of water.

Figure 23 shows under DRIFTS the carboxylic acid is still present but more hydroxyl groups are showing. It is also possible to compare the historic sample which exhibits the same peaks around 1700 cm⁻¹ shows carboxylic hydroxyl groups which the soot also shows. This indicates that the historic sample is also acidic.

When applying PCA it was found that petrol and coal soot had the most variability when using DIFFUSE 4300, as shown by the confidence ellipse in Figure 24. As pure soot and fly ash was able to be analysed on 4100 the PCA on this data is more revealing. Figure 25 shows that pure mixed wood and pine wood show similar results and that fly ash is more distinct. This shows how much cotton was picked up in the reference samples.

More interestingly in Figure 26, the direction of difference is shown acutely. In this, the historic sample is as distinct from the pure cotton as the pure soot, which indicated that the heavily sooted sample allowed for better detection by the FTIR than the reference sooted samples. As the historic sample is further from the wood soot than fly ash this suggests the soot is neither wood nor coal, from which the fly ash is derived. This strongly implies that the sample could have lamp soot present.



Figure 24: Confidence ellipse of PCA DIFFUSE 4300



Figure 25: Spider application for PAC DIFFUSE 4100



Figure 26: PCA of DIFFUSE 4100 PC 3 against PC 1

5.5 SUMMARY

As the fibres behind the soot are more visible, the condition of the fibres may be better to assess than the soot itself. It could be argued that if any potentially damaging chemicals are absorbed inside the soot particles then they are not in contact with the textile fibres directly. Without solvents or wet cleaning there should be no harm to the object. This would make it safe to retain soot on historic textiles. However, factors such as cumulative concentrations of small levels of potentially damaging chemicals or degradation products across a high number of carbon particles have yet to be understood. The solubility of these compounds and ease of migration (lability) with high air moisture and temperature is also unknown. From this trial, it can be concluded that analytical study with DRIFTS and from previous research by ATR-FTIR²²¹ that IR spectroscopy has limited application for sooty soiling characterisation in textile conservation.

²²¹ Meller, 'A Preliminary Investigation into the Characterisation of Sooty Soilings on Historic Textiles'. P48

6.1 THE ROLE OF POLYCYCLIC AROMATIC HYDROCARBONS AND NITRO POLYCYCLIC

AROMATIC HYDROCARBONS

There is evidence, at least in diesel soot, of a large variety of NPAHs being present. The NO_2 - on the PAH can hydrolyse into nitric acid in contact with water:

NO_2 -+ $H_2O \rightarrow HNO_3$ +H

It is therefore plausible that aqueous wet cleaning would lead to an acidic bath, as is often observed and commented on in textile conservation²²². There is evidence that NPAHs in the atmosphere have a diurnal pattern in which the air temperature in the daytime increases and the amount of NPAHs decreases and the amount of NO₂ in the atmosphere increases. When the temperature decreases the inverse occurs. As NO₂ is a gas it would not be considered to remain deposited onto the textile. However, as there is also evidence of soot having a slight porosity, it is possible that this gas may be absorbed into the porous carbonaceous structure. If this happens then the creation of nitric acid in water is viable, although, if the NO₂ is released into the atmosphere, over time the soot may become safer to wet clean.

6.2 THE USE OF ANALYTICAL TECHNIQUES ON HISTORIC TEXTILES

Chromatography with mass spectroscopy is a powerful tool for analysing and characterising fresh soot from various different fuel sources. However, as many of the chemical components such as PAHs can breakdown over time or by exposure to UV, more research into historic samples would be needed to compare fuel samples in a more relevant way.

FTIR analysis of soot on textile surfaces is unable to detect low quantities of organic components relating to the soot source even with DRIFTS. Only the surface of the soot particles is analysed and therefore less information can be determined if the diagnostic compounds are within the porous structures. DRIFTS may instead offer a more useful role in assessing the chemical condition of the fibres below the sooty soiling.

²²² Thompson, Coupar, and Benner, "Most I Saw Were Very Dirty, Some Very Ragged and All of Very Coarse Cloth". P44

SEM and TEM have been used to assess the morphology of the sooty soiling. In these results there is a difference between different fuel sources. As electronic microscopy is a non-destructive technique this is ideal for identifying the size and shape of soot on historic textiles.

