

NORFOLK

Wood Tar

**PROJECT
REPORT**

Funded by **Leader II** and **MAFF**

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Centre for Environmental Risk
Forest Enterprise
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Norfolk WOOD TAR Project Report

Wood Tar

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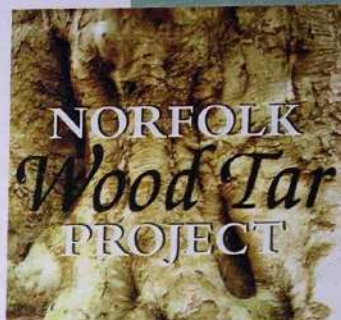
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Acknowledgements

I would like to thank the following individuals for their help and encouragement over the last few months. Jenny Aspenburg in Halsingborg for all the Swedish contacts she gave me and for translating very difficult text. Also Staffen Claesson in Goteborg, whose enthusiasm and knowledge of wood tar is second to none. Peter Fiddy for his patience and ingenuity in adapting the incinerator and for staying up all night! Chris Nix, for helping to get the initial bid together (including splendid spreadsheets) and encouraging me to keep going through the bid making process. Simon Malone and Paul Bond at Forest Enterprise for supplying the raw material and the site for the live experiments. Dirk Bouwens for stimulating my interest in the subject following our work together in Gotland and for his advice in getting the experiments going. Dr Chris Foxall for arranging all the chemical analysis and Susan Ferguson for her advice and help in putting together the final report and helping me to achieve my targets on time. Don Kelly in Sheffield was also a mine of information concerning the commercial production of charcoal and it's by-products in the UK over the last couple of centuries.

Finally, I must thank Norfolk County Council and specifically the Department of Planning and Transportation for allowing me the time to undertake and complete the project and MAFF (through the LEADER II initiative) for jointly financing the project.

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Glossary of Terms

Pyrolysis is the thermal degradation of organic matter in the complete absence of oxidising agent, or with such a limited supply that gasification does not occur to an appreciable extent. In the latter case, the process can be referred to as partial gasification. It should be noted in this context that steam, itself a potential oxidant, will also be produced from the water contained in the biomass feedstock during pyrolysis.

In pyrolysis, the volatiles are thermally driven effects-out of the substrate, resulting in char, condensable liquids or tars and gaseous products. The conditions employed are designed to maximise the yields of liquids such as oils and tars and minimise the proportion of feed stock converted to char and gaseous products.

Heat can either be supplied indirectly by heating the retort or in the case of the more traditional kiln, the thermal energy is provided directly from the wood itself. Even in the case of indirect heating methods, some direct heat can be provided by recycling gases resulting from the pyrolysis process itself back into the retort.

Carbonisation is a particular type of pyrolysis process which maximises the yield of solid products (char) by employing slow reaction rates and relatively low temperatures. Such carbonisation processes can, eg. be used to produce specific types of solid fuels such as coke or anthracite.

'Destructive distillation' is an alternative name for pyrolysis and carbonisation. The name was commonly used by late 19C and early 20C chemists but is now rarely used.

Gasification is strictly the conversion of solid and liquid residues derived from the thermal decomposition of organic matter (pyrolysis) with oxidising reactants and yielding mainly low molecular mass gaseous products.

The main objective of gasification is to transfer the maximum usable chemical energy from the feedstock to the gaseous fraction of the products. Air, oxygen and steam are most commonly used as oxidants, but carbon dioxide and hydrogen may also be used. The use of steam as an oxidant was introduced as a way of improving the amount and quality of gas derived from coal gasification plants in the 1880s and was widespread by the early 20C.

PyNE - The Biomass Pyrolysis Network - is a global network of active researchers and developers of fast pyrolysis biomass. It has been established to discuss and exchange information on scientific and technological developments on biomass pyrolysis and related technologies of the production of liquid fuels, electricity and chemicals.
<http://www.pyne.co.uk/over.htm>

Wood Tar

Chapter 1

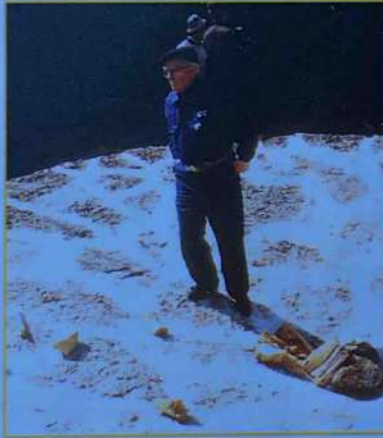
INTRODUCTION

In 1998 I led a small group of three individuals to take part in an EU RAPHAEL Project called TRADIMA, studying the manufacture and uses of traditional materials in the conservation of buildings and structures.

Following a planning meeting in Bornholm in March it became clear that the first part of the practical 'hands-on' experience was going to be very interesting and unusual. It was the first time I had heard about wood tar and I saw the first practical application of it in Bornholm on a number of fishing sheds and some very old cottages close to the sea.

The proposal was that all participants would gain first hand experience of making wood tar in the very traditional and locally distinctive way on the Island of Gotland off the South East Coast of Sweden. During our stay, participants would also gain valuable experience in the production of wood burnt lime and linseed oil. During the 14-day stay, we also had the opportunity to see these materials in use.

So it was, that at a small site in the forest, in the parish of Hejnum, we were introduced to the method of wood tar production as practiced for many centuries on the Island. The site is managed by Byggnadshyttan, (who are a company owned by a foundation in Visby) They are closely involved with the conservation of historic buildings throughout Gotland and operate on a non-profit making basis. The man who was actually going to supervise the operation (known as the Sojdegubbe) was one of only a small number of people in Sweden who have practical experience of the process.



A big advantage of this traditional small scale of production, is that it is easier to control the process from the start and to rigorously select only the best raw material and ensure that the roots and stumps of these 15 to 20 year old pine trees (*Pinus Silvestris*), were cleaned of bark and any other detritus that was not essential to the production of high quality tar.

The 'Sojde' comprised a circular dished area of limestone with a central hole to allow the tar to flow via a water-trapped pipe into the collecting vessels. The site was on a slope and the diameter of this construction was approx. twenty feet. Upon this area, we piled the small pieces of wood all pointing towards the centre in the shape of a cone. The whole pile was then covered with a layer of pine branches and finally covered with sawdust to exclude air from entering the pile. The volume of wood used was about twenty cubic metres.

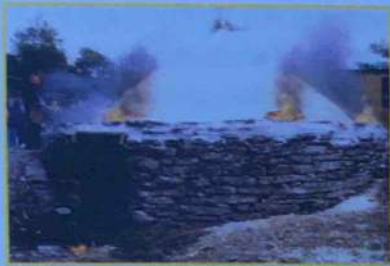




This wood burns very easily and once one or two pieces were alight the temperature very soon rose to between 700 and 800 degrees centigrade. A large quantity of moisture is driven off at the beginning and this causes quite a lot of smoke. However, after a day or so it becomes less and less until by the third day it

has virtually disappeared and changed from white to blue. The tar began running after twenty-four hours, or so and the final quantity was a little short of 1000 litres.

The resultant thick brown liquid contains upto 250 different compounds and has been used for centuries as a timber preservative. Nearly all the old dwellings are constructed from softwood and even on stone built churches, there are still large areas of exposed timber that need protecting. There is evidence on Gotland of 800-year-old church doors still in use and most of the roofs are left as bare timber, their only protection being wood tar.



Having seen the product in action protecting timber over many centuries, not only in Gotland, but elsewhere in Scandinavia, the idea that there might be a market for this Eco-sensitive product in England, began to

crystallize. The Thetford Forest area in Norfolk possesses many hectares of an identical species of pine to that in Gotland and currently the trees are de-stumped after felling and the roots are piled up in 'windrows'. Could they too be turned into a useful timber preservative, that was the question?

To discuss this question, a meeting was arranged with Forest Enterprise (who manage the Thetford Forest area on behalf of the Forestry Commission). They agreed that here indeed was an idea that had merit. It was explained that they have to lift all the stump material and roots out of the ground to prevent the spread of a fungus that will cause damage to new plantations if allowed to remain in the soil. The area subsequently taken up by this material takes out of commission about 15% of the potential growing areas for new trees. Therefore, any activity that might yield a return on this 'waste' would be a bonus.



Forest Enterprise agreed to support an application for European funding to enable further research to take place and to contribute five working man-days towards the partnership funding required. An application to the LEADER II programme was then prepared and submitted in the autumn of 1998. The overall aim being, to establish whether there might be a commercially viable method of producing good quality wood tar from the waste material currently produced as a result of their activities.

In order to achieve this overall aim the following detailed objectives were identified:-

- Identify and quantify the availability and quality of rootstocks on the area.
- Carry out detailed chemical analysis on samples of different tars.
- Examine the effects of stump maturity on the quality of tar produced.
- Investigate the commercial production of wood tar elsewhere.
- Investigate the existing market for timber preservatives and see if other new markets might be created.
- Identify any legislative changes in the 'pipeline' that might affect the marketability of wood tar and the future of existing chemical preservatives.



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Gotland University College

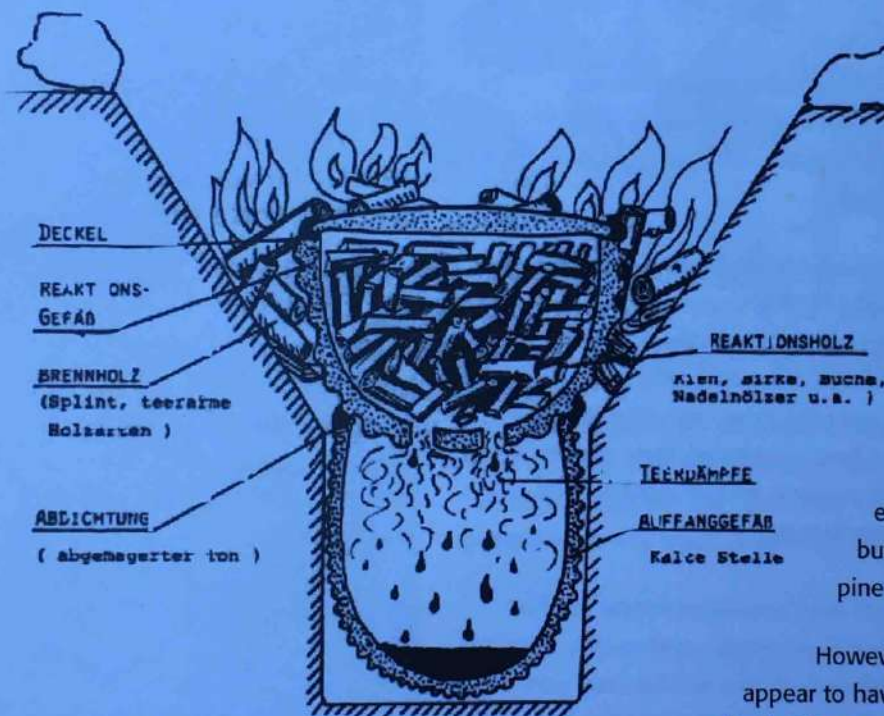
EC LEADER II Programme
applications dated
2.12.98/7.4.99/29.4.99.

Wood Tar

Chapter 2

A Short History of Wood Tar

Wood tar has many different uses beneficial to man. Through contact with Prof. Dr M. Fansa at the Staatliches Museum in Oldenburg, a small working group of archaeologists at the Musemsdorf Duppel were identified, who have been recreating and studying early methods of tar production. It has apparently been manufactured by man since Mesolithic times, initially as an adhesive for gluing flint to wooden shafts for use as arrows and other tools. It was later used as a lubricant (for Roman chariots and other horse drawn vehicles); for medicinal and veterinary use and as a timber preservative (especially of wooden ships and their rigging). Following further processing, many other useful products can be extracted that can then be used for example as additives in the manufacture of rubber tyres/perfumes and many other products.



The main centres of production in recent times have been located close to where the raw material grows. As *Pinus Silvestris* (known in the UK by its common name the Scots Pine) is the preferred species and this tree naturally grows in a wide belt from Scotland across the North Sea through Scandinavia, into North East Europe and Russia; then it is not surprising, that it is within these areas that most wood tar is produced. Some wood tar was also extracted from Birch and other softwoods, but in the main, it is the tar produced from pine that is most sought after.

However, although Sweden, Russia and Finland appear to have been the main centres of production for the last few centuries, Britain's colonies in North America were also encouraged to produce pine tar and pitch for later shipment to England, particularly at the beginning of the 18th century when England was cut off from its Scandinavian supplies by Russia's invasion of Sweden and Finland. Nevertheless, this was not the first time wood tar had been produced in North America. According to John Evelyn writing in 1664 it was made, he recorded, 'from the American pitch pine, which grew on barren hills and plains. These often blew down and when the ground was burnt annually by the Indians, the bodies of the trees were consumed, leaving behind knots of timber from the joint at which the boughs joined the trunk. The latter were collected and fired in a furnace made with a sloping clay floor, which had an outlet for the tar. The knots were piled on this in a similar manner to that employed in charcoal-burning and covered with clay.' By 1725 four fifths of the tar and pitch used in England came from the American colonies and this remained constant until the American Revolution in 1776, when England was again forced to trade with the Dutch for Scandinavian products.

However, later in the century, yet again England found itself unable to import adequate supplies from Europe due to the naval blockade during the Napoleonic wars and so worried was the Admiralty, that it offered a reward to any manufacturer who could develop and manufacture sufficient wood tar for their needs. Unfortunately, the records about which companies might have been successful were destroyed by bombing during the Second World War. However, one particular company that was founded at this time and which continued to produce wood tar until the 1970's was the Shirley Aldred Company in Worksop, Nottinghamshire.



Shirley Aldred Factory, Worksop

During the 19th century the construction of wooden ships increased tremendously as England's Navy and those of her close neighbours, grew. The demand for wood tar also increased, reaching its peak in the middle of the century when it was a major export for Sweden.

However, as sailing ships began to be replaced by steam, the demand for tar and pitch for protecting their wooden hulls and rigging, dropped quite significantly. This had quite a damaging effect on many rural areas in Sweden in particular, where tar making was a useful sideline. This was particularly true in a country where farming, forestry and fishing were the most important industries and where the market economy had not yet been introduced. Here people lived on their own produce or on the exchange of products and tar distilling, was one of the many sidelines that could bring in extra income.

Chapter references:

Woodland Crafts in Britain

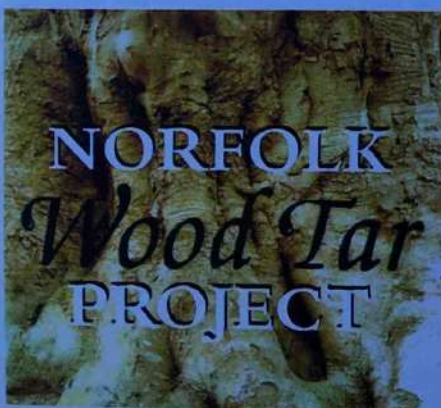
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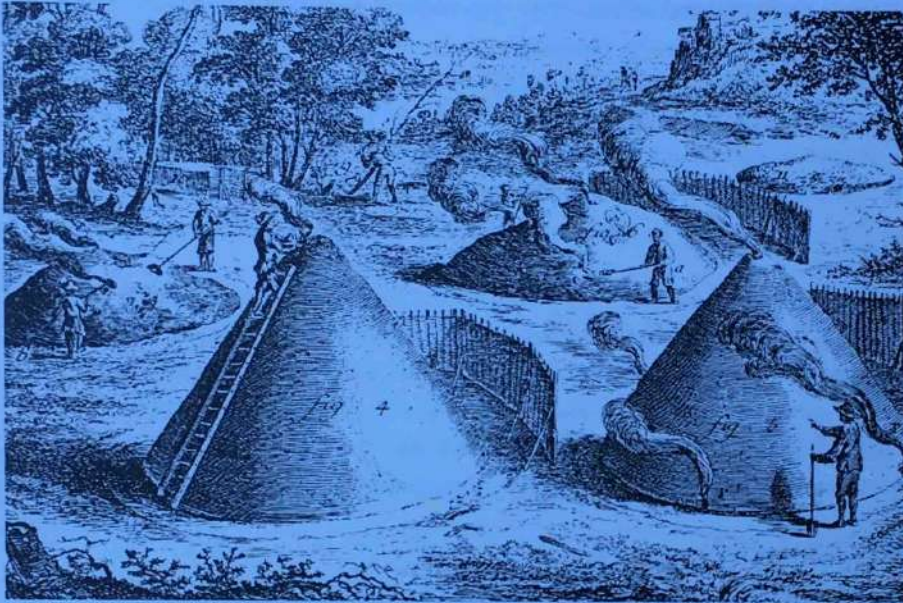


Wood Tar

Chapter 3

The Current Scene

Many different methods have been used to produce wood tar but they mainly fall into two categories. The direct burning method, where the wood is set alight in a pit or chamber and air is excluded by covering the whole pile with earth/turfs or sand. This is very similar to the traditional way of producing charcoal and is similar to that method described above by John Evelyn.



Charcoal Burning the 'traditional' way

commands a premium price (see Claessons attached price list in Appendix One). A full description of the traditional Swedish method, translated into English from the original Swedish text taken from Fredrik Westman's book 'Tar Burning', is attached to this report (Appendix Two).

Portable retorts developed from the earlier fixed retorts in the latter half of the 19th century. Now timber could be loaded into separate containers, which were then lowered into a brick chamber incorporating a firebox. Distillation proceeded and on completion the cylinder was withdrawn by a travelling hoist system on an overhead gantry and replaced by a fresh container of wood. This method became the most commonly adopted method this century, both in the UK and elsewhere.

Whilst it was hardwood charcoal that was the primary end product for these systems, other by-products were available including Acetic Acid, Methanol and Hardwood Tar Oil and Pitch. They have many different industrial applications (see following paragraph). Softwood, on the other hand, yields mainly wood turpentine and tar oils (known in the USA as Naval Stores).

According to Don Kelly (author of 'Charcoal and Charcoal Burning' and past M.D. of Shirley Aldred and Co Ltd) acetic acid (known as wood vinegar) was the main by-product and it was used for various industrial uses. These included the manufacture of rubber products and (when mixed with iron borings), as a mordant for the dyeing industry. The industry was centred in the Forest of Dean area, an area in north Nottinghamshire, Liverpool and Glasgow. Now, all large-scale production has ceased in the UK due largely to the import of cheaper

The other way is to heat the wood indirectly in a container or retort. This method is variously known as 'destructive distillation' or 'steam distillation' (USA) but is more generally known today as 'pyrolysis'. (For a full description of these terms refer to glossary).

There is no doubt that the earlier method was the most common, particularly in Scandinavia and the more rural parts of Europe and is still carried on by a handful of individuals and small local groups today. This method produces small quantities of very high quality wood tar that

charcoal from South and Central America and South East Asia. In addition, the development of the petrochemical industry with its many by-products during the 1960's and '70's also adversely affected the demand for charcoal by-products, as they were able to produce synthetic versions much cheaper. However, there are still a few companies trading in Scandinavia and Europe.

Only two main companies have been identified. These are Skogens Kol in Sweden and Bertrand Navarre in France. Unfortunately, none of the firms contacted would discuss in any detail their manufacturing processes, products or by-products, despite requests to visit them. But details of the processes and equipment used are given in Dumesny and Noyer's book detailed below. They also list a number of secondary products of wood distillation, namely: Chloroform, Methyl Nitrate, Ethyl Acetate, Acetone and wood creosote. One Swedish company that only recently closed (Perstorps in SW Sweden), listed the following different wood tar products:-

- **Crude Beechwood Tar No 1.**
Described as Pyroloem Fagi (a tar produced during carbonization, containing approx. 20% pyroligneous acid).
Used for pharmaceutical purposes.
- **Beechwood Tar No 111.** (a tar produced from Tar No 1 and from which the pyroligneous acid has been removed by distillation).
Used for regeneration of rubber and for impregnation purposes. Also used for carbolineum.
- **Beechwood Tar No 112** (a tar product from which the pyroligneous acid has been removed by distillation).
Used for impregnation and for coating of trees as a protection against fungus growths. Also used in the electricity industry.
- **Beechwood Tar No 123** (a black syrupy liquid) Used in the rubber industry.
- **Tar Oil No 3** (a clear brown oil which darkens in the presence of iron or upon exposure to light)
Used in the production of creosote and for flotation uses.
- **Tar Oil No 4** (a dark oily liquid)
Recommended for extraction and flotation purposes.
- **Beech Pitch** (a blackish-brown, hard brittle pitch, which can be powdered at normal temperatures)
Used as a raw material in the rubber industry; as a binding agent in compressed cork, fibreboards, fire briquettes etc, in the manufacture of electrodes; as an insulating material in dry cells; for grinding lenses etc.
- **Creosote** (a clear almost colourless, or faintly yellow oily liquid with highly refractive qualities. It has a penetrating odour of smoke, a burning taste and is neutral in reaction.)
Used for pharmaceutical purposes; the production of creosote carbonate, creosote lactate, vanillin and other products.



As part of my investigations in Sweden, I visited Staffen Claesson in Goteborg who sells over thirteen different varieties of wood tar for use as a timber preservative treatment on wooden boats and buildings. He buys his supplies from various outlets and in his list are included both commercial and traditionally produced tars.

Although there is no evidence of the superior quality of one over another, yet, he was quite emphatic about the merits of the old fashioned traditional tars over those produced commercially as a by-product from charcoal manufacture. This is particularly so when applied as a timber preservative. As a result of the visit, he



gave me several different samples (including a commercially produced 'Stockholm Tar') and I was also able to purchase in Halsingborg some of the tar produced in large quantities by Skogens Kol in the northeast of Sweden.

When any timber becomes wet, it is liable to attack by wood destroying fungi which eventually can cause wood to rot. Wood eating insects are also a problem. However, different timbers vary in their resistance to attack by wood destroying fungi according to the species concerned. Although there are some notable exceptions (English Oak for instance) many European hardwoods and all softwoods will fail if not treated in some way with a timber preservative.

The Building Research Establishment (known hereafter as the BRE) have been undertaking research in this field for over 60 years and have published their findings in three publications listed below. One describes the biological natural durability of timber (in ground contact). The other two describe the tests and results, of preserved timber in and out of ground contact.

One of the main sites for these tests is within the Thetford Forest area where thousands of stakes in ground contact have been monitored since 1929. The trials tested eight preservatives in pine stakes (as a softwood sample) and in beech stakes (as a hardwood sample). The specific timbers chosen were Corsican pine sapwood and European beech. Seven waterborne preservatives and one organic solvent-borne were selected. Unfortunately, no wood tar derived preservatives were tested.

The tests on timber out of ground contact have not been going such a long time (only since 1967) and were set up to provide data on the likely performance of exterior joinery work in buildings. Again, whilst this time, coal tar creosote was tested, there was no testing of wood tar.

Peter Koch in his two volumes on the Utilization of Southern Pine (chapter 22 vol II), also details tests carried out in the USA using both oilborne preservatives such as the creosote formations / crank case oils and wood-tar creosotes and also waterborne preservatives such as Boliden Salt/chromated copper arsenate and chromated zinc chloride.

Unfortunately, none of the preservation tests undertaken either here or in the USA tested the sort of traditional wood tar that this study is concerned with and no reference to any such tests have so far been discovered. Nevertheless, practical use of this material over centuries would seem to indicate that it certainly works well and maybe as a result of this report one of the research organisations like the BRE would be interested in putting wood tar into the 'frame' with the other preservative formulations.



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Utilization of Southern Pines by Peter Koch Volumes I & II published by US Department of Agriculture and Forest Service 1972.

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Pine Tar; History and Uses by Theodore P. Kay National Maritime Museum Association 1997.

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Long term field trials on preserved timber in ground contact (revised to 1993) by Smith and Orsler BRE Report 1995.

Wood Products: Distillates & Extracts by P. Dumesny and J. Noyer 1921

Wood Tar

Chapter 4

Production and Collection of Samples

Whilst it was always assumed that wood tar could be produced in this country from Scots Pine (*Pinus Silvestris*), it was not known whether Corsican Pine or indeed other woods would also be a useful source for wood tar. Furthermore, whilst the accounts of wood tar production in Sweden talk of using at least fifteen year old stumps (and in some cases much older), it was doubtful if there would be anything similar in this country.

With the help of Forest Enterprise staff, who produced information on felling and consequent destumping over a large area of the forest between 1980 and 1990, it was possible to identify particular sites where samples might be obtained.

These stumps are piled in 'windrows' in such a way as to encourage their decay, so there was some scepticism as to whether any of the older material would have survived. It should be understood that the climate in this part of the UK is quite different to that in Sweden and it was, therefore, with some surprise that under the outer layer of very rotten wood, a hard core of very resinous material remained.