6.3 SIGNIFICANCE FOR TEXTILE CONSERVATION

There is currently not enough data regarding the composition of historical soot exposure to long term environmental conditions to determine if the origin of the soot can be identified through scientific analysis. However the significance this could bring has been shown to be vast.

6.3.1 Historic / aged soot sampling

As many studies use new samples of soot for their analysis it would be useful to carry out analysis on aged soot. Historic samples are an important feature of this kind of research. However, to ensure the sources of soot are known, many samples will need to be artificially aged. Light aging machines are a possible way to create these samples. Analysis could then be carried out on the new and aged samples and compared.

The significance of the soot on the textile needs to be weighed up against the damage which the soot can cause. In order to understand the scale of the damage which the sooty soiling can cause, further research would be needed. There are many ways this can be achieved. One method would be to create two heavily sooted samples of each source of soot and a control with no soot. One of which will be artificially aged in a light aging machine. The samples can then be compared using tensile testing for strength. If the difference between new and light aged soot can then be compared and compared against the non-sooty sample. If a sooty sample is significantly weaker than the non-sooty sample then it is a strong indication that the soot is causing damage.

This information could be backed up by using DRIFTS analysis. As the DRIFTS analysis provides a good level of detail on natural fibres under the sooty soiling it would be possible to compare if the fibres from the artificially aged fabric had chemically degraded more or less than the non-sooty and also to compare the effects of different types of soot.

To investigate the damaging effects of the soot on the textile it would be useful to carry out an Oddy test. The purpose of an Oddy test is to find out if any VOCs are given off by a material. As NPAHs have the potential to release NO₂ into the atmosphere when the soot is
in the atmosphere it would be worth testing if in practice this happens when the soot is deposited onto a textile.

6.3.2 Morphology of soot

SEM and TEM are useful tools for imaging and assessing the morphology of the soot. Studies have then been carried out using ImageJ software to count the number of particles in each carbon agglomerate.

6.4 CONCLUSION

Although Sooty soiling is thought to be acidic in nature, if soiling can be used as a form of evidence of an event or of how the object was used then this is may change the debate between to clean or not to clean.

Very little research regarding soot has come out of the conservation field with many soot samples being taken from ambient air. This means gases which would not deposit onto a textile are analysed. The analytical techniques target diesel or gasoline derived soot with little focus on other fuel sources making it impossible to compare the results with other fuel sources.

Soot changes over time, through the presence of light and humidity and pollutants. For a historic item with historic soot the chemical composition of soot may have changed considerably over time.

As the majority of current research is focused purely on diesel soot, it is not always possible to compare different techniques of analysis to identify the source of soot. Despite this, there is evidence that syingol and guaiacol is detectable in wood soot only, which could be determined using chromatography with mass spectrometry if quantities are detectable. This is useful information to a social historian as the choice between coal and wood in the home has a long history.

When using DRIFTS the fibres behind the soot are more visible, meaning the condition of the fibres maybe better to assess than the soot itself. If any potentially damaging chemicals are absorbed inside the soot particles then they are not in contact with the textile fibres directly. This would make it safe to retain soot on historic textiles. However, factors such as the effect of potential degradation products and the solubility of compounds such as carboxylic acid are not yet known. FTIR both using ATR and DRIFTS has limited application for sooty soiling characterisation in textile conservation. The intrusive analytical methods of SEM and TEM to provide images of the soot particles may hold the key to identifying the source of the soot more effectively than chemical analysis and is worth exploring in the future.

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APPENDIX 1- GLOSSARY

Activated Carbon	Carbon atoms with a high surface area due to reaction with ga	
	to increase porosity.	
Activated Graphite	Carbon atoms arranges in a planar hexagonal structure with a high	
	surface area due to reaction with gases to increase porosity.	
Agglomerate	A cluster of Primary particles which are weakly bonded together.	

Carbonate

Carboxylic Acid	Functional group with a hydroxyl group and double bonded oxygen
	known as a carbonyl group. Solubility in water decreases as the
	size of the chain increases.

Destructive Sampling	where the sample used for analysis is destroyed in the process.
Gasification	
Graphite	Carbon atoms bonded to form layers of hexagonally arrange planer condensed rings.
Guaiacol	Product from Pyrolysis of lignin

Intrusive Sampling	where a sample needs to be physically removed from the object
	for analysis to take place.
Organic Carbon	Carbon bonded in an organic compound
Organic Compound	Carbon, Hydrogen and Oxygen bonded together with intramolecular forces
Poly Aromatic	Also known as polycyclic Aramaic Hydrocarbon. A compound made
Hydrocarbon	up of multiple aromatic rings containing on Hydrogen and Carbon

Figure 27 Pyrene:

Pyrolysis	Decomposition of organic material at high temperatures. T	
	Precursor to Gasification.	
Nitrated Polycyclic	Compound with multiple aromatic rings and at least one nitrile	
Aromatic Hydrocarbon	group	
Pyrene		
Syringol	Product from pyrolysis of lignin	

APPENDIX 2- SAMPLE MATERIAL

Material	Fragment of	
	cotton upholstery	Secol Dura
		XI TANYA
Thread Count	28 cm x 34 cm	
		2. 4. 50 6628
Weave	Plain weave	NASTRA AND
Origin	CTC reference	
	Collection	

Table 12: Details of cotton for soot samples

Material	Fine Bleached	
	Cotton	
Part Number	CD10	
Fait Nulliber	CDIO	
Batch	022783/111	
Duten	022/03/111	
		and the same and the same being the same and the
Thread Count	24 cm ²	
	_	
		PLACE REPORT OF THE PROPERTY O
Weave	Plain weave	
		and the second sec
Draducar	Mhalays	And the Low State and which the property of the second s
Producer	whaleys	

Table 13: Details of cotton for soot samples

APPENDIX 3- COLLATED DATA

soot sample	Diesel soot
1-NNAP	177 (pg m ⁻³)
2-NNAP	236 (pg m ⁻³)
2-NFLU	8.8 (pg m ⁻³)
9-NANT	<0.24 (pg m ⁻³)
9-NPHE	<0.11 (pg m ⁻³)
1-NPYR	1.81 (pg m ⁻³)
3-NFLT	<0.06 (pg m ⁻³)
6-NCHR	7.87 (pg m ⁻³)
7-NBaA	<0.23 (pg m ⁻³)
6NBaP	23.3 (pg m ⁻³)
3,1-DNPYR	<0.11 (pg m ⁻³)
1,6-DNPYR	<0.05 (pg m ⁻³)
Nirto-PAH (3,6)	455 (pg m ⁻³)
Nitro-PAH (3,4)	432 (pg m ⁻³)
PHE	66 (pg m ⁻³)
ANT	1.9 (pg m ⁻³)
FLT	74 (pg m ⁻³)
PYR	140 (pg m ⁻³)
ВаА	<0.8 (pg m ⁻³)
CHR	<0.7 (pg m ⁻³)
BbF	<0.7 (pg m ⁻³)
BkF	<1.2 (pg m ⁻³)
BaP	<0.4 (pg m ⁻³)
DbahA	<1.1 (pg m ⁻³)
BghiP	<0.5 (pg m ⁻³)
IND	<0.7 (pg m ⁻³)
РАН (3,6)	282 (μg g ⁻¹)
РАН (3,4)	282 (μg g ⁻¹)
РАН (5,5)	<4.6 (µg g ⁻¹)

Table 14: HPLC results for Diesel cars²²³

²²³ Schauer, Niessner, and Pöschl, 'Analysis of Nitrated Polycyclic Aromatic Hydrocarbons by Liquid Chromatography with Fluorescence and Mass Spectrometry Detection'.

Analysis	GC/MS
Material	Coal soot
Trimethyl benzene	0.0035
Naphalene	0.015
Benzothiazole	0.0091
Monomethyl naphthalene	0.0057
1,4 dichloro Benzene	0.003
Biphenyl	0.0075
Dimethyl naphthalene	0.018
Flourene	0.029
Diphenylmethane/biphenyl, monomethyl-/dibenzofuran	0.018
Naphthalene, trimethyl-	0.06
Anthracene/phenanthrene, monomethyl-	0.27
9h-fluorene, monomethyl-	0.07
Dibenzofuran, monomethyl-/4,4-dimethylbiphenyl-[1,1-Biphenyl]-4-	0.081
carboaldehyde/2-hydroxyfluorene	
Anthracene/phenanthrene, monomethyl-	0.5
9h-fluorene, dimethyl-	0.011
Pyrene	1
Naphthalene, 2-phenyl-	0.51
Phenanthrene, monoethyl-/dimethyl	0.33
2,6-Diisopropylnaphthalene	0.21
Fluoranthene, monomethyl-/pyrene, monomethyl-	0.25
Benzo[kl]xanthene	0.49
Butylated, hydroxytoluene	0.11
Triphenylene/benzo[a]anthracene	0.12
Pyrene, dimethyl-	0.065
Phenanthrene, tetramethyl-	0.62
Chrysene, monomethyl-	0.54
Benzo[a]pyrene/benzo[e]pyrene	0.11
Benzo[c]phenanthrene, 5,8-dimethyl	0.022