Why and how this happens is still a mystery, but it appears from observation that as the tree stump decays resin-acids are concentrated to the stumps. One theory is that it has to do with the tree's protective mechanism, as the same thing occurs when a pine is damaged by what the Swedes call 'torskatesvam' or tar-sting (see Fredrik Westman's account in Appendix 2) In fact in the Gotland situation the expert tar producer (the Sojdegubber), made reference to the fact that he found the stumps from wind damaged trees were more likely to release a high quantity of wood tar than those that had not.

Once the material had been extracted from the forest, the next task was to decide the method, which would be used to extract the tar. Some new

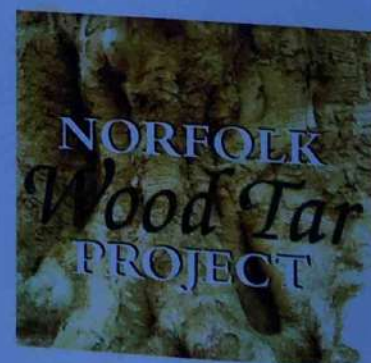
'Webster Retorts' had recently been installed at North Elmham in Norfolk and the owner was willing to allow us to load stump material into the retort chamber. But they

are quite big and would require approximately a ton and a half of timber. In addition, this plant is designed specifically for producing charcoal using the pyrolysis method described above, not tar and it was difficult to see how the tar might be collected, without some major adaptation.

Bearing in mind the number of samples that were intended to be produced, it was decided to abandon this idea. Fortunately, a new style of domestic incinerator was discovered and with a minimum of fuss, it was



'Windrows' in Thetford Forest





Webster Retort, North Elmham

quickly converted to serve a new purpose. It was loaded with some of the fifteen year old stump material collected from Thetford and after cleaning to remove lichen and other fibrous material, small pieces were loaded into the bin.

On April 26 in Norwich, the wood was lit. Once alight, the lid was replaced, but several times the temperature dropped and the fire went out. This was the first experiment and many lessons have subsequently been learned, including getting the temperature up to a good level before beginning to exclude the air from the bin.

However, following the application of a blow torch to the wood, it kept going all through the night and although there had been some indication of tar dripping from inside the lid in the early evening, it didn't start to run properly from the bottom of the vessel, until 10.45pm. Thereafter, it kept up a steady flow until 8.30am the next day and produced about a litre of good quality wood tar. (Full details of this experiment and other later ones are included in Appendix Three).



First experimental burn in Norwich

Following the success of the first experiment, more material was gathered from the Thetford area including some younger stumps of the Scots pine and also some Corsican pine, five and fifteen years old and some Silver Birch branches. Over a period of several days during June and July, the experiments continued and good tar was extracted from older stumps of both the pines, but the younger timber and the Silver Birch produced very little. What did come through also appeared black and brittle, i.e. more like pitch. This may have been because the samples became very hot towards the end of the process and it was very difficult to control this.

In order to meet one of the objectives of this study, other samples of both wood tar and other tars were obtained to see how they compared. Some of the samples were gathered in Sweden, others were purchased or obtained in this country from a variety of sources, although there appear to be only two main importers in the UK. These are Battle, Hayward and Bower Ltd and Teisen Products Ltd. The first company import what is called 'Stockholm Tar' and the second imports 'Beech Tar'. Both of these are sold mainly for use as veterinary products.



Wood Tar

Chapter Five

Discussion of Chemical Analysis of Tar samples

Compared to other groups of naturally occurring chemicals, wood tars have, to date, received relatively little attention. Such materials have a well-justified reputation of being extremely difficult to analyse. This is, in part, due to their physical characteristics which make them difficult to handle and purify, and partly because wood tars are chemically very complex and thermally unstable mixtures. The situation is compounded by the large numbers of different types of tar that exist. Owing to these analytical difficulties, relatively few data on the composition of wood tars are presently available.

Since the earliest analyses over a century ago, a number of analytical methods have been used in attempts to identify the components of wood tars. Techniques employed include infra-red spectroscopy (IR), thin layer chromatography (TLC) nuclear magnetic resonance (NMR), and High Pressure Liquid Chromatography (Heintzel 1880; Sandermann 1965; Hadzi and Cvek 1976). Such methods are not ideally suited however, to the unequivocal identification of the many individual components in complex mixtures, and thus have largely been superseded by combined gas chromatographic-mass spectrometric (GC-MS) methods. In such techniques gas chromatography is used to separate the individual components in the mixture, which are then identified on the basis of their accurately measured mass. The GC-MS technique is now the method of choice for analysing complex mixtures of organic chemicals such as wood tars (Robinson 1987; Reunanen 1989; Amen-Chen, 1997) and was therefore the method adopted in the present project. For further details on GC-MS techniques and their application to mixtures of natural organic materials the reader is referred to the work of Mills and White (1982) and more recently to that of Hayek and co-workers (1991).

The production of the tar samples has been described in the previous chapter. The sixteen tar samples analysed are listed above:

Sample Code	Description
TA-1	Gotland Tar
TA-2	Furutjara A (Fir Tar A-stub heartwood tar, Sweden)
TA-3	Dalbrandtjara (dal-burnt fir stubs/pinewood)
TA-4	Tratjara A (Wood tar A, oven burnt pure fir stub)
TA-5	Bjorktjara (Beech tar, oven burnt, veterinary use)
TA-6	Beech Tar (supplied by Teisens)
TA-7	Birch Tar (bark)
TA-8	Commercial tar (supplied by Skogens Kol AB, Sweden)
TA-9	Stockholm Tar (supplied by Battle, Hayward, Bowyer)
TA-10	Dried Sludge Tar (supplied by Waste Gas Technology)
TA-11	Scots Pine Tar (15 yr stumps, Thetford Forest, UK)
TA-12	as above-repeat pyrolysis
TA-13	Scots Pine Tar (5 yr stumps, Thetford Forest, UK)
TA-14	Corsican Pine (15 yr stumps, Thetford Forest, UK)
TA-15	Coal Tar (Fakenham Gas works, Norfolk)
TA-16	Dark creosote (retail sample, Homebase Ltd, UK)



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In drawing overall conclusions from the analytical data presented in Appendix Four, it is important to bear in mind that the final chemical composition of a tar sample depends on a number of factors including the nature of the starting biomass, the duration and severity of the pyrolysis process, the technology employed, the post-pyrolysis refining processes (if any) and the conditions and duration of storage of the tar so produced. Even minor variations in the conditions under which the tar is produced have the potential to effect changes in the composition of the final product. Considerable caution therefore needs to be exercised when comparing the chemical composition of one tar with another, particularly on the basis of relatively few samples.

Notwithstanding the above comments, the sixteen tars analysed during the present project have produced a considerable amount of useful data in tar composition and how this varies from sample to sample. The principal conclusions from the analytical data are as follows:-

- The two tars produced from 15 year old Scots Pine (*Pinus Silvestris*) stumps from Thetford during this project are very similar to tars traditionally made in Sweden from the same species e.g. Gotland Tar.
- Although the quantities of tar from 5 year old Scots Pine stumps (Norfolk) was less than from the more mature stumps, the composition of the tar produced was found to be broadly similar to that from the 15 year old material.
- The samples of tar obtained from the 15 year old Corsican Pine stumps were similar in composition to that from the Scots Pine. Corsican Pine, a tree commonly planted in Thetford Forest is thus a potential additional source of wood tar.
- The composition of wood tars is species dependent. Thus tars from beech, birch and pine analysed during the present project are quite distinctive, even though it is quite likely that the precise pyrolysis conditions used will have varied from species to species.
- Tars from different species within the same family (e.g. Scots Pine, Corsican Pine and Masson Pine) produce tars which, although similar in composition, appear to be distinguishable from each other.
- The tar from dried sewage sludge was unique amongst the samples analysed and the chemical composition of the product suggested that such tars might also be useful as wood preservatives

For further details and discussion of the chemical analysis of the 16 tar samples, the reader is referred to Appendix Four.

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Wood Tar

Chapter 6

Wood and Coal Tars: A Comparative Health Risk Assessment

A comprehensive health risk assessment even on a single chemical is rarely an easy assignment. The potential hazards to health will depend on the chemical, physical and biological properties of the substance, and the predominant pathways followed through the environment leading to human exposure. The transmission routes into the body, and the consequent impact on body organs and tissues will also determine the risks to human health

In the case of tars, comprised as they are of many hundreds of constituents, a complete assessment of the health risks arising from exposure to such complex mixtures is not at present an achievable objective. In such circumstances, the assessment is generally based on key active ingredients selected on the basis of their known toxicity or because they constitute a major component in concentration terms. Thus, for example, in the case of coal tar based creosotes, the levels of benzo(a)pyrene (a known carcinogen) and phenols (skin irritants and poisons) are used as product safety indicators. Chemical composition and level of exposure play key roles in determining the precise nature and severity of the health risks associated with exposure to particular types of tar. Duration of exposure also plays a significant part.

Some of the health impacts resulting from exposure to tars are short term (acute) whilst others are more characteristically long-term (chronic). In the sections that follow, these detrimental impacts will be reviewed and, where possible, related to the chemical constituents of the tars potentially responsible. The chapter concludes by considering strategies for minimising these health risks including compliance with the current health and safety regulations.

Acute toxicity of tars

The main classes of chemicals produced by the fast pyrolysis of wood are: organic acids, aldehydes, ketones, esters, phenols and furans and terpenes. If the pyrolysis temperatures are kept below around 500°C, the total amount of aromatic hydrocarbons in the tars is less than 1% by mass (PyNE 1997). Of these groups, aldehydes (formaldehyde, acrolein), furans (furfural alcohol) and phenols pose the greatest acute toxicity threat. The acute oral toxicity of such tars has been estimated (PyNE 1997) at around 700mg/kg body mass although no information is provided as to the test species used. Other acute toxicity tests indicated that, although the impact on skin was low, the eyes were particularly sensitive with probable corneal damage occurring from even low exposures. Lung damage was also reported, albeit at much higher concentrations. Such effects were attributed to the high content of organic acids, aldehydes and phenols in these tars. Although it is recognised that fast pyrolysis tars are quantitatively different in composition to the more traditionally produced tars, they contain a large number of the same compounds and are thus useful pointers to possible health hazards associated with the latter.

Similar acute effects on the eyes, mucous membranes and lungs have been documented for coal tar based creosotes (Ide 1996). Phenols are relatively easily absorbed through human skin and severe poisoning can occur as a result. Symptoms include nausea, vomiting and diarrhoea and, in gross exposures,



can be fatal. Dermal absorption of phenols from pine tars have also been reported (Schmid and Korning 1996) as being more pronounced than in coal tars, but it should be borne in mind that the concentrations of phenols in pine tars are significantly lower than in the coal based products.

Exposure of the skin to wood tars and coal-based creosotes can also result in acute irritations, which can be quite severe. If such skin contamination is followed by exposure to the sun's UV rays, a more serious condition, known as photosensitive dermatitis, may result. This condition, which can re-occur merely by further UV exposure, can be seriously disfiguring and difficult to cure. Recent work by Laaf and his colleagues (1992) has indicated that dermal exposure to wood tars can also cause severe skin irritations.

Chronic Toxicity of Tars

The long-term (chronic) health problem that causes most concern is the possibility that exposure to tars may induce cancer. Coal tars, and to a lesser extent wood tars, contain a range of polycyclic aromatic hydrocarbons (PAHs). Some of these such as benzo(a)pyrene (BaP) are known to cause lung and skin cancers in animals and probably in humans (IARC 1987). Although the levels of such carcinogens in wood tars are generally substantially less than those in coal tars, the possibility that the long-term exposure to wood tars could result in an increased cancer risk, however small, cannot be dismissed.

In this context, it is worth noting that medicinal ointments produced both from coal and wood tars have been used for many years to treat a wide variety of skin disorders including eczema and psoriasis. The practice of using of such products for medicinal purposes has, somewhat ironically, been shown to be potentially harmful especially if continued for long periods. The scientific literature contains a number of reports of skin cancers attributed to the prolonged use of ointments containing tars of various sorts. Thus, for example, Kushelev (1966) described a case of skin cancer resulting from the extended application of an antipsoric preparation containing 30% coal tar. Similar instances have been reported from the use of wood tars to treat skin conditions (Serkovskaya 1997).

Conclusions

The ultimate practical objective of any health risk assessment is to minimise exposure to the chemical or product in question and hence to reduce (or even eliminate) the detrimental health effects. As was emphasised earlier in this chapter, the achievement of this goal requires data from a number of areas including product composition, concentrations and toxicological activities of the active ingredients, principal environmental pathways and routes of human exposure and the nature of the interactions of the key chemical agents with target organs and tissues.

In the case of wood tars, the main groups of chemicals which are of potential concern are as follows:

- volatile aldehydes and furans
- phenols
- polycyclic aromatic hydrocarbons (PAHs)

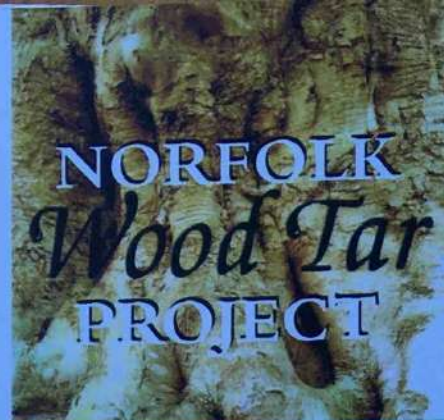
Of the above, the volatile aldehydes and ketones are present in very low concentrations in wood tars used as preservatives and would therefore not be likely to pose a significant risk to health in well ventilated premises.

The principal threat posed by the phenolic group stems from the relative ease with which such compounds are absorbed by the skin. These risks can, of course, be substantially reduced by wearing the appropriate protective clothing and adopting all necessary precautionary measures.

Wood tars generally contain relatively low levels of potential carcinogens such as benzo (a) pyrene. This, together with the low volatility of such compounds, suggest that the inhalation route is likely to pose a very low risk when such products are used under normal operating conditions. Dermal contact should, however, be reduced as much as possible.

In concluding this review of the potential health risks associated with the use of wood and coal tars, mention needs to be made of the role of the Control of Substances Hazardous to Health Regulations (COSHH 1994) in minimising the health risks associated with occupational exposure. These Regulations, which cover England, Scotland and Wales and which came into force in January 1995, apply to 'all very toxic, toxic, harmful, corrosive and irritant' substances and to all places of work. A useful summary of the Regulations is contained in the Pollution Handbook published by the National Society for Clean Air (NSCA 1999). Central to the regulations is the assessment requirement that an employer cannot carry on any work activity, which exposes employees to any hazardous substance unless a 'suitable and sufficient' assessment has been made. In the case of the wood tars, which are the subject of this report, this would involve assembling the sort of data detailed in the previous sections of this chapter and then putting in place the necessary working procedures to minimise exposure.

On the basis of the chemical compositions of the tar samples analysed during the present project, it would appear that wood tars used as wood preservatives are likely to pose substantially lower health risks than those based on coal tar. In view however of the complex nature of wood tars and the sensitivity of their chemical composition to the precise conditions used during their production, it is difficult to generalise. Ideally therefore health risk assessments of such materials need to be dealt with on a case by case basis.



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Wood Tar

Chapter 7

Legislative Aspects of Wood Preservatives

Control of Pesticides Regulations (COPR)

For the purposes of UK legislation, wood preservatives are classed as pesticides and therefore come under The Control of Pesticides Regulations (COPR) 1986 (SI 1510), as amended in 1997 (SI 188). Before any such chemical can be sold, supplied, stored, used or advertised it has to be approved under COPR. Approval is granted by the Ministers of the government department's signatory to the regulations. The registration process is carried out by the Ministry of Agriculture, Fisheries and Food (MAFF) and the Health and Safety Executive (HSE). MAFF is responsible for agricultural pesticides such as those used in agriculture, horticulture, forestry, food storage practice, animal husbandry and vertebrate control. The non-agricultural pesticides, including wood preservatives, surface biocides, insecticides for use in public hygiene areas, antifouling products etc., are the responsibility of HSE.

Under COPR, companies submit data such as environmental or mammalian toxicity studies, in support of product approval and the information supplied is used to carry out a scientific evaluation and associated risk assessment on the use of the product. This evaluation and risk assessment is then referred to the Interdepartmental Secretariat (IDS) and may then also be considered by the independent Advisory Committee on Pesticides (ACP). These bodies of experts make recommendations based on the submitted scientific assessment, and advise Ministers on the granting of approvals.

Each product approval is granted subject to specific Conditions of Approval, which are legal requirements and must be observed. These conditions are documented in the legal documents produced at the end of the approval application and are also reflected on the product label to ensure that it can be used safely with regard to both man and the environment. Following approval, products are subjected to an on-going review programme so as to ensure that the data on which approvals are based meets current safety standards. The costs of running the approval system are recovered through fees for each product approval and an annual levy on the UK sales turnover of approval holders. The levy presently stands at 1.2%.

Information on approved products is made publicly available by various means, including as mentioned above, the product label. Following the review of the pesticide active ingredient, or the first approval of a new active ingredient, a summary of the information considered by the committee is made publicly available. In addition, an annual publication is available from The Stationery Office, which lists all products holding an approval under COPR and also gives details of relevant legislation, the approvals process, any pesticidal ingredients that have been banned or severely restricted and lists the published evaluations available. The latest issue, Pesticides 1999, was published in June. Details of products approved since the latest annual publication went to print are published in monthly editions of the Pesticides Register.



The Marketing and Use Directive (M&U)

The Marketing and Use Directive was introduced in 1976 in order to harmonise restrictions on the use of certain hazardous substances across the Member States of the European Union. There have been numerous amendments to the Directive in order to introduce controls in the single market on groups of substances considered to present a risk to human health and/or the environment. Responsibility for the negotiation of these amendments on behalf of the UK rests jointly with three Government departments, namely: the Department of Trade and Industry, the Department of the Environment and the Health and Safety Executive.

Some wood preservatives known to contain active ingredients that are potentially toxic are subject to controls under the M&U Directive additional to those imposed under the COPR. Thus, for example, concerns regarding the carcinogenicity of creosote produced from coal tar were raised in 1994, when the use of the product in Europe were reviewed under Directive 94/60/EEC (14th amendment to M&U Directive). Although the decision was made to allow all existing uses of creosote to continue, the levels of the known carcinogen, benzo (a) pyrene (BaP), were restricted to <0.05% (500ppm) for industrial use and to <0.005% (50ppm) for professional and amateur use. In both cases, the water extractable phenols must not exceed 3%. For further details of the specification for creosote, the reader is referred to the current British Standard for Coal Tar Creosote for Wood Preservation (BS 144:1997).

Under the Directive, restrictions were also placed on the uses of coal tar creosote. Thus, wood treated with industrial grade creosote may not be used for children's playground equipment or food growing boxes. Creosote is not allowed to be used inside residential properties. To our knowledge, no controls and restrictions similar to those described above presently apply to preservatives or creosote generated from timber.

The Biocidal Products Directive

The Biocidal Products Directive 1998 (BPD) and associated Regulations, aims to remove barriers to trade in biocides by harmonising controls for the review, approval, marketing and use of such products throughout the European Union, whilst ensuring a high level of health and environmental protection. The Directive (98/8/EC) has now completed all its negotiating stages and the final text has been adopted by both the European Council and European Parliament. The importance and relevance of the Directive in the context of this report is that the new legislation will eventually replace COPR and thus the regulation of wood preservatives will come under the BPD rather than the COPR. The BPD has to be implemented in the Member States by May 14 2000.

A biocidal product is defined under the Directive as a chemical or biological substance or preparation used to control harmful organisms in situations other than to kill weeds or otherwise protect plants from pests. The Directive thus has a very wide scope: as well as non-agricultural pesticides currently dealt with under the COPR i.e. wood preservatives, public hygiene insecticides, masonry biocides etc, it also covers disinfectants and a number of other specialist products. The product types covered by the Directive are categorised into the following 4 main groups:





- Disinfectants and General Biocidal Products
- Preservatives
- Pest control
- Other biocidal products.

Wood Preservatives are listed as a separate category (Product Type 8) within main group 2 and are described as those used for wood from and including the saw-mill stage, and wood products (including both preventive and curative products). A full list of the 23 product types covered by the Directive has been published by the HSE (HSE 1997).

In order for the Directive to work, a list of biocidally active substances currently in use under existing legislation in the Member States will be required. The list from the UK, currently standing at 1500 entries, has been submitted to the European Chemical Bureau (ECB), and is expected to be available on the internet by the end of November 1999. Active substances on the list and products containing them will remain subject to the transitional arrangements of the Directive. This means, that, in the interim, wood preservative products in the UK will continue to be controlled under the COPR until all the active substances in an individual product have been considered under the BPD review programme. Any active substance not included on the above list will be considered as new and both it, and any product containing it, will have to meet all the appropriate provisions of the BPD before they can be supplied anywhere within the EU (HSE1999)

The UK proposes to implement the BPD by new Regulations, to be known as the Biocidal Products Regulations (BPR). These will be made under the Health and Safety at Work Act 1974 and the European Communities Act 1972. It is proposed that the main enforcing authorities for the BPR will be HSE and local authorities. Penalties for breaches of the BPR will be in line with other UK health and safety legislation. The BPR is expected to come into effect on 14 May 2000.

The precise impact of the new legislation on the wood preservative market is difficult to assess at this stage. Those general-purpose products already controlled under COPR are likely to have been transferred to the provisional list of biocidal active substances under the new Directive. However, as the HSE have acknowledged (HSE 1998), it is possible that there may be some existing active substances on the UK market that have not yet been submitted to the ECB. This may apply particularly to 'niche market' products such as traditional wood preservatives that are used in relatively small quantities.

Chapter references

BS 144 (1997)
Specification for Coal tar creosote for wood preservation (as amended in April 1998)
British Standards Institution, London

Health and Safety Executive (HSE) 1997:
Biocidal Products Directive, 98/8/EC: Fact Sheet No. 1

Health and Safety Executive (HSE) 1998:
Biocidal Products Directive, 98/8/EC: Fact Sheet No 3

Health and Safety Executive (HSE) 1999:
Biocidal Products Directive, 98/8/EC: Fact Sheet No 4.

Wood Tar

Chapter 8

Market Research

The UK market for brush applied timber preservative is somewhere between £30 & £35 million pounds per annum.

All the main timber preservative manufacturers in the UK were approached to ascertain from them their attitude towards a new product and to get from them an idea as to the size of the UK market. The companies approached were:-

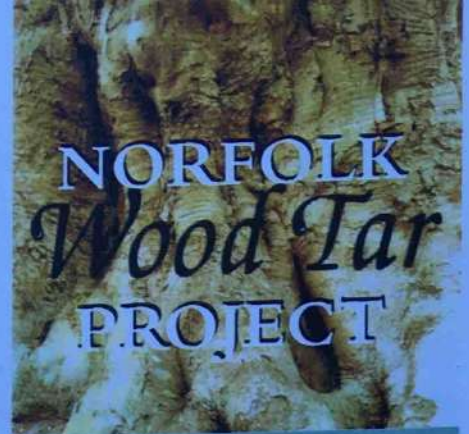
- Dulux ICI Paints
- Protim Solignum Ltd
- Sadolin-Akzo Coatings plc
- Ronseal Ltd
- Cuprinol Ltd
- Hicksons Ltd

Cuprinol were particularly helpful and indicated the market for creosote type products (which might in the future include wood tar), to be in the order of £5m per annum and for waterborne preservatives, some £20m per annum. Whilst Hicksons recognise the increased requirements of the Biocidal Products Directive, they were of the opinion that established manufacturers could easily provide the additional information required.

The hardware buyer at B&Q was very positive about the possibility of selling wood tar, especially if the environmentally friendly nature of the product could be emphasised. As he felt it would be more likely to succeed if it was part of an already established range, it would be helpful if one of the other 'players' in the field were to co-operate in marketing. B&Q have brokered similar partnerships in the past.

At a recent Sustainable Building Day at Waxham Barn in Norfolk, an opportunity presented itself for some of the wood tar samples to be presented to the general public. Over 1000 people attended the day and there was a lot of interest in the wood tar samples displayed, not just from the public but also from companies engaged in marketing and selling 'environmentally friendly' materials connected with the building trade.

One such company, Eco-Merchants from Kent were particularly interested and have been to Norfolk to discuss the availability and supply possibilities for wood tar. Their customers are people who tend to have a heightened awareness of environmental issues generally and the company feel that if such a product could be made available in reasonable quantities, then it would prove popular with their client base.