Table 15: GC/MS peak intensity for PAHs in coal soot²²⁴

²²⁴ Gao et al., 'A Comparison between the Vacuum Ultraviolet Photoionization Time-of-Flight Mass Spectra and the GC/MS Total Ion Chromatograms of Polycyclic Aromatic Hydrocarbons Contained in Coal Soot and Multi-Component PAH Particles'. P67

APPENDIX 4- DRIFTS RESULTS

Diffuse 4100 Exoscan



Table 16: DIFFUSE FTIR Cotton no soot averaged



Figure 28: DIFFUSE FTIR Cotton and Coal Soot all



Figure 29: DIFFUSE FTIR Cotton and Coal soot averaged



Figure 30: DIFFUSE FTIR Cotton and Wood soot All



Figure 31: DIFFUSE FTIR Cotton and wood soot Average



Figure 32: DIFFUSE FTIR Cotton and Diesel Soot All



Figure 33: DIFFUSE FTIR Cotton and Diesel Soot Average



Figure 34: DIFFUSE FTIR Cotton and Petrol Soot All



Figure 35: DIFFUSE FTIR Cotton and Petrol soot Average



Figure 36: DIFFUSE FTIR Cotton Pinewood Soot All



Figure 37: DIFFUSE FTIR Cotton Pinewood Soot Average



Figure 38: DIFFUSE FTIR Historic Cotton and Soot all



Figure 39: DIFFUSE FTIR Historic Cotton and Soot



Figure 40: DIFFUSE FTIR Mixed wood Soot all



Figure 41: DIFFUSE FTIR Mixed Wood Soot All



Figure 42: DIFFUSE FTIR Pine wood soot all



Figure 43: DIFFUSE FTIR Pine Wood Soot All



Figure 44: DIFFUSE FTIR 4300 Cotton No Soot All



Figure 45: DIFFUSE FTIR 4300 Cotton No Soot Average



Figure 46: DIFFUSE FTIR 4300 Cotton Coal Soot All



Figure 47: DIFFUSE FTIR 4300 Cotton Coal Soot Average



Figure 48: DIFFUSE FTIR 4300 Cotton Wood Soot All



Figure 49: DIFFUSE FTIR 4300 Cotton Wood Soot Average



Figure 50: DIFFUSE FTIR 4300 Diesel Soot All



Figure 51: DIFFUSE FTIR 4300 Cotton Diesel Soot Average



Figure 52: DIFFUSE FTIR 4300 Cotton Petrol Soot All



Figure 53: DIFFUSE FTIR 4300 Cotton Petrol Soot Average



Figure 54: DIFFUSE FTIR 4300 Cotton Pinewood Soot All



Figure 55: DIFFUSE FTIR 4300 Cotton Pine Wood Soot Average






Figure 57: ATR Cotton No Soot Average

ATR



Figure 58: ATR Cotton Coal Soot All



Figure 59: ATR Cotton No Soot Average



Figure 60: ATR Cotton Diesel Soot All



Figure 61: ATR Cotton Diesel Soot Average



Figure 62: ATR Cotton Wood Soot All



Figure 63: ATR Cotton Wood Soot Average



Figure 64: ATR Cotton Petrol Soot All



Figure 65: ATR Cotton Petrol Soot Average



Figure 66: ATR Cotton Pine Wood Soot All



Figure 67: ATR Cotton Pine Wood Soot Average



Figure 68: ATR Mixed Wood Soot All



Figure 69: ATR Mixed Wood Soot Average



Figure 70: ATR Pine Wood Soot All



Figure 71: ATR Pinewood Soot Average



Figure 72: PCA Analysis of DIFFISE 4300

Class 2_cotton and coal soot Class 3_cotton and wood soot Class 4_cotton and diesel soot