Chapter references:

Dulux,ICI Paints,
Wexham Road, Slough, SL2 5DS
01753 550555 www.dulux.com

Protim Solignum Ltd,
Fieldhouse Lane, Marlow, Bucks
01628 486644

**Sadolin - Akzo Nobel
Woodcare,**
Meadow Lane, St Ives, Cambs
PE17 4UY
01480 496868/01480 496801
woodcare@stives.deconorth.com
www.akzonobel.com

Sikkens - Akzo Coatings plc,
99 Station Road, Dicot, Oxon
OX11 7NQ
01235 815141/01235 819508
(see website above)

Ronseal Ltd,
Thomcliffe Park, Chapeltown,
Sheffield, S35 2YP
0114 246 7171/0114 245 5629
www.ronseal.co.uk

Cuprinol Ltd,
Adderwell, Frome, Somerset
BA11 1NL
01373 475000/01373 475050
(now ICI)

Hicksons
01977 671771
Dr David Aston 01977 556565

Conclusions

- The first conclusion to make is that it is now established that within the Thetford Forest area in Norfolk there are considerable reserves of mature stump material both of Corsican and of Scots pine.
- Wood tar of comparable composition to that traditionally produced in Sweden and elsewhere can be produced from Scots pine in this country.
- Corsican pine stumps (which are now the principal tree planted by the Forestry Commission) will also yield a wood tar comparable to that produced from Scots pine.
- Our experiments show that wood tar can also be obtained from less mature source material.
- The tar from dried sewage sludge appears to have similar preservation properties to those found in creosote.
- The project has demonstrated that tars of a comparable nature to those currently imported into the UK can be produced locally.
- There is large market for timber preservatives in the UK and a growing interest in sustainable products of this kind.

Proposals

The project to date has clearly demonstrated the viability and desirability of producing wood tar in this country, particularly where the resource is a waste material. The proposals listed below will enable further work to take place that will build upon the achievements of this LEADER II project.

1. That a pilot plant based on traditional designs be set up in conjunction with EcoTech and Forest Enterprise at the site in Swaffham to enable high quality wood tars to be made from locally available wood resources.

This proposal will have several immediate benefits:

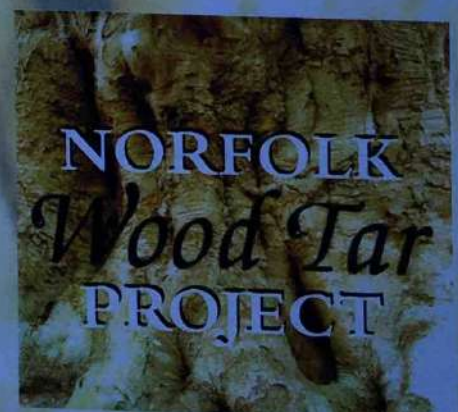
- It will highlight the production and uses of materials made from waste products.
- It will enable further work to take place to determine the appropriate pyrolysis conditions for producing the desired consistent product.
- It will broaden the base for EcoTech and be a valuable educational resource.
- In the shorter term the tars produced may help those engaged in the preservation of historic wooden ships, boats and other structures.

2. The project has shown that there may well be a use and a market for tars from other sources too, such as the dried sewage sludge tested.

Further work is strongly recommended to demonstrate the valuable potential of these tars.

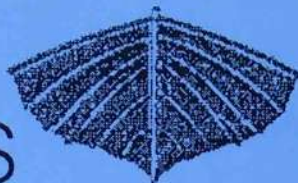
3. Further links need to be established between those involved with wood tar manufacture in the future and with those others working in the pyrolysis field today, including in particular those in the PyNE organization (see Glossary for further information and contact details), so that information can be disseminated more easily.

4. Urgent discussions should take place with the Building Research Establishment (or other similar research organisation) to further test the efficacy of wood tars (and other tars from alternative sources) as timber preservatives.



APPENDICES

CLAESSONS



TRÄTJÄRA

PRODUKTER FÖR SKEPPSBYGGARE OCH SKUTÄGARE, FÖR MARINT BRUK, BYGGNADSVÅRD
RENOVERING OCH RESTAURERING — SKYDDAR OCH KONSERVERAR



PRODUKT- & PRISLISTA 1999-1

NYHETER

HÖRLE BRUKS RÖDFÄRG — äntligen har vi hittat en traditionell **slamfärg** som uppfyller våra krav. Slamfärgen från Hörle Bruk finns i klassiskt ljus röd samt i ett antal traditionella kulörer — ljus ockra, kromoxidgrön, blått, grått och vitt. Färdig slamfärg i 12-liters plastspann.

LE TONKINOIS — trä och metallskydd på ren linolja utan kemiska tillsatser. Traditionell **linoljefernissa** av högvärdig linolja som kokats vid 270°C och med tillsats av Tungolja, fri från aromatiska, eteriska, klorerade eller skadliga lösningsmedel. Mycket bra golvfernissa!

MARINKITT — armerad, gummiförstärkt nåtmassa, spackelkonsistens har återkommit i vårt sortiment. Lättarbetad, mjuk och god vidhäftning.

KALKFÄRG SPECIAL — gör det enklare att kalkavfärga puts — 2 strykningar.

Lite tjärhistorik

Kolning är känt från början av järnåldern. Äldre "tjärfynd" är bl.a "Guldhøje Klapstole", daterad till ca 1400-1200 f.Kr. Skeppsfynd, som "Nydamskeppet", visar att man tidigt började behandla med tjära för att skydda och bevara rötkänsliga material. Vid tiden för de första kyrkobyggena i Norden var redan tjärtekniken högt utvecklad och man kan ju än i dag se resultaten av denna behandling på bland annat de norska stavkyrkorna som stått emot tidens tand i snart 1000 år med mycket glea underhållsintervall.

Trätjära har sedan medeltiden under långa perioder varit Sveriges tredje största exportvara och under 1600-talet tidvis den största exportvaran, speciellt då det stora skeppsbyggeriet i Europa medförde stor efterfrågan. Först mot slutet av 1800-talet minskar tjärans betydelse som exportvara, inte huvudsakligen på grund av "...mindre omsättning å världsmarknaden, utan derpå att öfriga tjärproducerande länder tillägnat sig bättre metoder som gifva en utmärkt vara...".

Kåda, hartssyror, är trädets sätt att skydda sig och reparera skador. Terpener är trädets eget lösningsmedel till kådan, bland annat för att underlätta stigningen i trädstammen och även för att påskydda oxidationen, förhartsningen när kådan tränger ur stammen.

Den bästa råvaran till tjära är gamla furustubbar, brutna ur sandig, stenrik mark. I stubbarna anrikas kådan efter det att trädet fällts och kan efter 10-80 år, beroende av klimatzon, uppgå till en mycket stor andel av stubbens vikt. Dessutom förmultnar ytveden och enbart en kådrik kärna, töre, finns kvar.

Efter det att törestubbarna är brutna, veden kapad, kliven och torkad vidtar själva bränningen. Tjårdalen byggs vanligen upp som en kon av granslanor som täcks med näver och slutligen täcks med lerjord för att bli tät. I botten placeras "skon" där tjäran samlas för att när tjärtappen dras ur rinna i en ränna till tjärfaten. Nästa steg är att lägga in veden efter givna mönster i dalen och att klubba veden. När veden bildar en kulle av rätt storlek täcks den först med spinkved som tjänar till att få igång förbränningen. Efter detta täcks dalen med torv, mossor eller jord för att bli lagom lufttät.

Bränningen startas med att veden antänds vid kullens bas runt om dalen genom hål i täckningen. Förbränningen regleras sedan med hjälp av att öppna och stänga dessa lufthål samt att man klubbar dalen under tiden. Elden skall jämt sprida sig i det yttre skiktet till kullens topp för att sedan långsamt sprida sig nedåt inåt i dalen. Tjärbrännaren måste hela tiden reglera lufttillförseln utifrån de tecken dalen ger ifrån sig i form av rökens färg, hastigheten och senare färgen och viskositeten på tjäran. Det är först när förbränningen nått in i dalen som tjäran visar sig, först i form av "pärman", tjärvatten, för att snart övergå till den bästa rena ljusa tjäran. Mot slutet mörknar tjäran och blir trögflytande beaktad.

Efterbehandlingen av tjäran bestod i "vräkning" och sortering av tjäran vilket utfördes vid "tjärhofen". En form av kontroll var att sticka ett blankt järn i tjärtunnan och med ledning av utseendet hos de olika delarna av tjäran bestämma kvalitén. Fin, ordinär och grov eller prima, sekunda och tertiär var använda klassificeringar.

Trätjära har haft stor medicinsk användning, både för invärtes och utvärtes bruk. Än idag används trätjära som aktiv beståndsdel i hudsalvor och till veterinära ändamål brukas tjäran i ren form till sårbehandling och även som förebyggande "hudsalva".

Som slutord vill vi använda landets främste "tjärforskare" Hilding Bergströms ord som efter att ägnat ungefär ett halvt sekel åt studier av kolningsprodukter sammanfattar tjärans provning med:

För bedömning av kvaliteten på såväl trätjära som terpentinjära finns ej några allmänna använda analysmetoder. Således bedömes tjäran mest efter yttre egenskaper. Ett av tjärbrännare ofta använt prov består däri, att tjäran utstrykes på en hyvlad träyta, då tjärans färg, konsistens och torkningsförmåga kan iakttagas, liksom även om tjäran är fri från vatten eller ej".

Lite tjärhistorik

(A historic look at wood tar production in Sweden)

Charcoal burning is known to have taken place from the start of the Iron Age. Old tar finds have been made at "Guldhøje klapstole" dated to about 1400 – 1200 BC. Ship discovery sites such as "Nydamsskeppet", show that the practice of using tar as a means of protecting and preserving from wood-rot began many years ago. The tar technique was already well developed when the first church buildings in the Nordic countries were constructed and it is possible today to see the result of this treatment. The Norwegian stave churches have stood against the wear of time over a period of almost 1000 years despite very long maintenance intervals.

Wood tar has been Sweden's third biggest export product during long periods of time since the middle ages. Within the 17th century it was at times the biggest export product - a period in history when ship building in Europe placed large demands. It is first during the end of the 18th century that wood tar as an export product lost its significance. This was not so much due to reduced use on the world market, but due to the fact that other tar producing countries had refined their tar producing methods and produced a higher quality product.

Resin and resin-acids are means for wood to protect and repair damage. Terpene is the solvent for the resin that is also naturally present in wood. Amongst other things it allows a freer rising of sap within the tree stem and a quicker oxidation and hardening of the resinous substance when the resin seeps out of the tree stem.

The best raw materials used for the production of wood tar are old fir stumps broken from sandy, stone rich ground. The resin becomes enriched after the tree has been felled and can after a period of 10-80 years – dependant on the climate zone – reach a level equivalent to a very high percentage of the total weight of the tree stump. At the same time the outer wood rots and only the resin-rich heart and resinous pinewood remains.

After the resinous pine stubs have been pulled up the wood is cut, divided and dried before the burning takes place. The tar pile is usually built up as a cone of fir that is covered, first with birch-bark and then with clay soil, in order to give a tight surface. At the bottom of this a "shoe" is placed to collect the tar before the plug is pulled and the tar runs through a channel into the collection barrel. The next stage is to place the wood in a given pattern in the pile and to club the wood. When the wood has formed a pile of the right size it is first covered with easily burnt wood "swedish - spinkved" which will enable an easy start to the burning process. The pile is then covered with peat, moss or earth in order to be properly airtight.

The burning is started by lighting the wood around the base of the pile through holes in the pile covering. Closing and opening these air holes while continuously clubbing the pile will then regulate the burning. The fire should spread itself over the outer layer from the bottom up and then slowly burn through the pile inwards and downwards. The tar burner must continuously regulate the burning by way of the air holes in accordance with the signs that the pile gives in the form of the colour and speed of the smoke and later the colour and viscosity of the tar. It is first when the firing has reached the center of the pile that the tar starts showing itself, first in the form of tar water (Swedish - "pärman") which is soon replaced by the best, pure, light tar. Towards the end the tar becomes more viscous and pitch-like.

The after-treatment of the tar comprises eviction and sorting of the tar - a process that is carried out in the "tjärhof". One form of control is to stick a polished iron pole into the tar-barrel and by noting the covering of the different parts of the pole decide the quality. Fine, ordinary and coarse - or prime, second and tertiary were the classifications used.

Wood tar has a big medical use, both for ingestion and for external use. Even today wood tar is used as an active part of skin lotions and within veterinary circles a pure form of tar is used for treatment of sores and even as a preventative skin salve.

As a final word we would like to quote Sweden's main tar researcher Hilding Bergström. He has spent half a century studying the products of the coaling process and sums up the testing of the quality of the tar in this way:

The quality of both the tar and the terpentine-oil cannot be judged by generally used analysis methods. Therefore the tar is mostly judged after outer characteristics. A method mostly used by tar burners is one whereby the tar is brushed along a smooth wood plank so that the colour, consistency and drying capacity can be observed. At the same time it is possible to observe if the tar is free from water or not.

Examples of wood tar available in stock 1999:

Product	Per liter	Barrel-liter/SEK	25-liter/SEK	5-liter/SEK
<i>DALBRÄNDTJÄRA</i> - Dal-burnt tar handicraft produced dal-burnt using fir stubs, resinous pinewood, Swedish	Day's price	SEK 49.40:-	Sek 55:-	Sek 60:-
<i>FINTJÄRA</i> - Fine tar dal-burnt extra pure and light fir stub tar, syrup consistency, golden yellow	Day's price	60:-	66:-	74:-
<i>FURUTJÄRA A</i> - Fir tar A stub heartwood tar, dal-burnt type, easily thinned and low water content, brown		25.20:-	32.80:-	40:-
<i>TRÄTJÄRA A</i> - Wood tar A oven burnt pure fir stub tar, high resin content, varied red-brown, most often difficult to thin		22:-	28.20:-	36:-
<i>TRÄTJÄRA B</i> - Wood tar B oven burnt pinewood tar, high resin content, dark brown, difficult to thin		19.60:-	25.20	33.40:-
<i>BJÖRKTJÄRA</i> - Beech tar oven burnt, veterinary use, dark brown/black		23.20:-	30:-	38.80:-
<i>BALNDTJÄRA</i> - Mixedwood tar oven burnt using fir and leaf tree wood, veterinary use, dark brown/black		21.40:-	27.40:-	35:-
<i>SPECIALTJÄRA</i> - Special tar of pine wood, refined, freeflowing, easily thinned, light mid-brown		19.20:-	25:-	33:-
<i>BÅTSMÖRJA</i> - Boat grease "Roslags mahogany" - blend of fine tar, raw linseed oil and balsam terpine		36.40:-	42:-	50:-
<i>BRYGGSMÖRJA</i> - Pier grease blend of fir tar, raw linseed oil and balsam terpine		23:-	28.60:-	36.40:-
<i>BECKOLJA</i> - Beck oil old Norrland mosquito deterrant of dal-burnt tar	* 16 bottles/25ml			34:-
"NORDIC SUMMER" - "Nordic summer"back oil, djungel oil and "tjukolja" in paste	*20 jars/40g			38:-
<i>BECKOLJEBLANDNING</i> - Beck oil blend of dal-burnt tar, rape oil etc. for animals	*12 bottles/0.5l			164:-

APPENDIX 2

English Translation from Swedish Publication on Traditional Tar Burning

Tar burning

By: Fredrik Westman

Preface

This folder presents knowledge about the fine craft of distilling tar. At the same time I will show how it is possible to produce this natural impregnation medium in a simple way.

A few of the old trade expressions contribute to the atmosphere around the tar production.

However, the right atmosphere can only arise after the pile has been lit and the tar-fragranced smoke lies heavily over the forest in the cool of the midsummer evening.

Good luck!

Fredrik Westman

About tar production

Tar is reckoned as one of the Sweden's most important exports during the 17th and 18th centuries.

The tar production reached its peak during the middle of the 1850's, with a gradual decline over the following years. However, it was still an important commodity in the mid 1880's.

The decline was primarily due to the new materials which were entering the market and which did not need tar for impregnation. Another reason was the decreased use of rope and hawser as the sailing ships were replaced by steam. Pit tar of high quality was in fact the only effective impregnation medium within rope making.

Until the end of the 19th century, farming, forestry and fishing were the most important industries in Sweden. Market economy had not yet been introduced and people lived on their own produce or on the exchange of products. Each household therefore had a limited possibility of acquiring cash. Tar distilling was one of the many sidelines that could give an extra income. During some years, i.e. when the harvest was bad, this extra income was of vital importance. It is possible to discern this when reading the old account books from the bad Swedish harvest years of the late 1830's.

Compared with the production of nitric acid and potash, tar distilling as an extra income was not so lucrative. It is believed that the work input was 10 working days for one barrel of tar.

However, even if the profitability was relatively bad, it did give the people work. Apart from the handling of the tar wood and the actual distilling process, labour was needed for the transportation of the barrels. This was partly carried out by land and partly by rafting.

When rafting, 100-200 barrels were bound together to form a large raft. This was then rafted down to the storage place, the so-called tar court. The rafting was very dangerous, and it took a skilled crew of rafters to coax the raft over rapids and still water.

If the waterfalls were too big, the rafts had to be dismantled and the barrels manhandled past them.

At still water the crew would row the raft forward.

The handling of tar therefore created a variety of occupations. The extra income derived in this way was often of very great importance, especially for the part of the population who did not own and farm their own land, i.e. crofters.

Tar is distilled even today, but the tar pits are few and far between. Times have changed. On calm evenings in yesteryear, round about midsummer time, old and young alike would meet in an atmosphere of festivity when the tar piles were fired. Now the same places are desolate and covered by thick forests.

However, the toll of time has not managed to destroy the tar channels. They still lie there, well impregnated and reminding us that, after all, tar is an excellent impregnation medium.

Resin-acids in tar wood

A pine contains several low-viscosity resin-acids that flow in the "veins" of the tree.

When a pine is felled, this flow is stopped leading to a concentration of resin-acids in the tree stump - not so much in the outer layers but mainly in the core of the stump and below ground level.

Since the outer layers of the tree and the small roots contain little protection (resin-acids) against rot, most of these parts will have rotted away within 15 - 30 years. This makes it much easier to tear up the stumps and remove the surface wood.

This is the time to "harvest" the stumps, to chop them and dry them.

It is still unknown why the resin-acids are concentrated to the stumps. One theory is that it has to do with the tree's protective mechanism. The same thing occurs when a pine is damaged by "törskatesvam" - so called tar-sting "*tjärgadd*" when resin-acids collect at the damaged part, which can very well be used for tar wood.

It is also possible to deliberately damage the pine by barking it a few meters above ground level, leaving a narrow strip towards the north. This method, called "*katning*", was used before but is now forbidden by law.

It is also possible to extract tar from spruce the yield will be smaller. However, from a chemical point of view, pine tar is identical to spruce resin.

The firing of the tar must take place using a limited air supply - otherwise the tar pile would burn up. Through the heat, the resin-acids are distilled from the wood. At the same time, there is a chemical reaction changing the free flowing resin-acids into the more viscous tar, which will eventually enter the tar channel ("*tjärrännan*").

If the tar pile is too hot, the chemical reaction will go too far resulting in very viscous and pitchy tar. On the other hand, if the temperature is too low, the resin-acids will have time to evaporate, giving a reduced yield.

Since the firing takes place using only a limited amount of air - so called dry distillation - all the wood is not burnt but turns into charcoal. The tar pile produces approx. 15 % charcoal and 4-5 % tar reckoned on the original volume of wood.

It is important to get the landowner's permission before taking stumps and peat. The landowner also has to be consulted about the location of the tar pit. The fire brigade must be contacted when the pile is to be fired.

Mini tar pile

The tar-wood is taken from 15 - 30 year-old pine stumps that are sawn and chopped to a suitable size. The part containing the most tar is the sturdy root that leads vertically straight down into the ground. The parts above the ground level, particularly the upper parts, contain less tar but can nevertheless be used. The small roots - on the other hand - contain very little tar.

Pine stumps can be found on clearings that are 15 - 30 years old. Enquiry around can give the age of the clearing but it is also possible to count the number of branch tiers on the new pines. A new tier of branches is formed each year.

The ground should preferably be hilly and stony. However, reasonably good tar stumps can even be found in sandy ground. Boggy ground and marshland should be avoided. Stumps found here mainly produce so called *tar-water*.

A pointed iron lever, spade, axe and saw are needed to break up the stumps.

The stumps should then be sawn and chopped into pieces that are 10cm long and 2cm thick.

The rotted outer wood must be removed and can be used to start the firing process. When the tar wood has dried (taking about a week in room temperature) the process of building the mini tar pile can be started.

When constructing a full-size tar pit, roofing shingles are used as a base for the tar wood.

When constructing a mini tar pit it is however more suitable to use plate metal. Otherwise it is very difficult to achieve a completely airtight pile, which is vital.

Cut the thinnest grade of plate metal to a 1m square. Find the centre of the square.

Measure out the largest possible circle on the square.

Cut out the circle with a pair of metal shears.

Now make a funnel. Cut the plate from the periphery (the outer border) to the centre point of the circle.

Let the cut ends overlap until a cone is formed with an angle of 130°

Rivet the cone tightly so no tar can run through the joint.

Drill a hole, 6mm in diameter, through the point of the cone.

The volume of the cone decides how much wood can be stacked there and thereby how much charcoal and tar can ultimately be extracted. If you cannot calculate this yourself perhaps it is possible to get help.

The shoe

Saw off two 30cm long wooden planks with a width of 10cm and a thickness of 5cm.

Plane off one side of each plank so that it is completely smooth leaving no gap if these two sides are placed against each another.

Hollow out a channel in the smooth side of each plank to a depth of 2cm and a width of 2cm. This hollow must not extend all the way to the short ends of the planks.

Drill a 10mm hole down to the hollowed out channel in one of the planks.

Carve the hole out with a knife so that the plate metal cone fits the now conical hole.

In the other plank drill a 10mm hole from the short end to the hollowed out channel as shown in the illustration.

Cut a notch from this hole to channel the flow/drops of tar.

Nail the two halves together sealing the joints with paste or glue.

The plugs

Make two plugs, approx. 7cm long, which are to fit exactly into the hole where the tar leaves the shoe.

The *tightening plug* shall block the hole completely. Air must not be allowed to enter the tar pile by way of the shoe.

In the other plug, the *tar plug*, a groove must be made on the underside so that, when the tar runs out, the groove is filled with tar and preventing air from entering the pile.

The tar channel

Saw off a 70cm long plank with a width of 10cm and a thickness of approx. 5cm.

Hollow out a 2cm wide and 2cm deep channel. This channel must not extend to the ends of the plank.

Drill a 10mm hole from the underside of the plank down to the channel joining it just before its end. This channel shall eventually be placed in such a way so that the tar running from the groove in the tar plug that is attached to the shoe runs down to this channel.

The other end of this tar channel (the end with the 10cm hole) is placed over a barrel or another vessel in which the tar can be collected.

The fundament for the mini tar pile

Dig a hollow in a slope that is sheltered from wind. The hollow shall accommodate half of the metal cone while the other half shall lie free of the slope.

The exposed part of the cone must be supported by planks, so called far wood ("*Sw. Farved*"), which lie across ribs fanned out from the point of the cone. These ribs must be held in position by supporting poles.

Earth (preferably clay-bound) shall then cover the planks and be pounded flat.

In this way a conical earth funnel has been made - on the one side formed by the hollowed out slope and on the other side supported by a wooden construction.

The edge of the earth cone must extend at least 2dm further than the edge of the metal cone.

Dig away earth from below the point of the cone to accommodate the placing of the shoe.

Make sure that a hole exists at the bottom of the metal cone.

The mounting of the metal cone, the shoe and the tar channel

When mounting the metal cone on the shoe it is important to make sure that earth does not block the entrance to the shoe.

Place the metal cone in the earth funnel so that the open point is pushed through the hole at the bottom of the funnel.

Fill up with earth so that the metal cone fits tightly in the earth funnel and the cone is well supported.

A tight insulation material (e.g. rockwool) must be used before aligning the hole at the point of the metal cone with the hole in the conically carved upper part of the shoe.

Pack earth around the shoe so that it sits steadily. It can be covered almost up to the tapping hole.

Check that no scrap is blocking the shoe by pouring a small amount of water into the metal cone.

Put the tightening plug in place.

Mount the tar channel and a vessel for collection of the tar.

The laying of the mini tar pile - (Sw. "Bära ned tjärdalen")

First of all, place a 3dm long wooden pin carefully in the hole at the bottom of the cone.

Place a layer of relatively straight tar wood in a fan-shape around the pin.

Stack a 1dm cube, (Sw. *töreln*), of small tar wood bits around the pin.

Carefully pull out the pin.

It is now time to build up the so-called main cushion. Use lower grade tar wood as this will to a great extent be burnt up in the firing process.

The main cushion is built up by laying the wood just outside the upper edge of the metal cone. Each piece of wood shall lie in the same direction of the tangent, i.e. following the border of the metal cone.

Place a new layer across (at right angles to) the first layer. In this way a small firing place has been constructed (A) whereby it is possible to set fire to the tar pile.

Continue by placing the tar wood to cover the whole of the metal cone pointing towards the centre of the cone in a fan shape. Remember also to place the tar wood over the main cushion so that an even, round border is formed around the whole of the tar pile.

The wood must be carefully stacked so that the tar pile contains as little air as possible and as much tar wood as possible.

When the stacking is completed, the pile must be even and round. If any wooden piece sticks out it must be beaten into place by means of a wooden club or similar.

At the top of the pile, tar wood splinters and chips are placed (these were formed when splitting the wooden stumps).

The sealing of the tar pile

A 5cm layer of forest peat, preferably not sandy, shall cover the tar pile. Each peat block shall measure 50x50cm.

It is easiest to dig up these peat blocks using a prechopping axe (Sw. "*förhuggaryxa*") and a claw digger (Sw. *klogräv*), but an ordinary spade can also be used. It is important to

remember to dig up twice as much peat as is needed for the sealing of the pile, because some of the peat is destroyed during the burning process and must be changed out.

During the sealing of the pile the peat is packed tightly so that only a little air can penetrate. The green peat surface should be facing downwards.

A 5cm broad ring must be left free from peat at the outer perimeter of the pile, all around the tar pile. This ring is called the firing shot (Sw. "eldskottet").

Make sure that you have a supply of earth to shovel onto the pile when necessary. Damp sawdust can also be used.

The firing of the tar pile

Glowing charcoal is preferable when firing the tar pile, but even glowing or burning wood can be used. Always have water readily available.

Light a small fire a few metres from the tar pile and let the fire burn fiercely. If charcoal is available then this should be placed on the fire until it glows.

Lift back the whole of the bottom row of peat blocks with a wooden pin supporting each block.

Place burning wood or glowing charcoal at the firing place underneath the main cushion around the whole tar pile.

When the tar pile's wood has started to burn the peat turf is lowered into place again and the firing shots are gradually closed as well except at 4 places where 3x3cm openings are left.

Peat should be used to close off the firing shots. At a later stage of the firing process earth can be shovelled into place to tighten the pile.

The distance between the openings should be approximately the same.

Remember that, dependent on how the firing has succeeded, the tar wood can burn very intensively. If this happens, the oxygen supply to the fire must be quickly choked to prevent too much of the tar wood from burning up.

The burning of the tar pile

The burning of the tar pile shall proceed in two stages.

During the first stage, a rather careful monitoring must take place until the firing has reached the top of the pile.

When the second stage starts - meaning a burning through the pile - a slightly faster burning process can be used; it is now that the tar will start appearing. In a small tar pile however, the tar can start to run even during the first phase.

During the firing, it is important that no wind blows on the tar pile, as the burning becomes more intense due to the increased oxygen input on the windblown side of the pile and the burning becomes uneven - it misfires. If it should start blowing once the pile is lit then a windshield of some sort must be erected.

The first phase of the burning process

When the ignition of the pile has been completed, it is important to carefully adjust the size of the openings so that the fire spreads at an optimal speed.

A sign that the burning process is too intense is dark smoke, meaning that the tar is burning. White smoke means that it contains steam. The smoke should preferably be a blue-white colour.

To ensure an even burning process within the whole pile, the four first openings can be closed and four new openings can be made.

The level that the fire has reached can be measured by observing where the smoke leaves the pile.

One way of ensuring that the fire works its way up the pile is to tread gently or beat the peat covering about 25cm below the site where the smoke is leaving the pile. A crushing sound will indicate that charcoal has been formed and that the fire has passed that point.

When the smoke has reached the top of the pile, the time has come for the burning process to move into another phase as the fire spreads deeper down into the pile. (Sw. "*ta om tjärdalen*")

During this phase, the tightening plug should be taken out after about 45 minutes to see if the distillation process has started and the tar has started to run. If this is the case then it is time to change to the tar plug.

The second phase of the burning process

When the smoke has reached the top of the pile the air inlets can be opened somewhat to allow more air to enter the pile. It is important to move the location of the inlets continuously. This is the stage where the main distillation of the tar takes place. Continuous monitoring must ensure that the smoke does not become too dark.

It is even possible to monitor the burning process by observing the character of the tar. A free flowing tar means correct temperature. Viscous, pitchy tar tells that the tar pile is too hot.

During this stage of the burning process it is important to keep the pile in good repair using earth, damp sawdust or peat turf. The fire must not be allowed to break through the peat covering, only the smoke must do that.

As the burning process continues, tar is not the only resulting substance produced - charcoal is an equally important product. The size of the pile decreases and an on-going process of treading or beating the peat surface is necessary. The surface will then sink inwards and downwards while a crushing sound is heard from the charcoal.

The smothering of the tar pile

A few hours after the tar has ceased to run, the tar plug must be removed and be replaced *carefully* by the tightening plug.

If the burning has been successful, only a small mound of the original tar pile will remain.

It is now time to set in the charcoal stroke (the shut down) (Sw. "*kolastöten*"). This means that earth or damp sawdust must be shovelled over the pile and be trodden down so that the flow of air is stopped and the burning ceases.

The tar pile must now be monitored several times a day during a three-day period until the charcoal has finished burning and cooled down.

Then the earth and the peat can be removed. If the burning process has been completely successful, excellent smithy charcoal, (Sw. "*Dalkol*"), will remain at the bottom of the metal cone.

A full-sized tar pile

If the mini tar pile was successful, it is perhaps time to move on to try making a larger tar pile made in the old fashion.

A description of how this can be accomplished follows here. When it comes to the instructions for the different steps in the process, a reference must at the same time be made to the instructions given previously in relation to the mini tar pile.

Stump collection

The raw material, the pine stumps, are preferably collected during the autumn before the earth becomes frozen.

When pulling up the stumps, a pointed iron lever, spade, axe and saw can be used or a stump puller. The most rational method is to let a forest tractor pull up the stumps. A method used in times gone by was to blast up the stumps using explosives.

Splitting and drying

After pulling up the stumps, they must be transported to the place where they will be used for the burning (the tar pile location). There they must be pre-cut into larger pieces ("*lompas*"), preferably during a cold winter day, as they will split easier then.

Towards the spring, a second splitting must be carried out, ("*spöning*") when the wood is finely split in lengths of 40-60cm and a thickness of about 5cm. During this process the rotted wooden parts and earth are removed.

Following this process the wood must be graded in two different qualities. The better quality is composed of straight tar-rich wood.

Then, the wood is piled and dried until around midsummer, when it is time to construct and burn the tar pile.

The tar pit

The tar pit, half of which consists of a funnel-shaped timbered base, is located on a hillside where it is dug in. The tar pit position should be chosen so that it is close to a water supply.

The tar pit - base for the tar pile

The tar pit must be prepared as a circle with a diameter of 4-12m, dependant on the planned production volume.

The free-lying part of the pit shall be timbered using ridges that fan out from the pointed base of the pile. The ridges shall stand at a 25° angle to the horizontal plane. Each ridge must be held in place by 3 - 4 supports.

Wooden planks or boards (Sw. "*farveden*") must be laid across the supporting ridges. If it is difficult to construct a completely tight surface, a layer of birch-bark can be added.

A layer of clay-bound earth should then top off the birch-bark covered boards. This should be pressed into position by treading on it so that the whole of the base of the pile is completely tight.

The shoe and the tar channel

The shoe should be positioned at the lower point of the tar pit construction. It shall be constructed in such a way that it allows the tar to leave the pile while air is locked out. ONE way is to drill two holes at a 90° angle to one-another through a log, and to place this log at right angles to the direction of the tar channel.

Two plugs must fit the opening in the shoe, a tightening plug and a tar plug. The tar shall run from the shoe, into the tar channel and further into a barrel.

The laying of the tar pile - ("Bära ned tjärdalen")

Just before the burning is commenced, the bottom part of the tar pile must be covered with wet roofing shingles. These should be laid like tiles on a roof, working from the bottom and upwards (one row laid clockwise, the next anticlockwise etc). The overlapping of each shingle should be approx. 5cm.

The topmost layer should overlap the layer beneath by at least 10cm. Gently bend each shingle before placing it down to make sure that the fibres are pointing downwards and inwards towards the hole leading to the shoe. The completed work should look like a big fan-shaped construction with the pointed base of the tar pit as the epicentre.

As it is today difficult to get hold of roofing shingles, it is possible to try using Masonite or thin plate metal as a base for the tar wood.

When laying the tar wood in place it should be fine weather. To start the work, a pole, 1m long and with a cross-section of 10x10cm, shall be placed vertically over the hole leading down to the shoe. This prevents the hole from being blocked when the work continues.

The wood should be positioned in a direction pointing down towards the centre of the tar pile. It is important to lay the straightest shingle pieces closest to the shingles. It is practical to use special wood stretchers when carrying the wood to the stacking place, especially when the pile starts getting higher.

The work commences by building up a little square pile (Sw. "*töreln*") at the bottom of the pit around the pole, closest to the shoe, with each side measuring approx. 1m. Twisted and bent wooden pieces should be used for this. A lifting device should then be used to remove the central pole.

The groundwork can now be continued by laying the wet roofing shingles as previously described, working from the bottom up until just below the rim of the cone. After this, the so-called main cushion should be laid.

When this work is finished, it is time to start laying the tar wood in place starting from the top at the main cushion and working down towards the cubic pile of wood at the bottom of the pit. Layer should be added to layer until the tar pile has attained the proportions desired.

During the stacking of the tar wood it is important to remember a few vital points:

- The pile should not lean inwards too much from the main cushion.
- The stacking should be carefully carried out so that a minimum of air is left within the pile.
- It is important that the pile retains its round shape and that its sides are even - otherwise there is a risk for uneven firing and the tar pile misfires.
- Wood chips and splinters from the splitting of the wood must be laid over the top of the pile.

- The pile should never be bigger than a size allowing a 70cm wide path around the whole of the rim of the tar pile.

Beating

To ensure that the wood mass sits really tight and that the pile is as round as possible, it should be beaten with a wooden club if necessary. This beating should also be done during the laying of the wood.

The sealing of the tar pile

The sealing of the pile should be carried out in the same way as described in the instructions for building up the mini tar pile, with the difference that the peat turf covering should be made bigger and thicker. The fire shots should also be larger. A suitable size here is about 15cm.

Firing, burning and smothering of the tar pile

The firing of the tar pile should preferably take place on a calm evening.

The firing, burning and smothering (the charcoal stroke) or shutdown is covered by the previous instructions for the mini tar pile. The difference is that there should be 6 to 7 openings where the air enters the pile and that these should be larger - about 15x15 cm.

When a full-size tar pile is fired, the first stage takes about 6 hours. Not until then will the tar start to run.

The first tar which flows is "tar water" which is not of the best quality. The best tar quality is achieved in the in-between stage. During the final stages the tar is viscous and black.

To be able to avoid standing on the pile during the burning and treading or beating the surface to ensure even burning, a long stick with a club furthest out is used (Sw. "*köreln*"). This is also used to make any extra air holes in the pile.

The length of the burning time is dependent on the size of the tar pile and the speed of the burning process. As an example it can be mentioned that a tar pile of the size two "barrels" (Sw. "*tunnor*") can burn effectively for about 24 hours. 1 barrel = 125 litres

A tar pile of the size 60-70 "barrels" achieves the best yield in relation to the amount of tar wood used. A tar pile of that size can take between 3-5 days to burn.

Grading the tar

Following the burning, the tar must be evicted (Sw. "*vråkas*") i.e. the tar water must be separated out. At the same time the tar is graded.

Prime tar is the least viscous. It is not granulated and it is frothy when it is poured.

Secondary tar is somewhat granulated and a little more viscous than prime tar.

Tertiary tar is coarse and often very granulated.

Smithy charcoal ("*Dalkol*")

The burning process also produces charcoal (Sw. "*dalkol*"). This is reckoned to be the best charcoal by blacksmiths.

It is important that this charcoal is not exposed to rain, as it easily absorbs water. If this has occurred and the charcoal is used for firing, it crackles and spatters in an unpleasant way, making it difficult to use.

The time needed for the tar pile to cool down can be between 1 and 4 weeks dependent on the size of the pile.

By this time, two end products have been extracted from the pine stumps: both an excellent impregnation medium - tar - and a high quality smithy charcoal ("*dalkol*").

To distil tar is a fine old craft. Today, tar piles are still burnt but they are few and far between. Fredrik Westman through his instructive directions in the folder "Tar burning" (Sw. "*Tjärbränning*") aims at teaching the art of building a tar pile.

The end products of the fired tar-wood are prime smithy charcoal, so called "*dalkål*" and of course nature's own impregnation medium - tar.

Rydebäck, 22 September 1999

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APPENDIX 3
Information and Results of Norfolk Tar Burning Experiments

WOOD TAR PROJECT - Results of First Firing - 26 April 1999

Wind easterly. Daytime temperature 13-15 deg C.

Fuel - 28kgs 15 year old Scots pine roots collected 4 days earlier from Thetford Forest

Time	Top deg C	Bottom deg C	Funnel deg C	Comments
2:15 PM				Ignition
2:45 PM	35			White smoke but less than at start
3:15 PM				Very little smoke. Reignited. 5mins later a roaring fire
3:30 PM				Cracking sound
3:45 PM	60	21		Removed string again to increase combustion
4:15 PM	90	52		Rope on and off to keep combustion going Plenty of white smoke. Much tar deposited on top stone.
4:45 PM	79	44		Still going strong. Bottom warming up. Tar appearing around the base beneath string and dripping from top lid.
5:15 PM				Temperature dropping, water trap removed. Blow lamp applied below but 'fire' is nearly out. Removed lid - applied blowlamp to top. Inferno! Foil gasket fitted.
5:45 PM	33	35		Temperature building up slowly. Cold underneath but good smoke out of chimney. Tar not dripping down outside.
6:15 PM	63	44		
6:45 PM	63	40		Temperature boosted again!
7:20 PM	194	67		Following another relight - top gasket removed
7:45 PM	185	70		
8:15 PM	175	114		Fibreglass jacket fitted. Less smoke but some steam. (Dirk Bouwens now in attendance)
8:55 PM	122	100		
9:15 PM	168	64		Weather now very cold with keen easterly blowing. Removed bottom string to let in more air.
9:30 PM	196	126		Built up bricks and curtains around outside to keep out cold winds. Gas outlet temperature 171 degrees C.
9:45 PM	190	131		Moved top damper - open a little
10:00 PM	200	123		
10:15 PM	200	150		
10:30 PM	>200	106		
10:45 PM	>200	165		First tar drips.
11:00 PM	>200	122		
11:15 PM	>200	120		
11:30 PM	>200	170		Tar dripping faster. Bottom dlsh 50 deg.
11:45 PM	>200	175		
12:30 AM	>200	150		
1:00 AM	>200	179		
1:30 AM	>200	>200		Tar running slowly/steadily, and thickly.
2:00 AM	>200	>200	41	Tar running better now.

2:30 AM	>200	>200	42
3:00 AM		>200	61
3:30 AM	>200	>200	>100
4:00 AM	>200	>200	>100
4:30 AM	>200	>200	>200
5:00 AM	>200	>200	>200
5:30 AM	>200	>200	
6:00 AM	>200	>200	>200
6:30 AM	>200	>200	200
7:30 AM	>200	>200	187

8:30 AM

Tar has stopped dripping. Insulation material removed.

Damping down commenced. Wood level in bin reduced to half original - all charcoal. Burnt tar on sides. Tar very thick

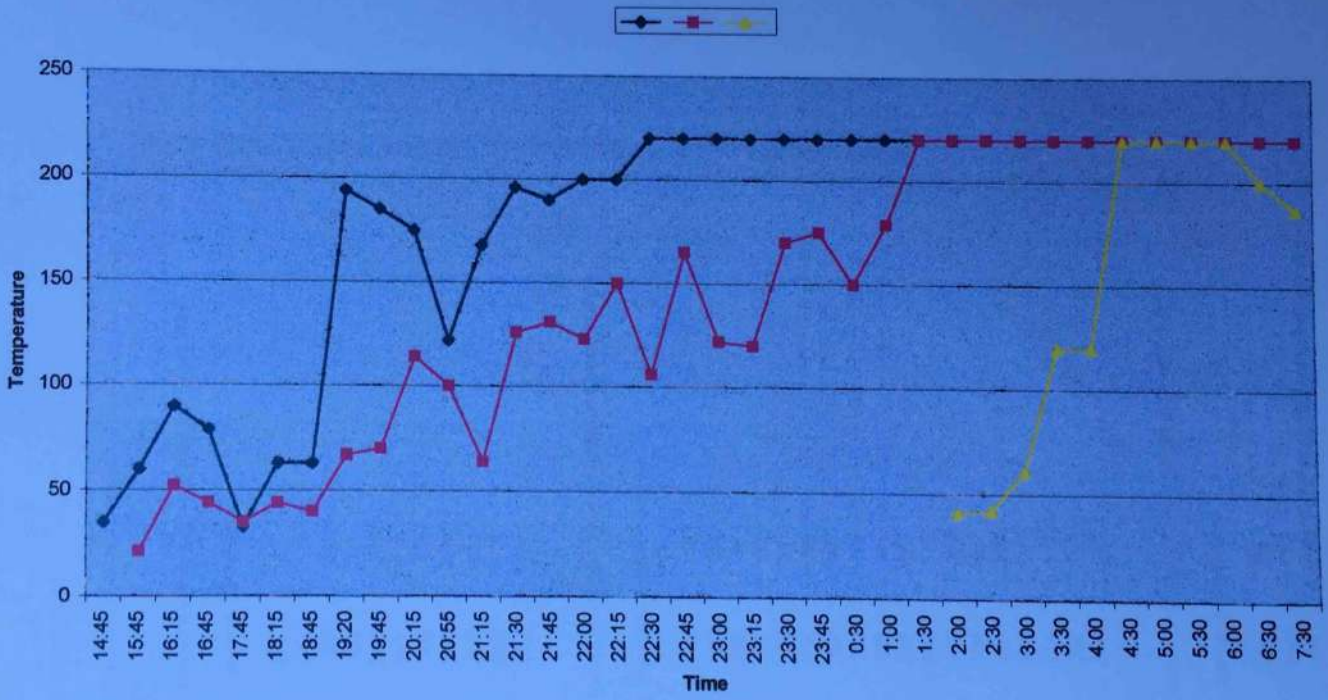
Concluding remarks:

Insulation improvements - need to keep tar collection warm.

More heat needs to be generated at start to prevent closing down.

Shorten funnel to increase diameter of spout.

Wood Tar Project - First Firing



WOOD TAR PROJECT

Thetford Forest Test Burns June 1999

Test Burn One - 21st June 1999 - 15 year old Scots Pine

time	top temp	btm temp
11:30	211	21
12:00	249	111
12:30	226	333
13:00	303	324
13:30	288	281
14:00	337	339
14:30	386	359
15:00	377	401
15:30	328	411
16:00	380	411
16:30	387	467

Test Burn Two - 22nd June 1999 - 15 year old Corsican Pine

time	top temp	btm temp
10:45	142	13
11:00	180	20
11:15	265	34
11:45	317	63
11:55	304	62
12:15	226	84
12:45	258	107
13:15	315	137
13:45	361	144
14:15	317	141
14:45	337	149
15:15	319	169
15:45	304	206
16:15	301	308
16:45	273	301
17:15	274	419
17:45	282	468
18:15	250	456

Test Burn Three - 24th June 1999 - 5 year old Scots Pine

time	top temp	btm temp
10:30	430	24
11:00	210	121
11:30	211	127
12:00	249	237

12:30	279	278
13:00	395	390
13:30	239	189
14:00	287	224
14:30	300	255
15:00	297	326
15:30	281	377
16:00	284	314
16:30	296	333
17:00	289	291
17:30	280	525

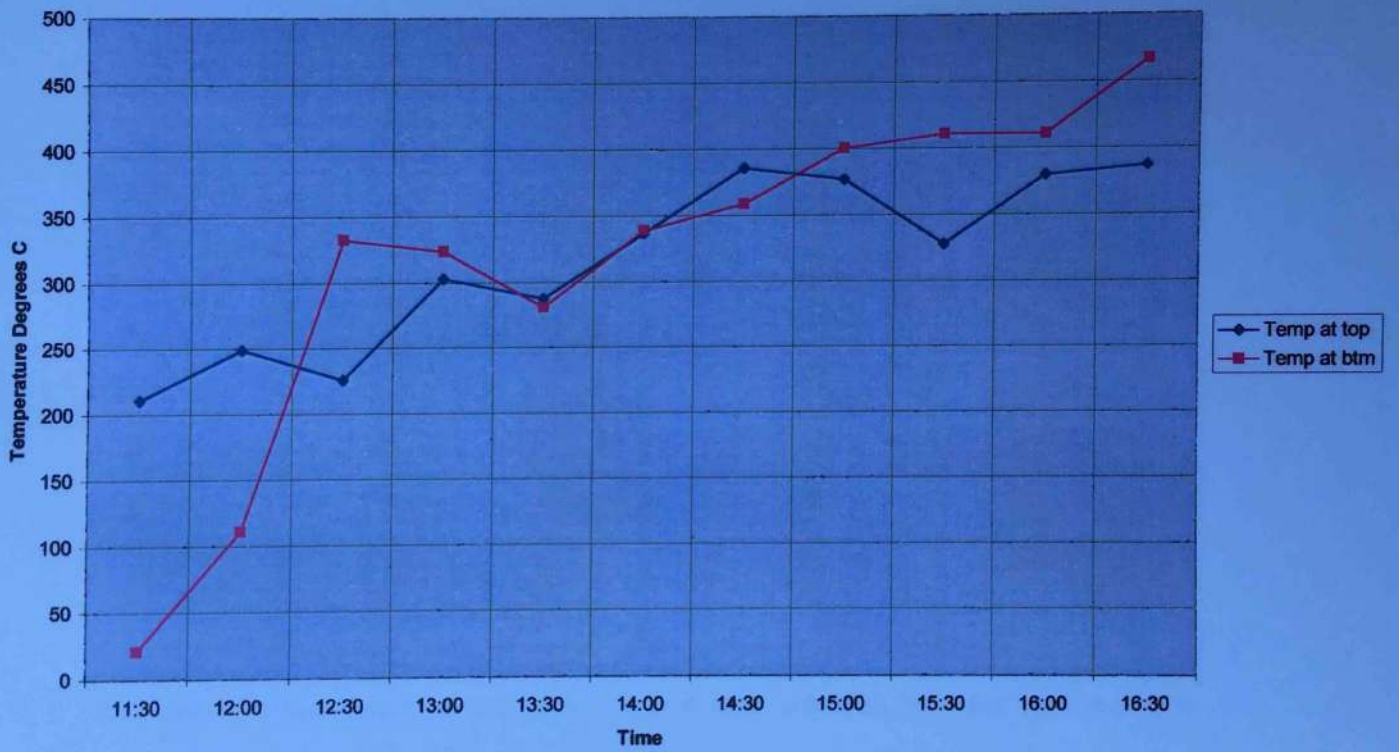
Test Burn Four - 28th June 1999 - 5 year old Corsican Pine

time	top temp	btm temp
10:30	581	15
11:00	512	16
11:30	375	43
12:00	351	69
12:30	342	85
13:00	426	104
13:30	350	126
14:00	376	156
14:30	392	202
15:00	366	222
15:30	364	240
16:00	321	580
16:30	269	588
17:00	269	619