Class 1_cotton ref



Figure 73: PCA results for DIFFUSE 4100

Class 2_cotton and coal soot Class 3_cotton and mixed wood Class 4_cotton and diesel soot

Class 1_cotton ref

Class 10_flyash 95% Confidence Level Class 8_mixed wood Class 9_pinewood Class 5_cotton and petrol soot Class 6_cotton and pinewood soot Class 7_cotton and historic soot

APPENDIX 5- SPECTROSCOPY REFERENCE PEAKS

Absorption cm-1	intensity	functional group
1100	medium	C-C-C bending
1675	strong	α, β-unsaturation stretching
1690	strong	aryl ketone stretch
1745	strong	cyclopentanone stretching
1780	strong	cyclobutanone stretching
3030	strong	Arenes C-H stetch
3300	strong	Alkyne C-H stretch
1000-1250	Medium	Amines C-N stretch
1100-1040	strong	Carboxylic aid O-C stretching
1210-1320	medium-strong	carboxylic acid O-C (sometimes 2 peaks)
1250-1000	strong	Amines C-N stretch
1360-1350	strong	α-CH₃ bending
1390-1370	medium	Alkane CH3 deforming
1430-1330	Medium	Alcohol O-H Bending
1440-1395	medium	Carboxylic acid C-O-H bending
1450-1400	strong	α -CH ₂ bending
1470-1350	medium	Alkane ch2, ch3 deforming
1560-1500	medium	N-H (2i-amide) II band bending
1600-1500	Medium-weak	Arenes C=C in ring stretch
1650-1550	medium- strong	Amines NH2 Bending
1650-1590	meduim	N-H (1i-amide) II band bending
1680-1630	variable	Aklene C=C stretch
1700-1500	Medium	Aromatic C=C Bending
1720-1705	strong	Carboxylic acid C=O stretching
1720-1710	strong	Ketone C=O Stretch
1740-1690	Strong	Aldehyde C=O Stretch
1740-1720	strong	Aldehyde C=O Stretch
1750-1680	Strong	Ketone C=O Stretch

1750-1735	strong	C=O stretching
1750-1735	Strong	Ester C=O Stretch
1780-1710	Strong	Corboxylic Acid C=O stretch
1815-1785	strong	Carboxylic acid C=O stretching
1820-1750	strong	carboxylic acid C=O (2 bands)
2000-1900	strong	Aklene C=C asymetric stretch
2250-2100	variable	Alkyne C=C symetric stretch
2260-2100	variable	Alkynyl C=C Stretch
2260-2220	medium	nitrile C=N stretch
2260-2240	meduim	nitrile C=N stretch
2270-2100	medium	-N=C=N-, -N3, C=C=O stretching
2840-2690	medium-strong	Aldehyde C-H stretch
2950-2850	medium-strong	Alkyl C-H Stretch
3000-2500	broad variable	Amine N-H Stretch
3000-2850	strong	Alkenes CH3, CH2 stretch
3030	variable	Aromatic C-H Stretch
3100-3010	medum	Alkenyl C-H stretch
3100-3020	Medium	Alkene C-H or CH2 stretch
3300	strong	alkynyl C-H Stretch
3300-2500	strong	carboxylic acid O-H (very Broad) stretching
3400-3300	weak	Amines N-H stretch
3500-3400	weak	Amines N-H stretch
3550-3200	strong	Alcohol/phenol O-H stretch
3550-3200	Broad strong	Alcohol/phenol O-H stretch
3650-3580	variable	Alcohol/phenol O-H stretch
3700-3500	medium	Amide N-H Stretch
700-600	strong	Alkyne C-H deforming
725-720	weak	Alkane Ch2 rocking
730-675	medium	Alkene RCH=CHR deforming
770-660	variable- weak	Alcohol O-H Bending (out of plane)
850-780	medium	Alkene C-H, CH3 deforming

860-680	strong	Aromatic C-H Bending
900-660	variable	Amines NH2 & N-H Bending
900-690	strong	Arenes C-H bending and ring puckering
995-880	strong	Alkene C-H, CH2 deforming

Table 17: Reference for FTIR peak analysis^{225,226}

²²⁵ 'IR Absorption Table', accessed 19 July 2016, http://webspectra.chem.ucla.edu//irtable.html. ²²⁶ 'Infrared Spectroscopy', accessed 13 August 2016,