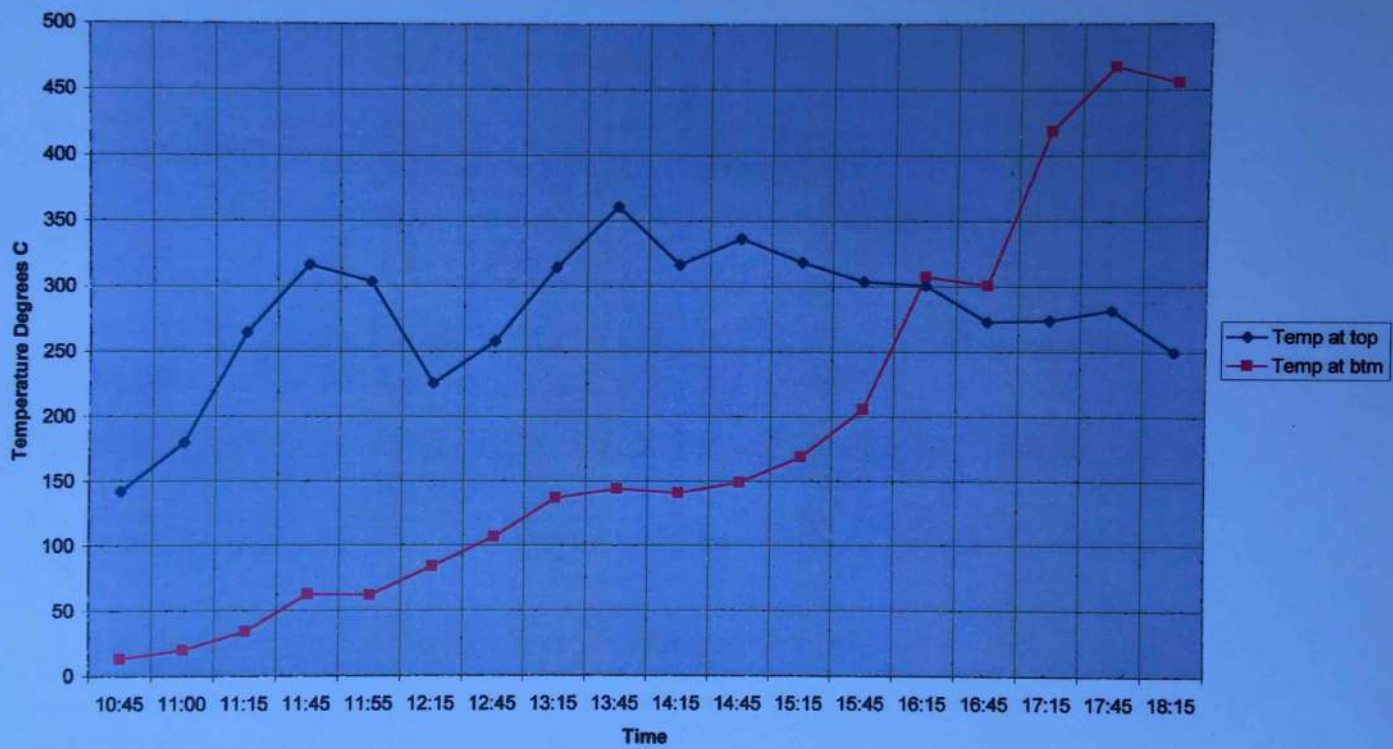
Test Burn Five - 5th July 1999 - Silver Birch Logs

time	top temp	btm temp
11:15	805	18
11:45	230	21
12:15	291	35
12:45	232	76
13:15	226	93
13:45	244	118
14:15	266	150
14:45	248	126
15:15	278	144
15:45	274	133
16:15	281	181
16:45	313	229
17:15	324	434
17:45	305	493

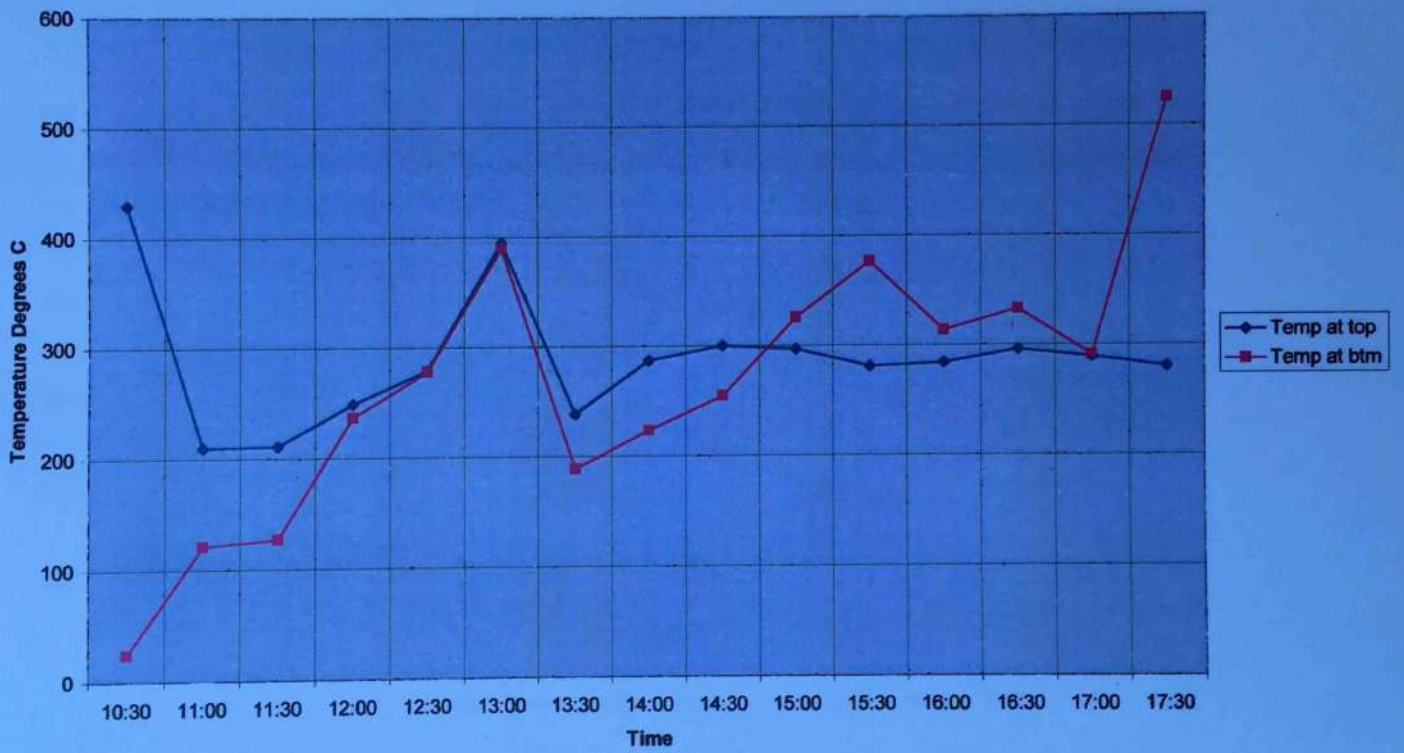
Test Burn 21st June 1999 15 year old Scots Pine



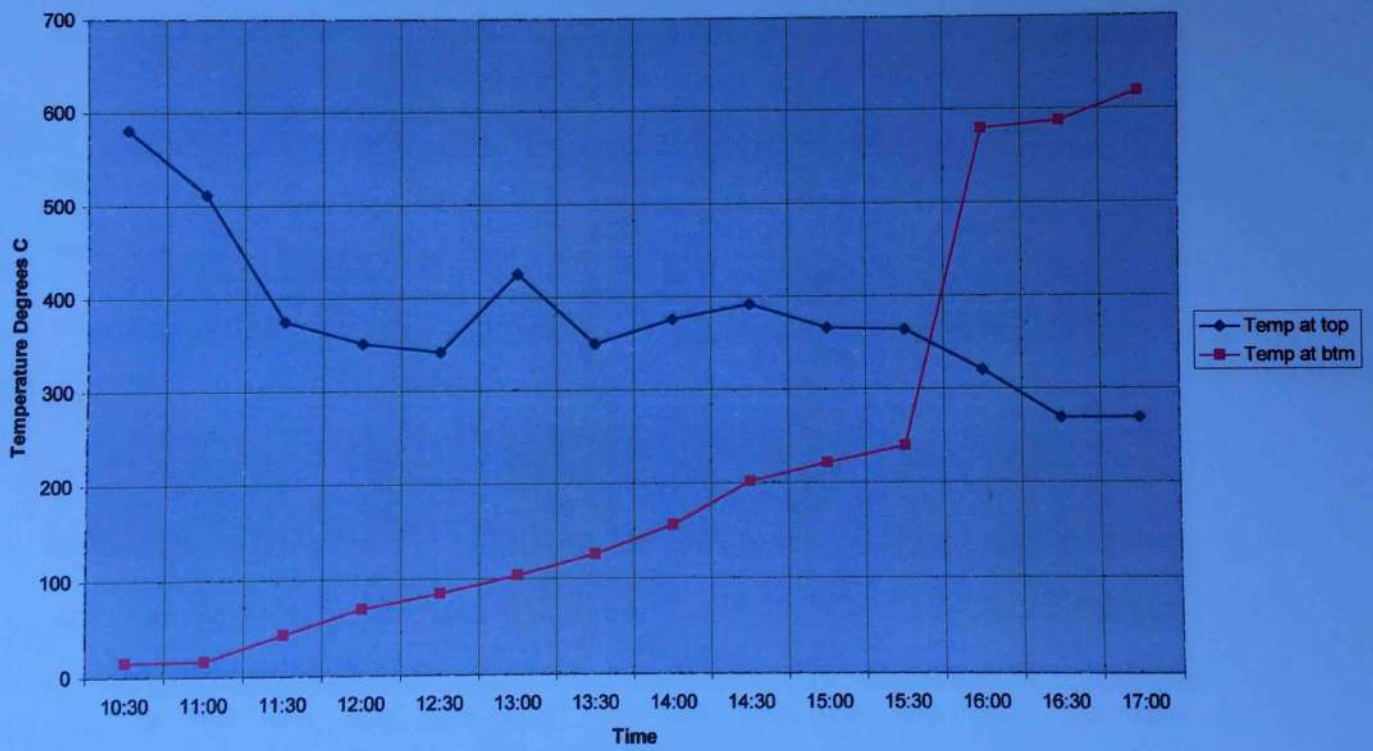
Test Burn 22nd June 1999 15 year old Corsican Pine



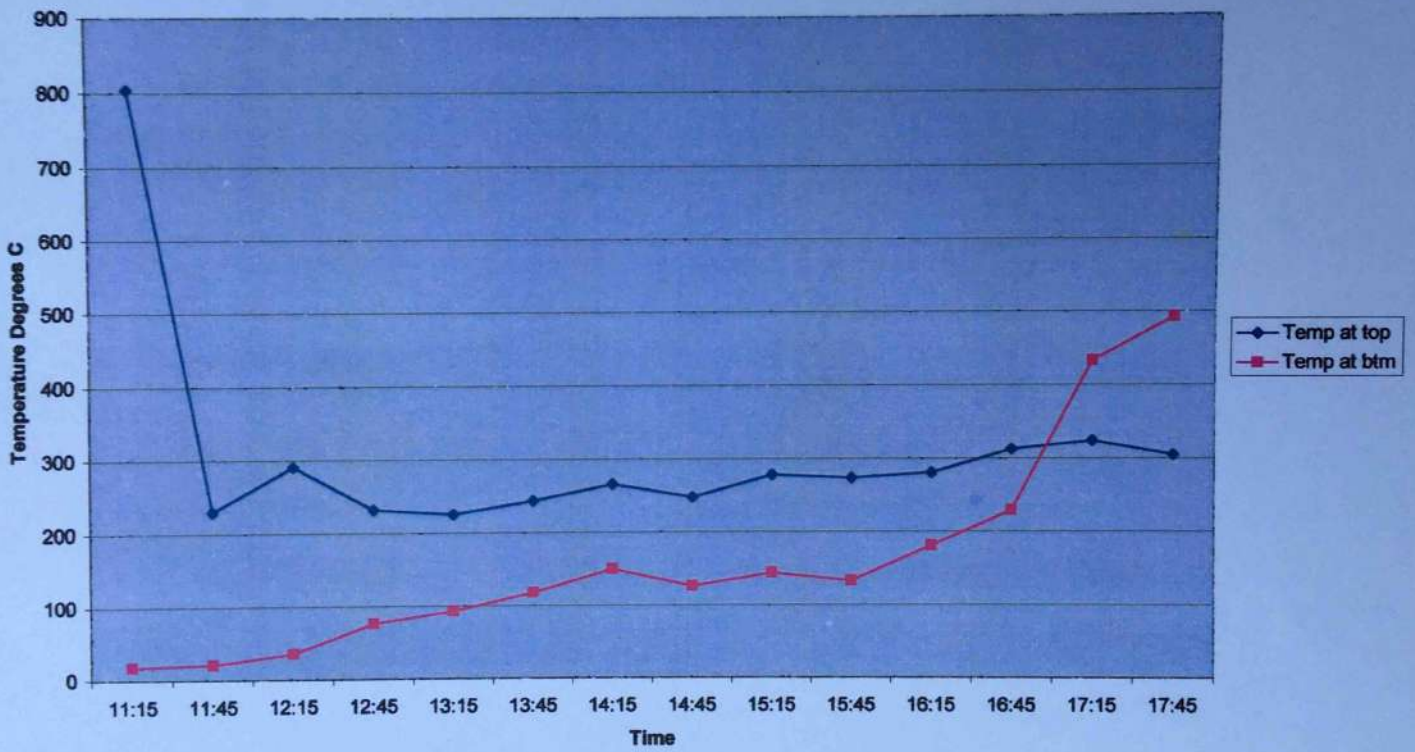
Test Burn 24th June 1999 5 year old Scots Pine



Test Burn 28th June 1999 5 year old Corsican Pine



Test Burn 5th July 1999 Silver Birch Logs



APPENDIX 4

Detailed Chemical Analysis of Tar Samples

APPENDIX FOUR

Detailed Chemical Analysis of Tar Samples

Introduction

The production of the tar samples has been described in Chapter Four. The sixteen tar samples analysed are listed below:

Table A: Tar samples analysed by GC-MS

Sample Code	Description
TA-1	Gotland Tar
TA-2	Furutjara A (Fir Tar A-stub heartwood tar, Sweden)
TA-3	Dalbrandtjara (dal-burnt fir stubs/pinewood)
TA-4	Tratjara A (Wood tar A, oven burnt pure fir stub)
TA-5	Bjorktjara (Beech tar, oven burnt, veterinary use)
TA-6	Beech Tar (supplied by Teisen's)
TA-7	Birch Tar (bark)
TA-8	Commercial tar (supplied by Skogens Kol AB, Sweden)
TA-9	Stockholm Tar (supplied by Battle, Hayward, Bowyer)
TA-10	Dried Sludge Tar (supplied by Waste Gas Technology)
TA-11	Scots Pine Tar (15 yr stumps, Thetford Forest, UK)
TA-12	as above-repeat pyrolysis
TA-13	Scots Pine Tar (5 yr stumps, Thertford Forest, UK)
TA-14	Corsican Pine (15 yr stumps, Thetford Forest, UK)
TA-15	Coal Tar (Fakenham Gas works, Norfolk)
TA-16	Dark creosote (retail sample, Homebase Ltd, UK)

Samples TA-1 to TA-5 were supplied by Claessons's Tratjara, Gothenburg, Sweden.

As can be seen from the above Table, of the total, thirteen were wood tars, one was derived from dried sewage sludge, one was a coal tar and the remaining sample was a commercially available sample of creosote. A sample (approximately 20g) of each tar was transferred to a cleaned 100ml-glass bottle and the samples despatched to a laboratory. The samples were analysed by Hall Analytical Laboratory Ltd, Manchester, who have considerable experience of dealing with such complex materials. All samples were coded before despatch, so the analysts were unaware of their identity.

The samples were all treated in an identical manner for the purposes of the analysis. A 0.1ul aliquot of each sample was taken up in an SGE 1ul syringe for injection into the GC-MS system. A Micromass Instruments 70S Series high resolution gas chromatograph mass spectrometer system was utilised for the sample analysis. A fused silica capillary column of 30 metres length and 0.25 mm i.d. coated with DB5 stationary phase was utilised for the sample speciation. Helium carrier gas was employed at a head pressure of 10 psi and split injection with split ratio of 30:1 was used. The injector temperature was held at 280 C and temperature programming was utilised from 45C to 300C at a programme rate

of 6C/minute. The mass spectrometer was scanned from m/z 600 to m/z 50 at 1 second per decade at a resolution of 2,000 (5% valley). All raw data were stored for subsequent data reduction and library search was made using the NIST library database.

The multiplicity of individual compounds found in each of the samples TA-1 to TA-16 is depicted in the GC-MS chromatogram figures attached to this Appendix. The vertical axis of each chromatogram is broadly representative of the relative concentrations of the individual components. The horizontal axis is indicative of the molecular mass – thus the smaller more volatile components are to be found to the left-hand side of the trace and the larger molecules are to the right. An examination of the various traces clearly indicates, as expected, that each tar contain several hundred individual components.

To identify every one of these components in each tar would constitute a huge analytical challenge, and is well outside the scope of this project. It was decided therefore to concentrate only on the categorisation and identification of the major components evident in each tar sample. The results of this exercise for the 16 tar samples are presented in the Tables attached to this Appendix.

The elucidation of the identity of an individual component in a wood tar sample from the GC-MS trace is, conceptually at least, relatively simple. Each peak on the chromatogram represents a specific chemical to which a mass can be accurately assigned. By a comparison of this mass value to a computer database containing thousands of substances and their accurately known masses, the identity of the unknown can be deduced. In practice however, the situation frequently arises where there are a considerable number of very similar but structurally slightly different substances each with the same mass. In this situation, without employing more sophisticated analytical techniques, it is only possible to identify the type of compound rather than its precise identity. Thus, for example, in sample TA-1 a dimethylbenzene of mass 106 (M^+) been identified. There are, however, a number of dimethylbenzenes of the same mass, which differ from each other only in the way the methyl groups are attached to the benzene ring. In order to identify each of the dimethylbenzenes present it would be necessary to inject pure samples of each compound into the GC-MS instrument so as that direct comparisons could be made with the unknown compounds in the wood tar. Substances such as phenol and naphthalene, each of which have single unequivocal structures, are however somewhat easier to identify with certainty. Thus for example the presence of peaks at mass (M^+) 94 and 128 respectively, can be taken as clear-cut evidence for the presence of phenol and naphthalene in the wood tar sample.

As will be abundantly clear from the Figs. and Tables attached, the wood tars analysed are, as expected, very complex mixtures which contain a wide range of individual components. The complete identification of all the compounds present in the various tars would require a major analytical programme which would be very time consuming and costly. However, considering the intractable nature of the samples, a very substantial amount of data on the nature and chemical composition of the tars has been generated during the present project. **Indeed, to our knowledge this investigation, involving as it does the analysis**

of sixteen tar samples from a wide variety of sources, represents the most comprehensive comparative study of such materials yet carried out.

Results and discussion

Prior to embarking on a detailed discussion of the analytical results, it is useful to restate the principal aims of this section of the project. These were to:

- compare the composition of tars made from 15 year old stumps of Scots Pine from Thetford Forest with those traditionally made from the same and other species in other countries
- investigate whether comparable tars could be made from younger (five-year-old) stumps of Scots pine from the same source.
- ascertain the chemical nature of wood tar produced from another softwood species, Corsican Pine, commonly grown in Thetford Forest
- compare the general chemical characteristics of handmade traditional tars with those of other commercially produced tars
- compare the relative health risks associated with the use of the wood and coal based tars, on the basis of the nature and levels of the potentially toxic active ingredients present

General interpretation of GC-MS chromatograms (wood tars)

All of the samples analysed show several clusters of peaks which reflect the following general chemical compositions:

Cluster	Retention time (minutes)	General composition
a	3-12	benzene derivatives volatile terpenes phenols
b	16-22	naphthalenes and other bicyclic ring compounds
c	30-50	sterols polycyclic aromatic hydrocarbons (PAHs) and PAH carboxylic acids

Retention times are a measure of the mass and hence molecular size of the individual components in the mixture and are thus useful for identification purposes. The lighter more volatile constituents have smaller retention times and appear at the left-hand side of the chromatogram. The larger polycyclic

aromatic hydrocarbons (PAHs), which are mainly produced during the pyrolysis process itself, have higher retention times and therefore appear towards the right-hand side of the chromatogram. The more central group of peaks is predominantly made up of naphthalenes and similar sized bicyclic ring compounds.

Wood tars from Scots Pine (Pinus Silvestris), Thetford Forest

Inspection of the GC-MS chromatograms (TA-11 and TA-12) for the two samples of tar produced from 15 year old stumps of Scots Pine reveals the following information. Three groups of peaks are evident in TA-11, although it is clear from the compounds identified that the sample is mainly composed of sterols and the larger hydrocarbon ring compounds (retention times 30-48 minutes). Concentrations of the more volatile terpenes are low. In sample TA-12 however, the latter compounds are well represented in the mixture, suggesting that the pyrolysis process was less severe than that for TA-11. Apart from the differences in the earlier parts of the two chromatograms, it is clear that the two samples are, as would be expected, very similar in composition to each other.

An important aim of the project was to determine whether less mature (five year old) stumps of Scots Pine could also be used to produce a comparable wood tar. Analysis of the tar (TA-13) so produced indicates that although many of the compounds present are also to be found in the tars from the more mature material, the sample is relatively devoid of the naphthalene type compounds normally found in the central part of the spectrum. Overall however, it is clear that less mature stumps do in fact produce tars which appear broadly similar in composition to that produced from the older source material.

Wood tars from Corsican Pine, Thetford Forest

A tar sample (TA-14) was also produced from 15 year old stumps of Corsican Pine and analysed under identical conditions to the other samples. A visual comparison of the resulting chromatogram with the tars from Scots Pine (TA11, TA12 and TA13) shows that many of the peaks are common to both species. An examination of the compounds identified in the respective samples confirms the visual comparisons. Although care is needed when comparing results from small sample numbers, the similarity in composition of the 15 year old Corsican Pine to that of the 5 year old Pine tar is particularly striking. The present project has clearly demonstrated that wood tars can be produced locally both from Scots Pine and Corsican Pine and that the chemical composition of the latter is broadly similar to that of the Scots Pine, which in other countries, at least, has been the more commonly used source of traditionally produced wood tars.

Commercially available traditional wood tars

In addition to the tars produced from Scots Pine and Corsican Pine from Thetford Forest, a number of other traditionally produced tars were also obtained (see Table A) and analysed.

Two samples of beech tar were analysed. The first (TA-5) is described by Claessens, the Swedish supplier, as oven-burnt (Bjorktjara No 6) and the other (TA-6) was supplied by Teisens. It is evident even from a cursory examination of the chromatograms for the two tars, that the patterns of peaks, especially at the lower end of the mass range, are strikingly similar in both samples. Both samples are dominated by compounds containing oxygen, mainly phenol derivatives and contain very little in the way of volatile terpenes. The results clearly indicate that the chemical composition of beech tars is quite distinctive and significantly different to those from Pine and other wood tar sources.

A sample (TA-4), described by the supplier as an oven-burnt tar and referred to as *Tratjara A*, was also analysed. The chromatogram for this sample is in many ways strikingly similar to that of the beech tar TA-5 just discussed. The *Tratjara A* tar is dominated by phenol derivatives as are the beech tars TA-5 and TA-6, but in contrast to the latter, volatile terpenes and nitrogenous compounds are also much in evidence. The presence of nitrogen containing compounds in wood tar is relatively unusual and it is clear that the material is chemically distinct from other tars so far analysed. The species of wood used as a source is not known.

Tars TA-1, TA-2 and TA-3 are traditional tars supplied by Claessen's of Sweden. Sample TA-1 (Gotland Tar) is produced from Scots Pine, and indeed the chromatogram shows the clusters of peaks characteristic of wood tars produced from the *Pinus* Family. The sample was found to contain a relatively high concentration of volatile natural terpenes coupled with polycyclic aromatic hydrocarbons. Tar TA-3 was found to have a very similar chemical composition and pattern of peaks to that of Gotland Tar, and it is not unreasonable to suggest that it too is produced from Scots Pine. The composition of sample TA-2 (*Fir Tar A*) is quite different to that of TA-1 and TA-3, in that the dominant compounds are non-volatile terpenoids including sterenes. The polycyclic aromatic hydrocarbon, retene, is a major component. Various substituted phenols are also present as minor constituents.

A pine wood tar (TA-9) sold commercially as 'Stockholm Tar' from Battle, Hayward and Bower, Lincoln, UK was also investigated. An examination of the resulting chromatogram reveals an overall pattern of peaks that appears quite different to any of the other wood tar samples. Although there are some similarities, especially at lower retention times, to the sample from Norfolk Scots Pine TA-11 and to Gotland Tar TA-1 substantial differences in the pattern of peaks, are also clearly apparent. Further evidence that this sample of 'Stockholm Tar' may not come from Scots Pine, is provided by comparing the

chemical components identified in the Gotland and Stockholm tars. The latter contains substantially lower concentrations of the volatile terpenes, and also contains small amounts of nitrogen and sulphur compounds which are not found in Gotland tar. Full details of the main chemical constituents of the Gotland and Stockholm tars can be found in the relevant tables attached.

Although it is conceivable that such differences in composition might arise from differences in pyrolysis conditions, it is more likely that this sample of Stockholm tar was produced from another Pine species, and not Scots Pine. In this connection, it is interesting to note that in a recently published paper on wood tar analysis (Lazaro et al. 1999), a sample of 'Stockholm Tar', also supplied by Battle, Howard and Bower Ltd, was analysed. The paper indicates that the crude tar liquor from which the refined tar was made, was imported from Southern China. The liquor itself was produced from the Massen Pine (*Pinus Massonia*). It is therefore quite possible that the tar sample TA-9 analysed in the present project originates from the same species.

Tars from other sources: Dried sewage sludge and coal tar creosote

The tar sample TA-10 from dried sewage sludge (provided by Waste Gas Technology Ltd, UK) and the creosote sample TA-16 (Homebase Ltd, UK) were the only two products that were not produced from wood. These were included in order to provide a comparison with wood tars. In the case of TA-10, little interest has been shown to date in the potential of tars derived from wastes such as sewage sludge and consequently few data are presently available on the chemical composition of such potentially useful materials. It was therefore decided to include it among the samples investigated.

The chromatograms for the sewage sludge tar TA-10 and for the creosote sample TA-16, are clearly significantly different to those of the wood tars discussed in earlier sections of this Appendix. Chemically speaking, the composition of the sewage sludge tar is unique amongst the samples analysed for the wide range of nitrogen containing compounds and polycyclic aromatic hydrocarbons present. Relative to other samples it is depleted in oxygen containing substances and is virtually devoid of phenolic compounds. Creosote shows a similar lack of such compounds, but substituted naphthalenes and polycyclic aromatic hydrocarbons are however present in relatively high concentrations. The broad similarity in chemical composition of the tar from dried sewage sludge to that of creosote, suggests that the use of the former as a wood preservative may have some potential. Further work would however be required to establish the suitability of the material for this purpose.

The conclusions resulting from this analysis, together with the references used, can be found in **Chapter Five** of the main Report.

Results

LC 27818 TA-1

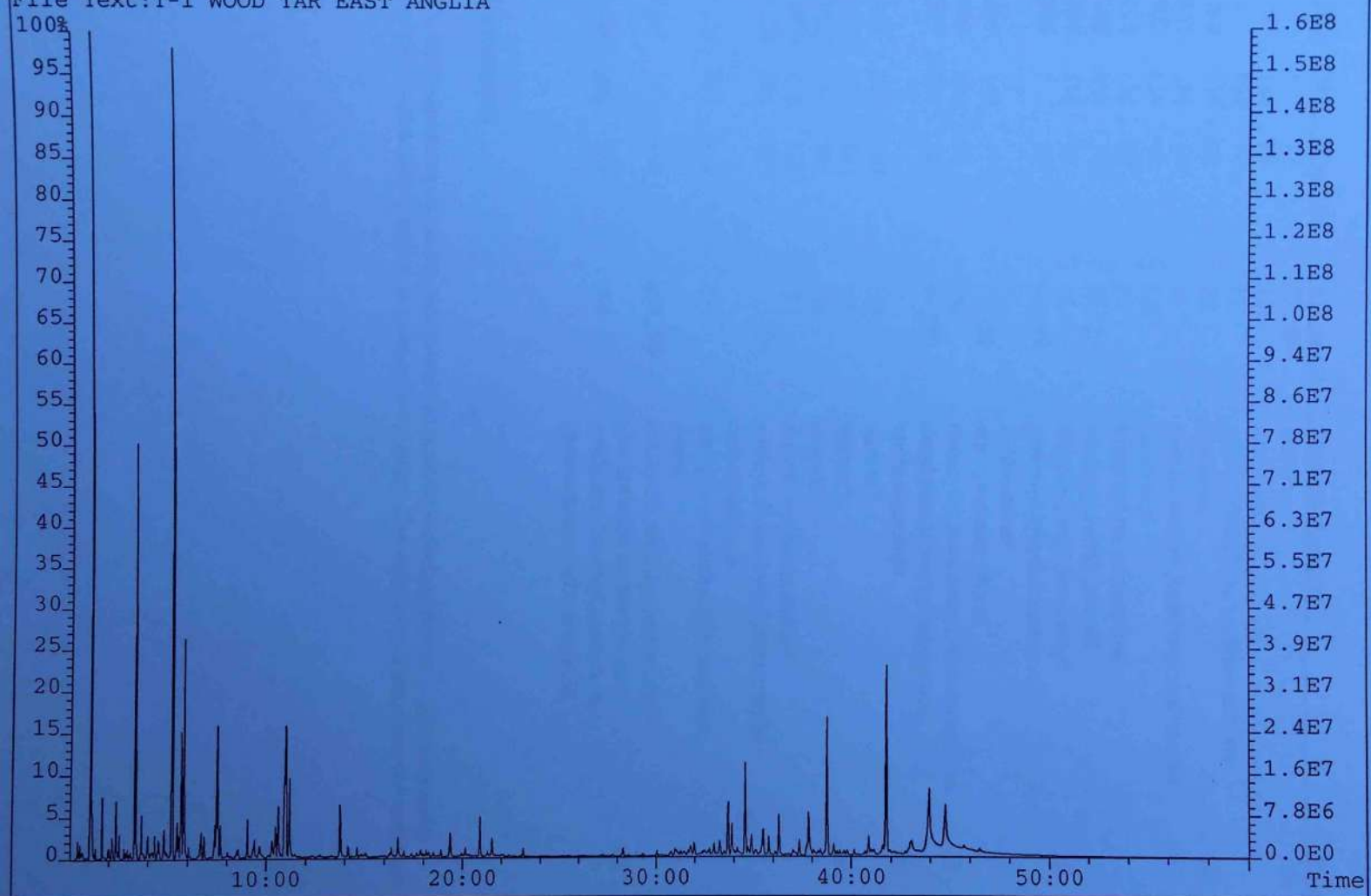
Scan	M+	Base ion	Fragments	General structure	Height
48	96	96	82	dimethylpyrazole	
63	106	91	77	dimethylbenzene	
74	104	104	91	ethenylbenzene	
91	136	93	77,105	carene	51
98	136	93	77,105	carene	
108	136	93	121	camphene	
118	110	110	81,96	methyl,furancarboxaldehyde	
128	136?	93	69	thujene?	
133	136?	121	105	tetramethylcyclohexadiene	
135	94	94		phenol	
142	136	93	69	bicyclo derivative	
155	136	93	121	bicyclo derivative	100
162	136	121	105	cyclohexene derivative?	
164	134	119	91	methyl,methylethyl,benzene	
168	134	93	119	methyl,methylethenyl,cyclohexane menthadiene	15
172	136	68	93	limonene	27
180	116	116	89	indene	
197	108	108		methyl,phenol	
199	136	93	121	methyl,methylethyl,cyclohexenol	
203	?	70	89,105	methyl,butylester,butanoic acid?	
219	136	93	121	menthadiene?	16
223	136	?	121	methyl,methylethylidene,cyclohexene	
228	132	132	117	methyl,methylethenyl,benzene	
239	148	133	105	ethyl,methylethyl,benzene cumene	
253	136	119	93	dimethylbenzenemethanol	
269	136	121	105	cyclohexene derivative	
280	136?	121		cyclohexene derivative	
311	128	128		naphthalene	16
316	136	93	121	cyclohexene derivative	
325	138	123	95	methoxy,methyl,phenol	
333	136	93	121	cyclohexene derivative	
410	152	137	122	ethyl,methoxy,phenol	
422	142	142	115	methylnaphthalene	
488	164	164	149	eugenol	
498	166	137	122	methoxy,propyl,phenol	
564	152	152	76	acenaphthylene	
578	164	164	149	methoxy,propenyl,phenol	
624	204	105	161	hexahydro,dimethyl,methylethyl naphthalene	

642	204	161	134	hexahydro,dimethyl,methylethyl,naphthalene	
690	184	169	154	methyl,methylethyl,naphthalene	
				eudalene	
1006	256	241	159	sterene?	11
1031	256	241	159	sterene?	
1084	238	223	181	dimethoxyphenanthrene	
1129	286	257	123	ethenyl,dodecahydro,phenanthrene	
				carboxaldehyde	16
1158	234	219	204	methyl,methylethyl,phenanthrene	
				retene	25
1247	314	314	239,299	octahydro,dimethyl,methylethyl,phenanthrene	
				carboxylic acid	
1312	300	239	299	octahydro,dimethyl,methylethyl,phenanthrene	
				carboxylic acid	
1336	302	302	256	?	

Comments

The sample contains a relatively high concentration of volatile natural terpenes (e.g., structures similar to limonene and menthadiene), coupled with polycyclic aromatic hydrocarbons. Nitrogen and sulfur compounds were not identified, oxygen being the only heteroatom.

File:LC27818 #1-2092 Acq:25-AUG-1999 08:02:40 Septum EI+ Magnet 70SE
TIC (+RP) Exp:MAGSCAN
File Text:T-1 WOOD TAR EAST ANGLIA



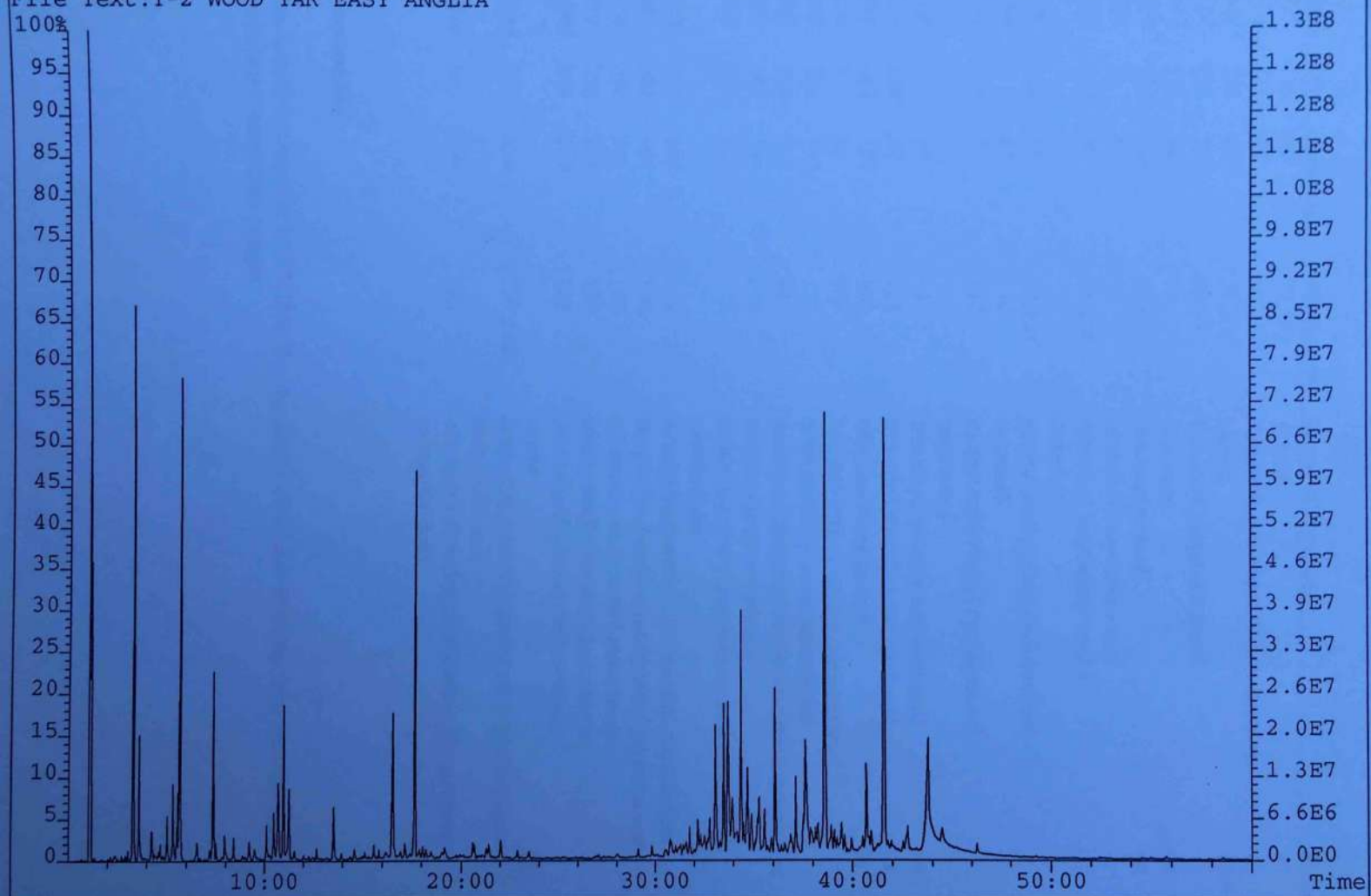
LC 27819 TA-2

Scan	M+	Base ion	Fragments	General structure	Height
98	136	93	77,105	carene	100
107	136	93	121	camphene	
159	136	121	93	methyl,methylethyl,cyclohexadiene	
169	136	68	79	limonene	89
220	136	121	93	methyl,methylethylidene,cyclohexene	35
302	154	95	121	isoborneol	
313	136	93	70	trimethyl,tricycloheptane	
320	138	138	95,123	methoxy,methyl,phenol	
328	136	93	68,121	trimethyl,tricycloheptane?	29
336	?	83	95,109	trimethyl,bicycloheptanone? norpinanone?	
405	152	137	91,122	ethyl,methoxy,phenol	
496	204	94	161	decahydro,tetramethyl,methanoazulene	28
527	204	161	94,189	decahydro,trimethyl,methylene, methanoazulene	72
988	258	243	187	sterene?	
1000	256	241	159	sterene?	28
1027	256	241	159	sterene?	46
1079	238	223	181	dimethoxyphenanthrene?	
1124	286	257	123,271	ethenyl,dodecahydrophenanthrene carboxaldehyde	
1153	234	219	204	methyl,methylethyl,phenanthrene retene	85
1243	314	314	239,299	octahydro,dimethyl,methylethyl, phenanthrene carboxylic acid	82
1308	300	239	299	octahydro,dimethyl,methylethyl, phenanthrene carboxylic acid	

Comments

The dominant compounds are non-volatile terpenoids, including sterenes. The polycyclic aromatic hydrocarbon, retene, is a major component. The only heteroatom observed is oxygen.

File:LC27819 #1-2092 Acq:25-AUG-1999 10:00:59 Septum EI+ Magnet 70SE
TIC (+RP) Exp:MAGSCAN
File Text:T-2 WOOD TAR EAST ANGLIA



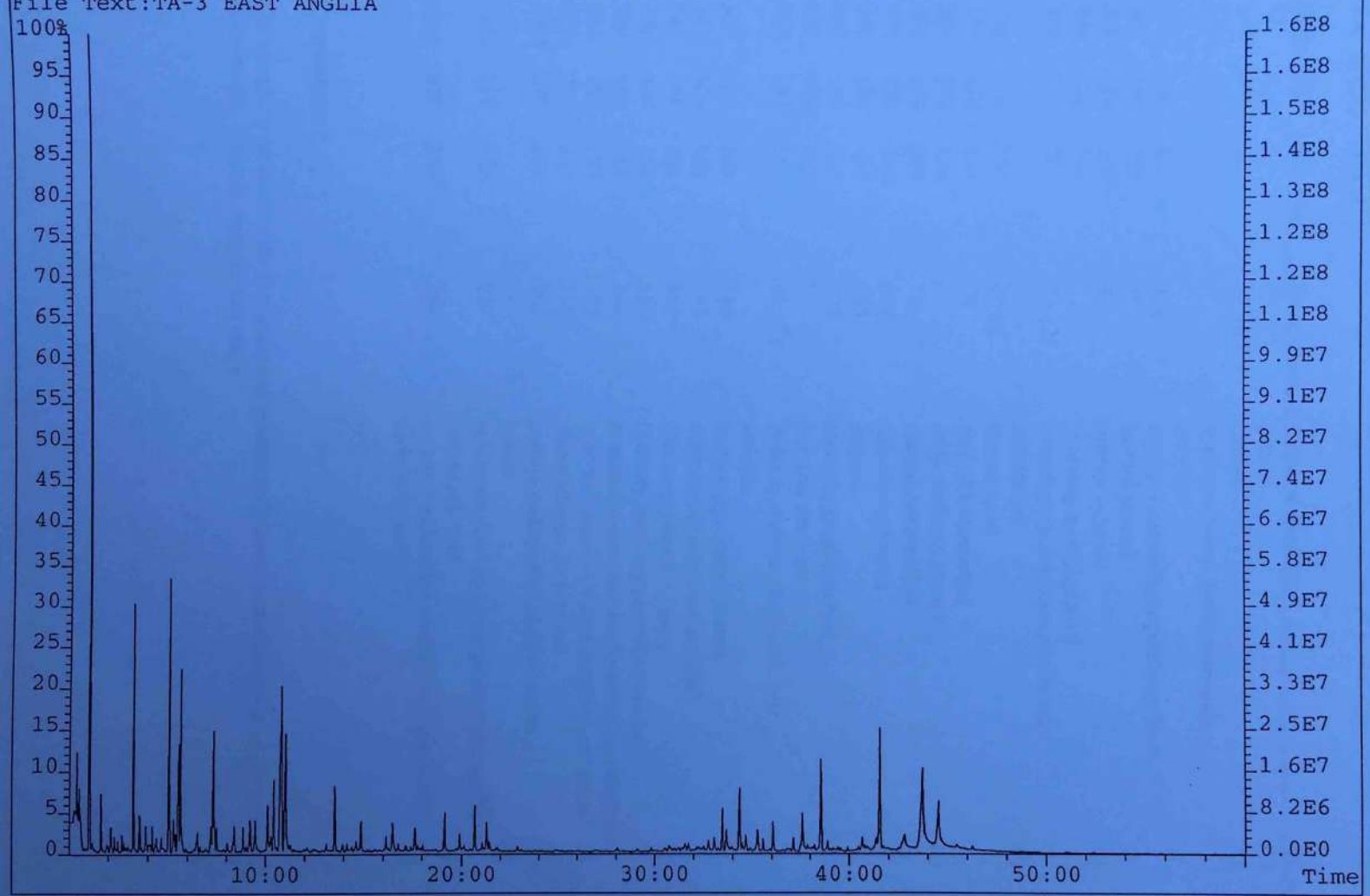
LC 27820 TA-3

Scan	M+	Base ion	Fragments	General structure	Height
92	136	93	77,121	pinene	91
101	136	93	107,121	dimethyl,methylene,bicycloheptane	
144	136	93	77,105	carene	100
157	134	119	68,93	trimethyl,bicycloheptenol	
161	136	68	93	limonene	65
209	124	124	109	methoxy,phenol	44
239	?	81	111	trimethyl,bicycloheptenol	
262	152	95	81,108	trimethyl,bicycloheptenone camphor	
270	136	71	93,121	methyl,methylethyl,cyclohexanol	
288	?	95	110	borneol?	
297	154	71	110	methyl,methylethyl,cyclohexenol menthenol	
308	?	93	59	trimethyl,cyclohexene,methanol	59
314	136?	59	121	trimethyl,cyclohexene,methanol	41
387	152	137	109	ethyl,methoxy,phenol	23
424	?	81	96	hydroxy,propyl,methyl,cyclohexanol	
469	166	137	122	ethyl,methoxy,benzenemethanol	
502	204	161	94	decahydro,trimethyl,methylene,methanoazulene	
545	164	164	149	methoxy,propenyl,phenol	
568	204	161	119	octahydro,methyl,methylene,methylethyl, naphthalene	
590	204	105	161	hexahydro,dimethyl,methylethyl,naphthalene	
607	204	161	134	hexahydro,dimethyl,methylethyl,naphthalene	
954	256	241	159	tetrahydro,hexamethyl,indacenone	
979	256	241	159	tetrahydro,hexamethyl,indacenone	
1098	234	219	102	methyl,methylethyl,phenanthrene retene	35
1184	314	314	239,299	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	44
1246	300	239	299	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	29

Comments

The sample is similar to LC27818 in the abundance of volatile terpenes, and the absence of heteroatoms other than oxygen.

File:LC27820 #1-2139 Acq:25-AUG-1999 12:41:05 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-3 EAST ANGLIA



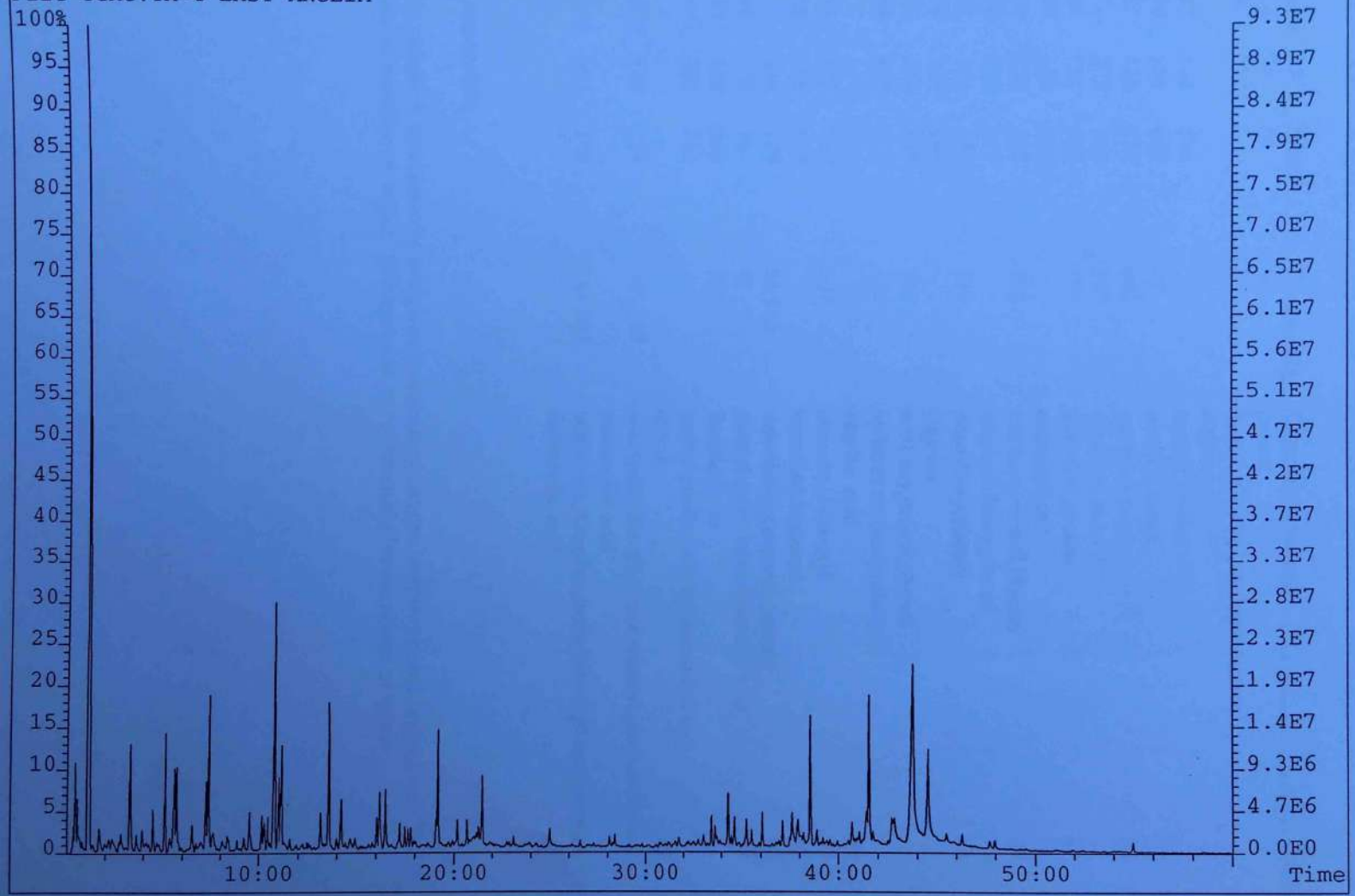
LC 27821 TA-4

Scan	M+	Base ion	Fragments	General structure	Height
93	136	93	77,121	pinene	43
144	136	93	77,105	carene	50
158	112	?		hydroxy,methyl,cyclopentenone corylon	
162	136	93	121	methyl,methylethyl,cyclohexadiene	
205	108	108	77	methyl,phenol	
209	124	109	81	methoxyphenol	63
306	138	138	123	methoxy,methyl,phenol	100
312	?	59	93,121	trimethyl,cyclohexene,methanol menthenol	40
316	110	110	64,92	benzenediol	
374	124	124	78	methyl,benzenediol	
386	152	137		ethyl,methoxy,phenol	60
405	124	124	78	methyl,benzenediol	
456	154	154	139	dimethoxy,phenol	
460	164	164	103	eugenol	
469	166	137	122	methoxy,propyl,phenol	
489	138?	123	77	benzene derivative	
497	152	151	81,123	hydroxy,methoxy,benzaldehyde vanillin	
506	164	164	149	methoxy,propenyl,phenol	
543	168	168	153	methoxy,nitro,benzeneamine?	
546	164	164	149	methoxy,propenyl,phenol	50
574	166	151	123	hydroxy,methoxy,phenyl,ethanone	
589	204	105	161	hexahydro,dimethyl,methylethyl,naphthalene	
612	180	137	122	acetylaminoethyl,amino,methylpyrimidine?	33
978	256	241	159	phenanthrene derivative?	
1098	234	219	102	methyl,methylethyl,phenanthrene retene	60
1184	314	239	299	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	63
1246	300	239	299	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	80

Comments

The sample is unusual in the dominance of phenol derivatives and abundance of nitrogenous compounds. Volatile terpenes are major.

File:LC27821 #1-2138 Acq:25-AUG-1999 14:15:48 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-4 EAST ANGLIA



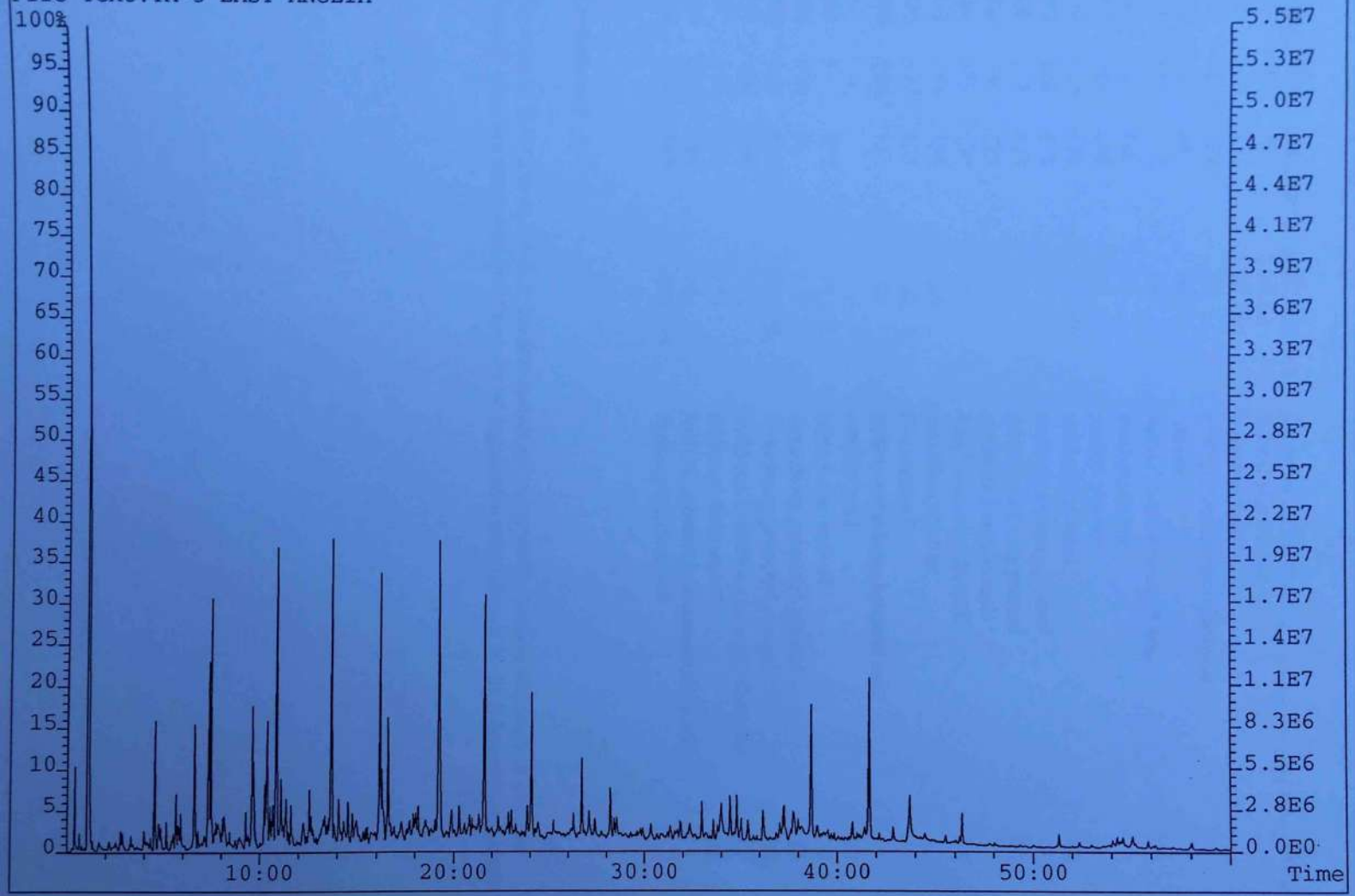
LC 27822 TA-5

Scan	M+	Base ion	Fragments	General structure	Height
128	94	94	66	phenol	
160	112	?	83	hydroxy,methyl,cyclopentenone corylon	
187	108	108		methyl,phenol	
208	108	108	77	methyl,phenol	
212	124	124	109	methoxy,phenol	79
273	122	122	107	dimethyl,phenol	
276	122	122	107	dimethyl,phenol	47
296	128	128		naphthalene?	
309	138	138	123	methoxy,methyl,phenol	95
390	152	137		ethyl,methoxy,phenol	100
461	154	154	139	dimethoxy,phenol	88
464	164	164		eugenol	
473	166	137	122	methoxy,propyl,phenol	
548	168	153	125	hydroxy,methoxy,phenol vanillic acid	97
615	182	167	107	dimethyl,biphenyl	79
686	196	167		trimethyl,biphenyl	51
761	194	179	91,119	dimethoxy,propenyl,phenol	
941	270	74	87	methyl ester, hexadecanoic acid	
1031	202	202	101	fluoranthene	
1102	234	219		methyl,methylethyl,phenanthrene retene	46
1187	314	239	141,197	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	51
1245	300	239	141,197	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	

Comments

The sample is dominated by compounds containing oxygen, mainly phenol derivatives. The volatile terpenes are minor. Nitrogen and sulfur heterocycles are absent or trace.

File:LC27822 #1-2139 Acq:25-AUG-1999 15:43:02 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-5 EAST ANGLIA



LC 27823 TA-6

Scan	M+	Base ion	Fragments	General structure	Height
47	96?	96	54,82	dimethyl,pyrazole	
80	110	95	56,86	butyrolactone?	
111	1110	110	53	methyl,furancarboxaldehyde	
128	94	94	66	phenol	
160	112	112	69	methyl,cyclopentanedione	23
185	108	108	77	methyl,phenol	
207	108	108	77	methyl,phenol	
210	124	124	81,109	methoxy,phenol	40
292	138	123	107	methyl,methoxy,phenol	
306	138	123	107	methyl,methoxy,phenol	50
366	140	125	97	methoxy,benzenediol	
386	152	137	121	ethyl,methoxy,phenol	40
458	154	154	139	dimethoxyphenol	100
470	137?	137	122	N-aromatic?	
544	154?	153	125	hydroxy,methoxy,benzoic acid	
				vanillic acid	90
613	?	107	77,123	phenol derivative?	77
677	194	91	119	dimethoxy,propenyl,phenol	30
758	194	194	91,179	dimethoxy,propenyl,phenol	30
778	196	196	181	hydroxy,dimethoxy,phenol,ethanone	
807	210	167	123	diphenyl derivative?	23
849	210	181	153	hydroxy,phenyl,benzeneacetic acid	
978	254	167	194,241	diphenyl derivative?	

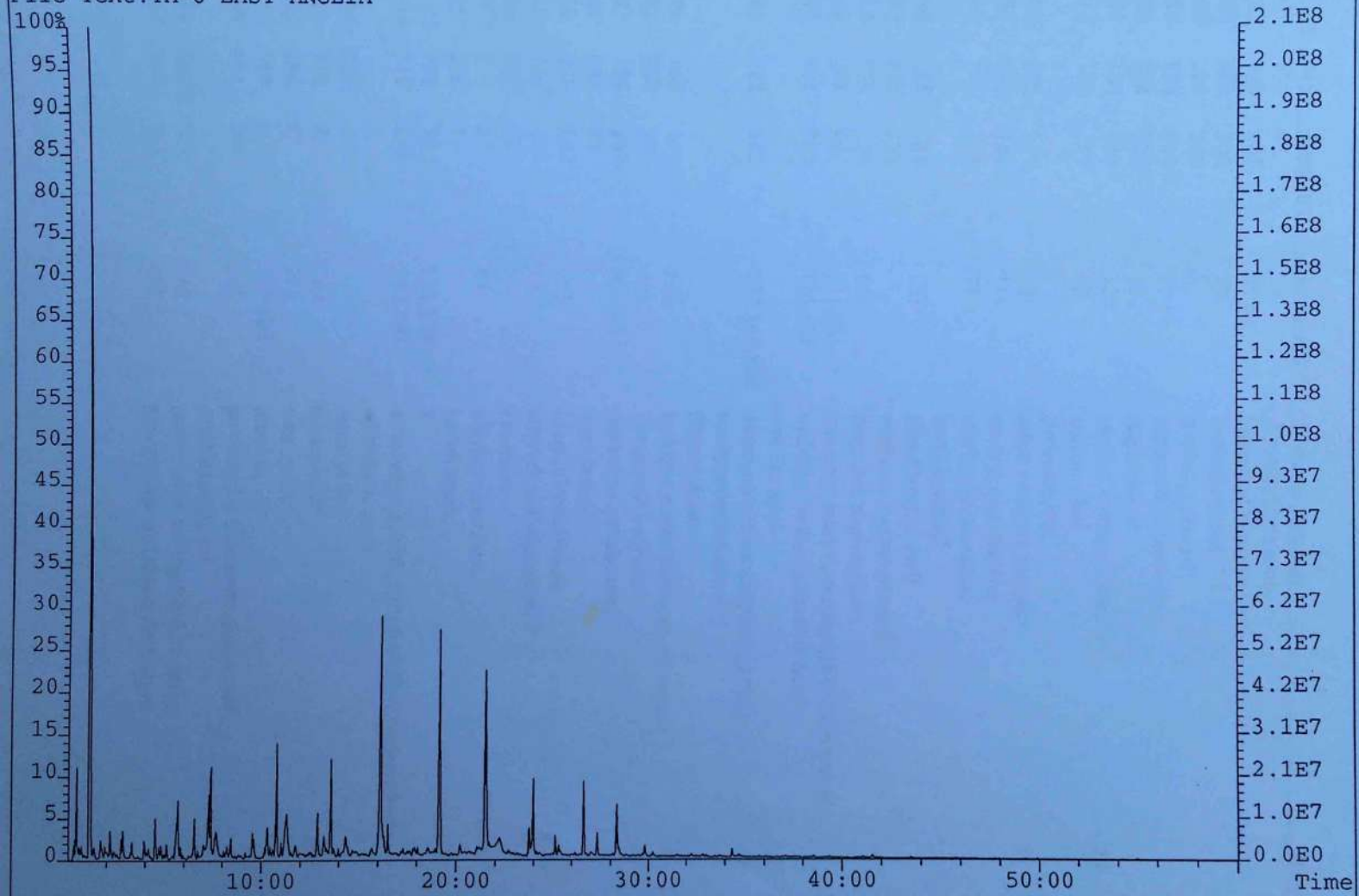
Comments

The sample is similar to TA-5 in the dominance of oxygenated compounds, such as phenols. Volatile terpenes are minor, and there are no significant quantities of N- or S-based compounds.

File:LC27823 #1-2138 Acq:26-AUG-1999 08:36:27 Septum EI+ Magnet 70SE

TIC (+RP) Exp:DEFAULT

File Text:TA-6 EAST ANGLIA



LC 27824 TA-7

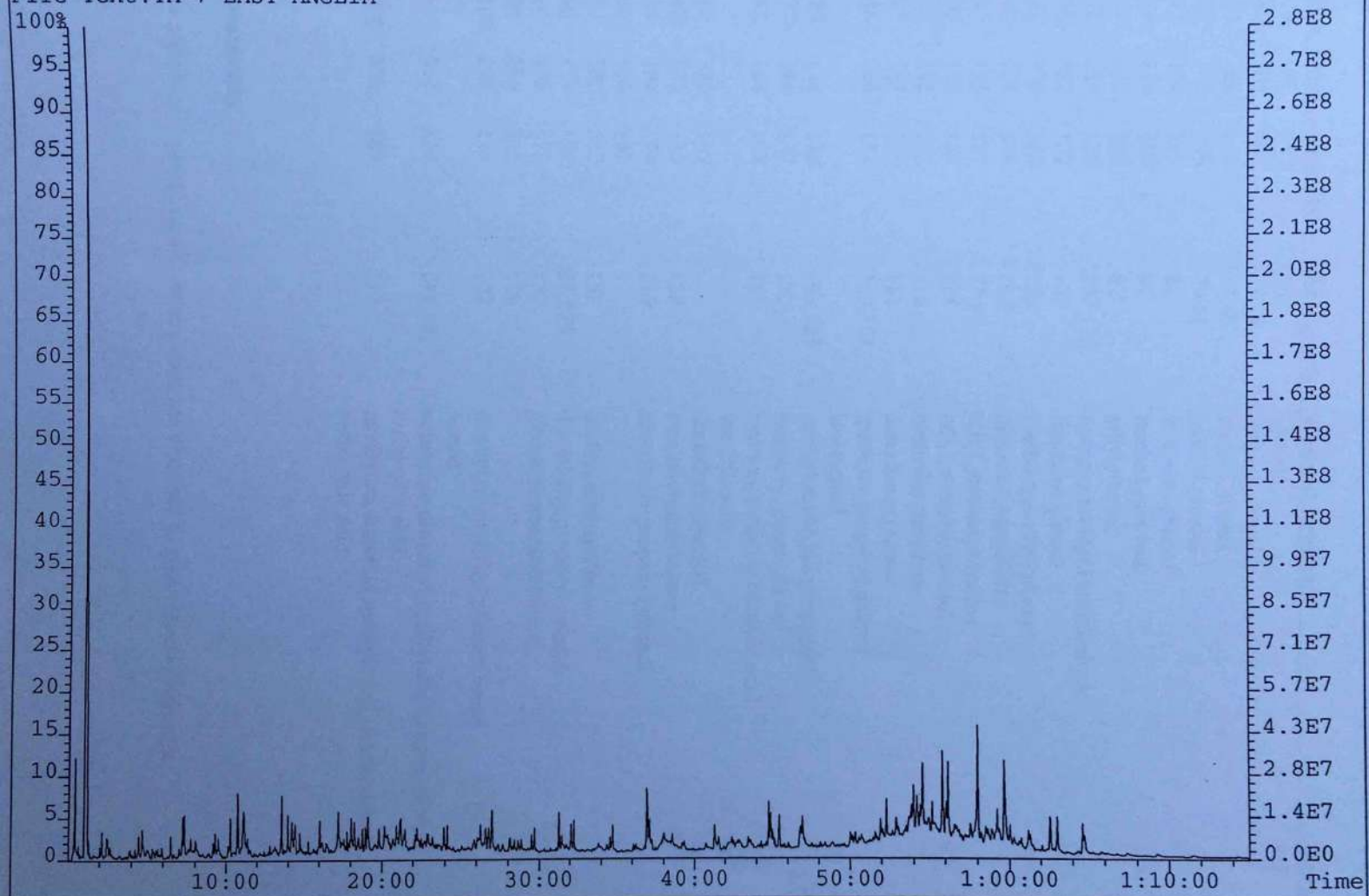
Scan	M+	Base ion	Fragments	General structure	Height
60	106	91	77	dimethyl,benzene	
132	120	105	77,91	trimethyl,benzene	
205	108	108	77	methyl,phenol	
208	124	109	81	methoxy,phenol	
264	134	119	77,91	tetramethyl,benzene	
292	128	128	102	naphthalene	
305	138	138	123	methyl,methoxy,phenol	50
317	110	110	92	benzenediol pyrocatechol	
386	152	137	121	ethyl,methoxy,phenol	51
398	142	142	115	methyl,naphthalene	
405	124	124	78	methyl,benzenediol homocatechol	
456	154	154	139	dimethoxy,phenol	
490	138?	123		methoxy,methyl,phenol?	
514	156	156	141	dimethyl,naphthalene	
519	204	94	121,161	dimethyl,methylpentenyl,tricycloheptane	
544	168	168	125,153	hydroxy,methoxy,benzoic acid vanillic acid	
564	122	122	107,161,189	decahydro,trimethyl,methylene, methanonaphthalene Seychellene	
574	166	151	123	hydroxy,methoxyphenol,ethanone	
602	204	57?	161	limonenol butyrate?	
682	196	167	97,111	tetraethylcyclohexane	
688	226	57		hexadecane	
756	220	107	163	longifolenaldehyde	
768	184	184	153	ethyl,dimethyl,azulene?	
989	282	57		eicosane	
1052	?	55	83	alkylcyclohexane	
1057	296	57		heneicosane	50
1177	296	55	111,239	?	
1184	310	239	143,299	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	
1276	326	107		tetracyclic?	
1280	326	95	189	tetracyclic?	42
1295	338	55	208	tetracyclic?	
1338	340	109	189,203	tetracyclic?	
1490	408	365	121	pentacyclic triterpane derivative neoleanadiene?	
1538	406?	363	135	pentacyclic triterpane derivative	55
1544	394	163	191	pentacyclic triterpane derivative	

1554	408	189	297	pentacyclic triterpane derivative	70
1590	424	381	161,245	pentacyclic triterpane derivative	82
1601	406	189	229	pentacyclic triterpane derivative	70
1652	424	134	189	pentacyclic triterpane derivative	100
1701	426	95	189	pentacyclic triterpane derivative	75
1783	440	440	369	pentacyclic triterpane derivative	
1796	442	189	288	pentacyclic triterpane derivative	
1842	442	189	411	pentacyclic triterpane derivative	
1845	484	189	135	pentacyclic triterpane derivative	

Comments

The sample is unique in the high concentrations of pentacyclic triterpenes, and in the trace amounts of normal alkanes. It appears to be relatively poor in O-, N-, and S-groups.

File:LC27824 #1-2138 Acq:26-AUG-1999 10:39:42 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-7 EAST ANGLIA



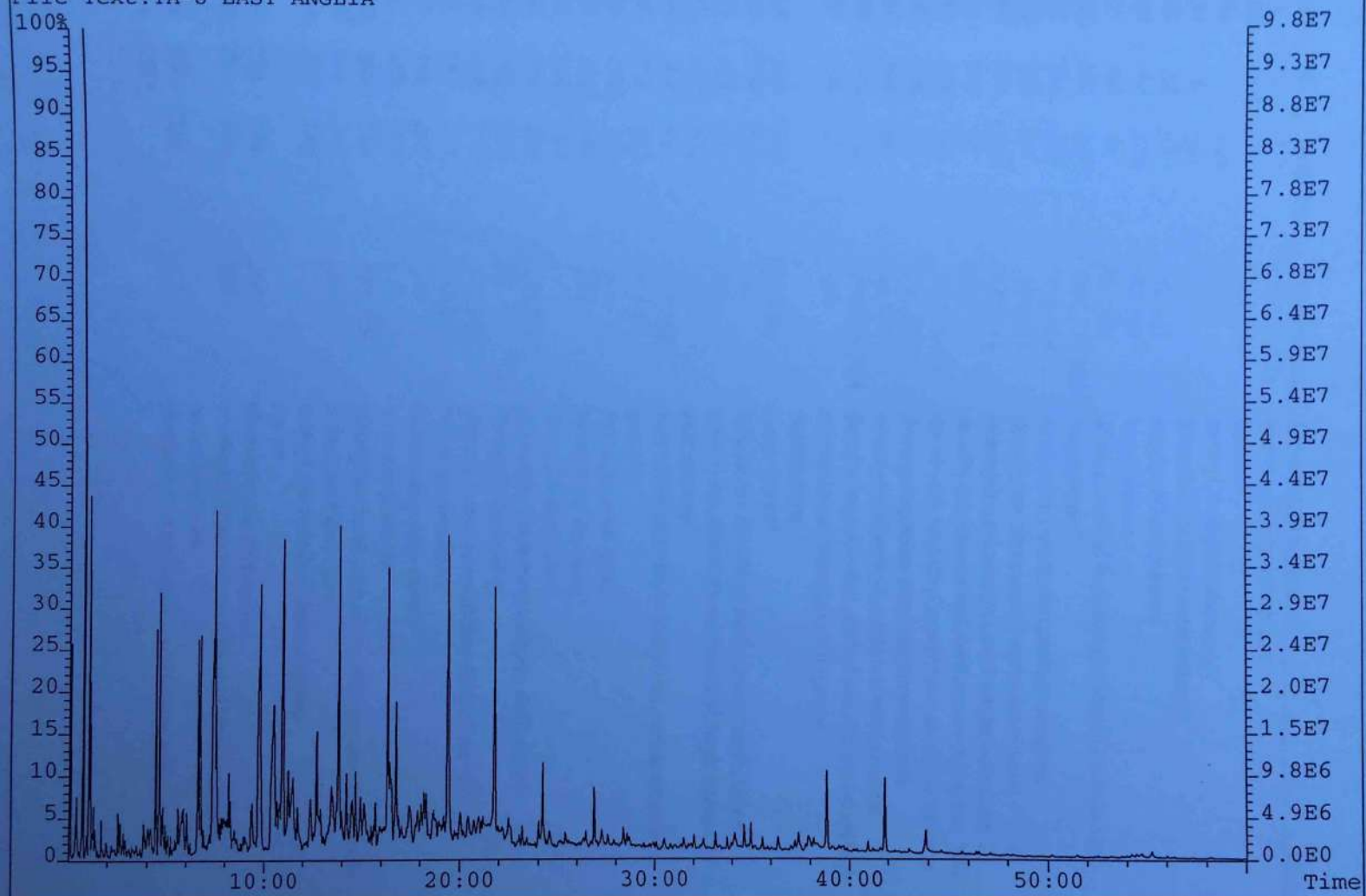
LC 27825 TA-8

Scan	M+	Base ion	Fragments	General structure	Height
126	94	94	66	phenol	62
187	108	108	79,89	methyl,phenol	60
190	108	108	79,89	methyl,phenol	
209	108	108	79,89	methyl,phenol	
211	124	109	81	methoxy,phenol	
214	124	109	81	methoxy,phenol	100
265	122	109	81	ethyl,phenol	
276	136	136	107,122	hydroxy,methyl,benzaldehyde	
278	122	122	107	dimethyl,phenol	76
312	138	138	123	methoxy,methyl,phenol	85
320	146	146	107	dimethyl,benzofuran	
361	136	121	77,91	ethyl,methoxybenzene	
394	152	137	121	ethyl,methoxy,phenol	92
405	142	142	115	methylnaphthalene	
465	154	139	111	dimethoxy,phenol	
468	164	164	103,121	methoxy,propenyl,phenol	
				isoeugenol	80
470	138	138	105,123	methyl,methylthiobenzene?	
477	166	137	122	methoxy,propyl,phenol	
552	168	168	153	hydroxy,methoxy,benzoic acid	
				vanillic acid	90
619	182	167		dimethylbiphenyl?	76
640	170	155	128	trimethylnaphthalene	
684	194	194	119	dimethoxy,propenyl,phenol	
690	196	167		?	
700	182	182	152	methyl,dibenzofuran	
765	194	194	91,179	dimethoxy,propenyl,phenol	
808	178	178	152	phenanthrene/anthracene	
986	256	241	159	?	
1106	234	219	102	methyl,methylethyl,phenanthrene	
				retene	
1191	314	239	141,197	octahydro,dimethyl,methylethyl,phenanthrene	
				carboxylic acid	
1250	300	285	239	octahydro,dimethyl,methylethyl,phenanthrene	
				carboxylic acid	

Comments

The sample is depleted in volatile terpenes, but enriched in phenols and O-groups.

File:LC27825 #1-2138 Acq:26-AUG-1999 12:41:04 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-8 EAST ANGLIA

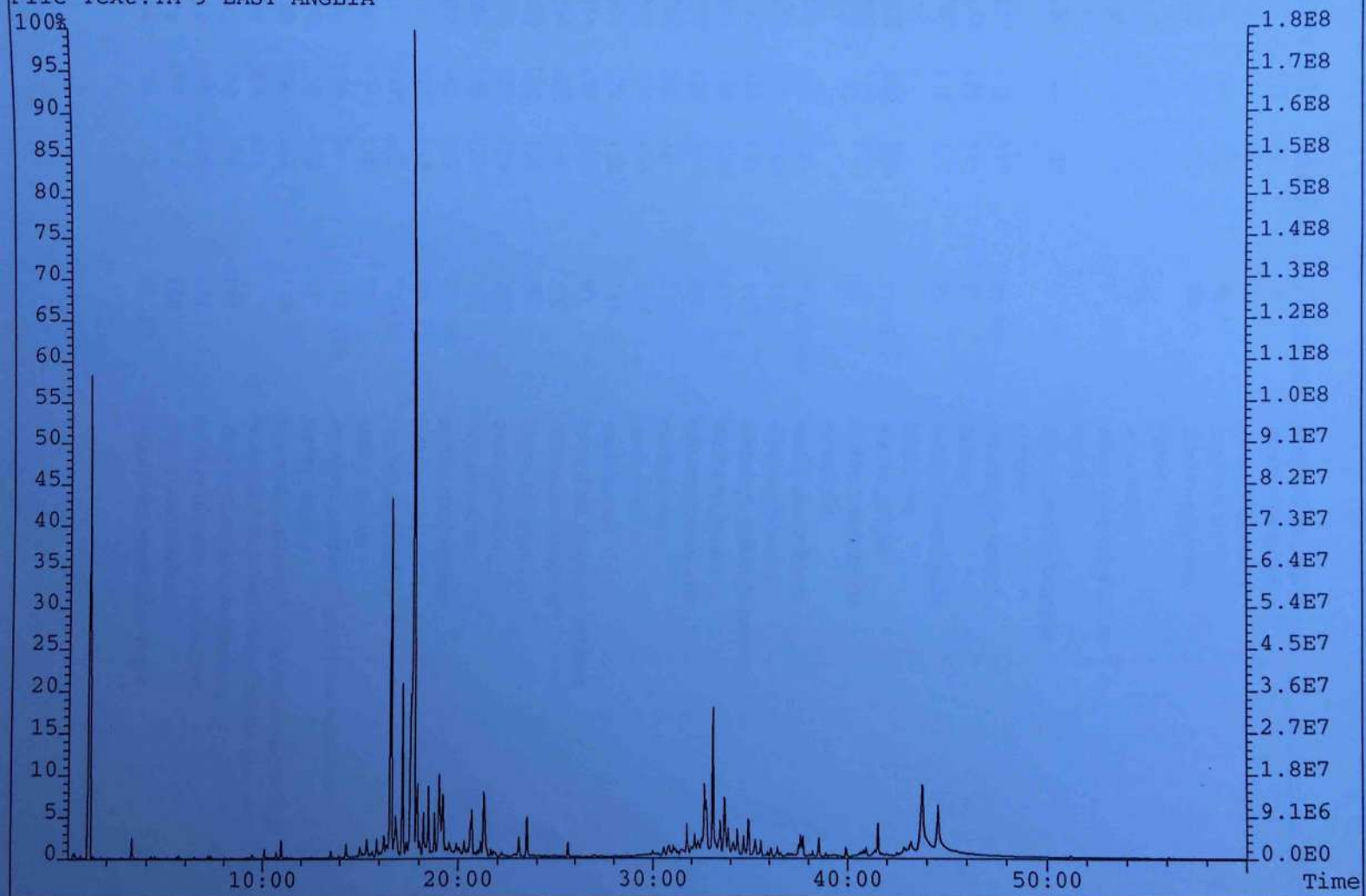


Scan	M+	Base ion	Fragments	General structure	Height
94	136	93	77,105,121	trimethyl, tricycloheptane	
288	154?	95	110,139	borneol	
306	138	138	123	methyl, methylthiobenzene?	
313	136	93	59,121	trimethyl, cyclohexenemethanol	
386	152	137	91,122	ethyl, methoxy, phenol	
408	150	135	95,107	butyl, phenol	
437	204	81	93,189	ethenyl, methyl, bis(methylethenyl), cyclohexane	
452	204	119	105,133,161	longipinene?	
462	204	161	119,189	octahydro, tetramethyl, methanoazulene	
472	204	94	119,133	decahydro, tetramethyl, methanoazulene	44
489	204	161	148,175	hexahydro, tetramethyl, methanonaphthalene	21
502	204	95	161	hexahydro, tetramethyl, methanonaphthalene	100
505	204	161	94,135,189	decahydro, trimethyl, methylene, methanoazulene	
520	204	94	133,161	decahydro, tetramethyl, methanoazulene	
527	204	81	93,189	octahydro, dimethyl, methylethenyl, azulene	
536	204	133	105,161,189	decahydro, trimethyl, methylene, cyclopropazulene	
543	204	122	107	octahydro, tetramethyl, cyclopropa naphthalene	10
548	204	119	93,133	longipinene?	6
590	204	105	161	hexahydro, dimethyl, methylethyl, naphthalene	
607	204	161	134	hexahydro, dimethyl, methylethyl, naphthalene	6
658	202?	187	159	cadinatriene?	
669	204?	95	119,189	decahydro, trimethyl, methylene, methanoazulene	
730	234	163	57,135	anisole?	
905	258?	190	243	?tricyclic derivative	
917	258?	190	243	?tricyclic derivative	
931	258?	243		?tricyclic derivative	9
934	258	258	147,215	phenanthrenecarboxaldehyde derivative?	
943	258	243	91	?tricyclic derivative	19
954	256	159	185,241	phenanthrenecarboxaldehyde derivative?	
966	258	258	133,215	?tricyclic derivative	
979	256	241	159	indacenone derivative?	
995	242	227	143	indacenedione derivative?	
1072	286	257	123, 271	ethenyl, dodecahydro, phenanthrenecarboxaldehyde	
1075	256	241	157	indacenone derivative?	
1099	234	219		methyl, methylethyl, phenanthrene retene	
1139	284	284	266	phenanthrene derivative?	
1184	314	239	299	octahydro, dimethyl, methylethyl, phenanthrene carboxylic acid	
1248	300	285	239	phenanthrene carboxylic acid derivative	9
1864	159?			?	

Comments

The composition is mixed, with some volatile terpenes, together with less volatile compounds. There are minor quantities of N- and S-groups. The obvious feature is the distribution of compounds by chromatography in to five clusters.

File:LC27826 #1-2139 Acq:26-AUG-1999 16:01:32 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-9 EAST ANGLIA



LC 27827 TA-10

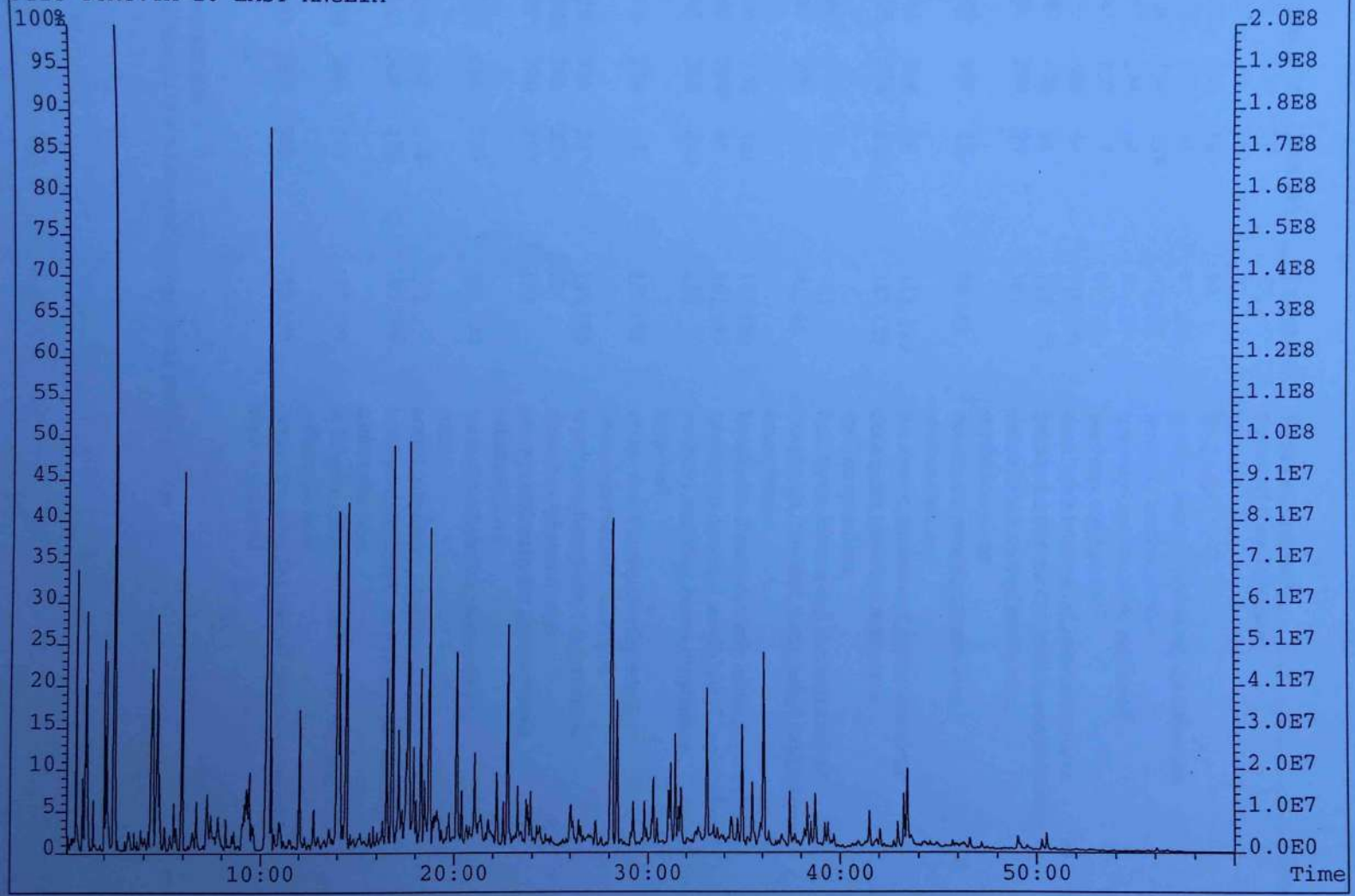
Scan	M+	Base ion	Fragments	General structure	Height
56	106	91	77	dimethylbenzene	
60	106	91	77	dimethylbenzene	
70	103	103	59,77	benzotrile?	100
91	107	107	79	dimethylpyridine lutidine	
125	103	103	76	benzotrile	
133	118	117	91,103	ethenyl,methylbenzene styrene	
136	118	117	91,103	ethenyl,methylbenzene styrene	
157	118	117	91,103	propenylbenzene?	
168	116	115	89	indene	46
190	117	117	90	methyl,benzotrile tolunitrile	
206	108	108	77,90	methyl,phenol	
211	117	117	90	methyl,benzotrile tolunitrile	
222	132	131	51,77,103	methyl,benzofuran	
233	130	130	115	diethenylbenzene	
242	132	132	117	dimethyl,ethenyl,benzene	
245	130	130	117	diethenyl,benzene	
257	117	117	90	benzeneacetotrile	
260	130	130	115	methylindene	
265	130	130	115	methylindene	
268	128	128	115	naphthalene	
274	130	130	92	methylene,propenyl,benzene	
296	130	130	102	dihydronaphthalene?	
300	134	134	89	benzo,thiophene	
342	129	129	102	benzopyridine	
363	129	129	102	benzopyridine	
398	142	142	71,115	methyl,naphthalene	
402	117	117	90	indole	
411	142?	142	71,115	methyl,naphthalene	41
464	131?	130	77	methyl,indole	
470	204	94	161, 189	decahydro,tetramethyl,methanoazulene	49
479	152	152	76	biphenylene?	50
488	204	161	130	hexahydro,tetramethyl,methanonaphthalene	
499	204	95		decahydro,trimethyl,methylene,methanoazulene	
502	156	156	141	ethyl or dimethyl,naphthalene	
510	156	156	141	ethyl or dimethyl,naphthalene	
521	154	154	128	ethenyl,naphthalene	
534	152	152	76,126	acenaphthylene/biphenylene	39

573	168	168	115,153	methyl,biphenyl	
599	153?	153	63,126	naphthalenecarbonitrile	
632	164?	163	83	phenalene	
642	166	166	83	fluorene	
663	166	166	83	fluorene derivative (e.g., acid)	28
682	166	166	83	fluorene derivative (e.g., acid)	
741	180	180	89,165	methyl,fluorene	
802	178	178		phenanthrene	42
809	178	178	89	anthracene	
833	179	179	76,151	fluorene-imine	
850	167	167	139	carbazole	
863	204	204	101	ethenylphenanthrene	
869	192	192		methyl,phenanthrene	
886	192?	192		methyl,phenanthrene	
889	192	192	95,165	methyl,phenanthrene	
896	190?	190	95,139,167	cyclopentaphenanthrene?	
900	181	181	77,152	methyl,carbazole	
904	192	192	95,165	methyl,phenanthrene	
943	204	204	101	phenyl,naphthalene	
979	204	204	101	phenyl,naphthalene	
988	204	204	101	phenyl,naphthalene	
995	202	202	88,101	pyrene/fluoranthrene	
1010	202	202	88,101	pyrene/fluoranthrene	
1028	202	202	88,101	pyrene/fluoranthrene	25
1065	230	230	115,152	terphenyl?	
1092	216	216	95,108	benzo,fluorene	
1104	216	216	95,108	benzo,fluorene	
1183	314	239	141,299	octahydro,dimethyl,methylethyl,phenanthrene carboxylic acid	
1224	226	226	100,113	benzo,fluoranthrene	
1233	228	228	114	triphenylene	
1238	228	228	114	triphenylene	
1398	252	252	126	perylene/benzofluoranthrene/benzopyrene	
1433	252	252	126	perylene/benzofluoranthrene/benzopyrene	
1440	252	252	126	perylene/benzofluoranthrene/benzopyrene	
1598	408?	189	134,229	pentacyclic triterpane derivative	

Comments

The composition is unique amongst the samples in the range of N-based compounds, and the polycyclic aromatic hydrocarbons. It is depleted in O-groups relative to other samples.

File:LC27827 #1-2138 Acq:27-AUG-1999 05:35:13 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-10 EAST ANGLIA



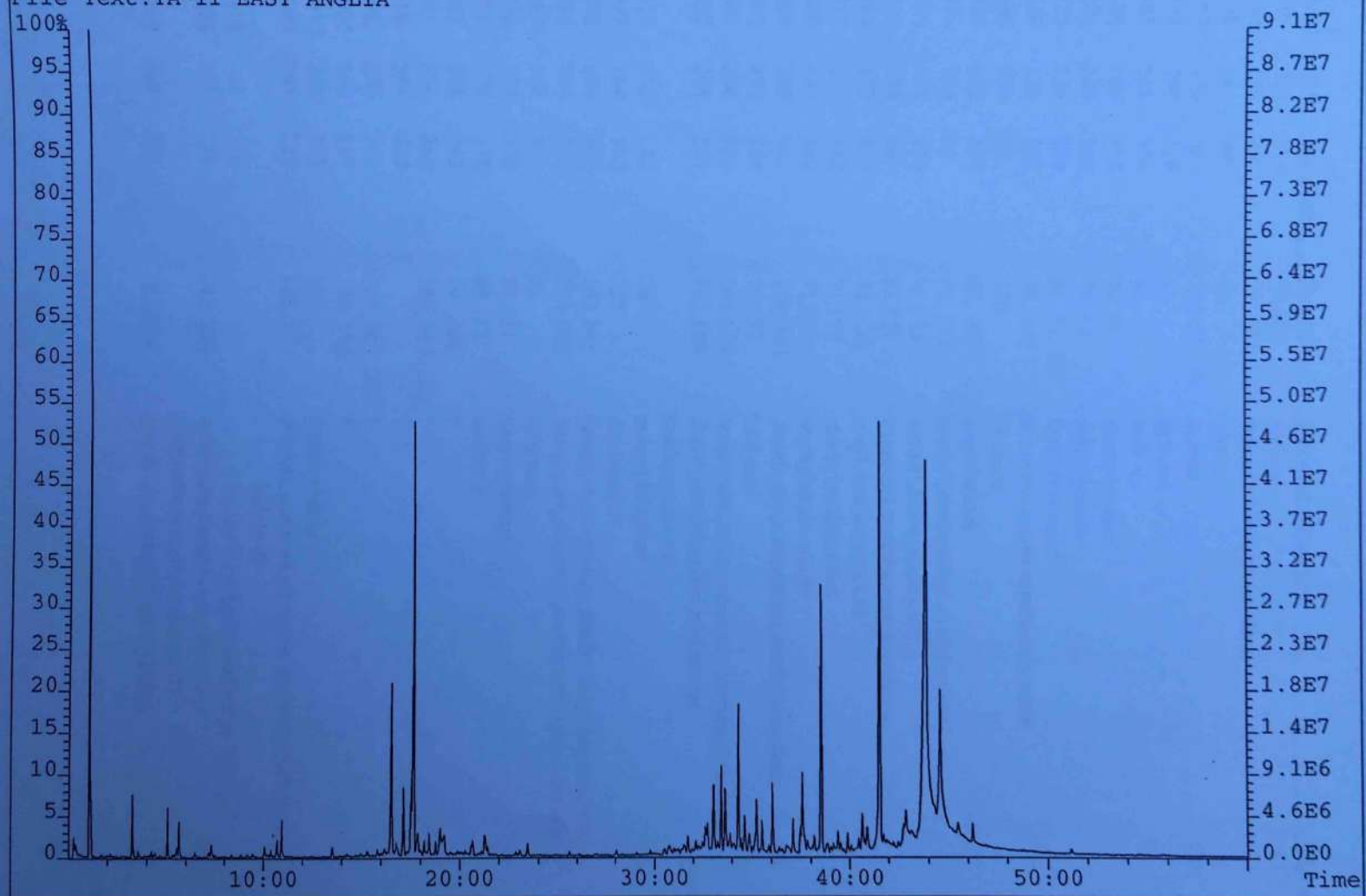
LC 27828 TA-11

Scan	M+	Base ion	Fragments	General structure	Height
92	136	93	77, 107, 121	trimethyl, tricycloheptane	15
144	136	95	71	carene?	
160	136	68	93	limonene	
208	136	121	93, 105	methyl, methylethylidene, cyclohexene	
304	138	138	95, 123	methoxy, methyl, phenol	
311	136	59	93, 121	trimethyl, cyclohexene, methanol	
385	152	137	91, 122	methoxy, ethyl, phenol	
470	204	94	119, 199	decahydro, tetramethyl, methanoazulene	21
487	204	161	148, 175	hexahydro, tetramethyl, methanonaphthalene	
499	204	95	161	decahydro, trimethyl, methylene, methanoazulene	
502	204	161	94, 189	decahydro, trimethyl, methylene, methanoazulene	100
508	204	94	113, 189	decahydro, tetramethyl, methanoazulene	
534	204	133	161, 189	decahydro, trimethyl, methylene, cyclopropazulene	
546	204	119	105	hexahydro, tetramethyl, methanoazulene	
588	204	105	94, 161	hexahydro, dimethyl, methylethyl, naphthalene amorphene?	
606	204	161	134, 189	hexahydro, dimethyl, methylethyl, naphthalene	
668	204?	85	161, 189	hexahydro, dimethyl, methylethyl, naphthalene?	
941	258	243	227	methoxy, dimethyl, benzo, dipyrone	15
952	256	241	159, 185	brayelin?	
978	256	241	159, 185	octahydro, dimethyl, methylethyl, phenanthrenecarboxaldehyde	
1028	238	223	181	tetrahydro, hexamethyl, indecenone?	31
1071	286	257	123	dimethoxyphenanthrene	
1098	234	219	102, 190	ethenyl, dodecahydro, phenanthrene carboxaldehyde	62
1158	248	248	233	methyl, methylethyl, phenanthrene retene	
1183	304	239	197, 299	acetyl, trihydroxy, naphthoquinone?	
1250	300	285	197, 239	octahydro, dimethyl, methylethyl, phenanthrene carboxylic acid	100
1271	302	302	197, 239	octahydro, dimethyl, methylethyl, phenanthrene carboxylic acid	95

Comments

The sample is a mixture of hydrocarbons and O-groups.

File:LC27828 #1-2138 Acq:26-AUG-1999 18:09:20 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-11 EAST ANGLIA



LC 27829 TA-12

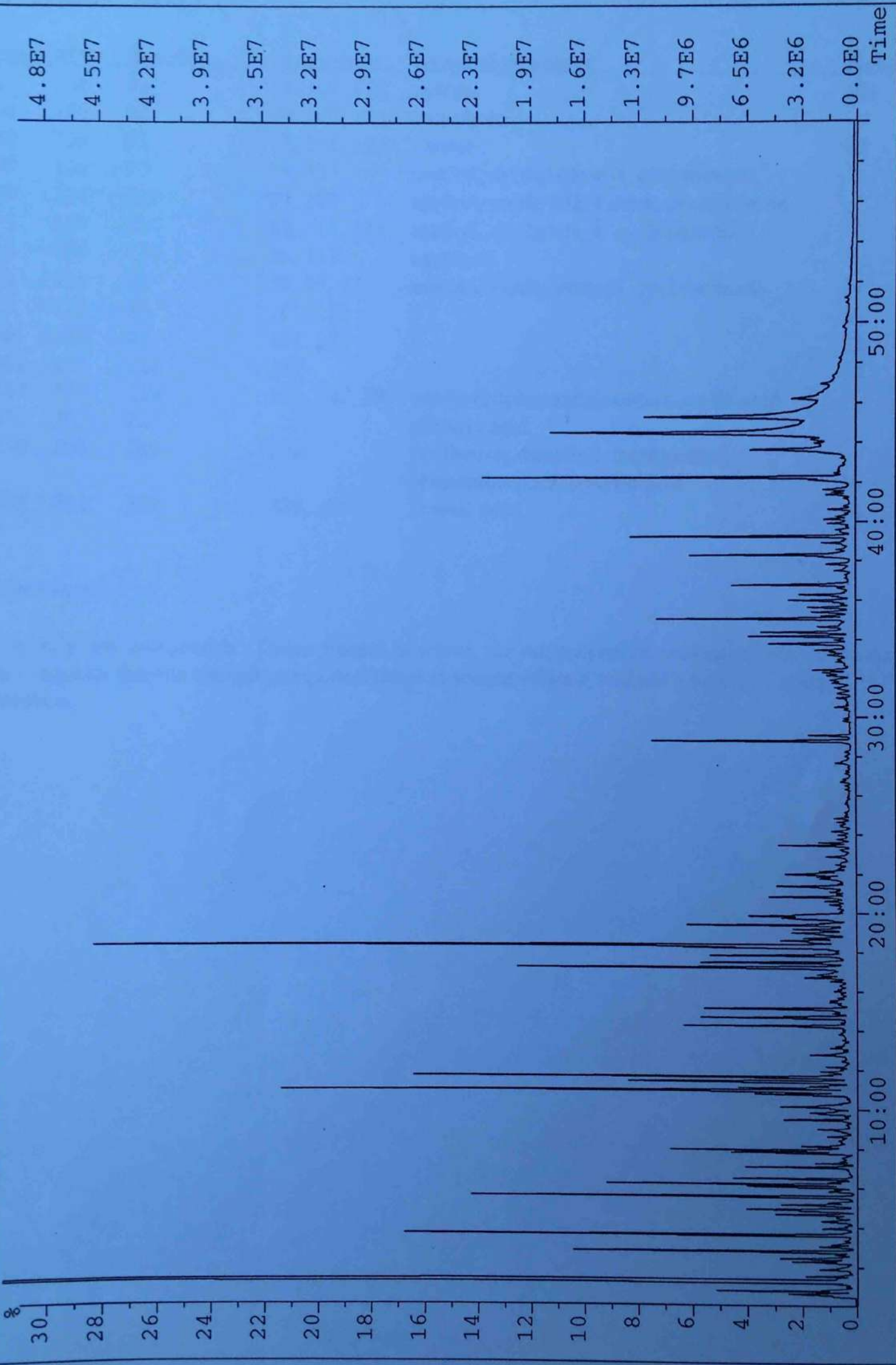
Scan	M+	Base ion	Fragments	General structure	Height
79	104	104	78,106	styrene	33
101	136	93	77, 107, 121	trimethyl,tricycloheptane	57
139	94	94	66	phenol	
157	136	93	77,107,121	carene	50
171	134	119	91	cymene	
183	116	116	89	indene	
200	108	108	79, 89	methylphenol	
221	108	108	79, 89	methylphenol	
225	124	124	81, 91, 109	methoxyphenol	
269	136	121	79, 105	trimethyl,methylenecyclohexene	
306	139	95	110	borneol	
310	128	128	64, 102	naphthalene	73
316	154	93	71, 111	methyl,methylethyl,cyclohexenol	
324	138	138	95,123	methyl,methoxyphenol	
331	136	59	93,121	trimethyl,cyclohexene,methanol	
405	152	137	91, 122	ethyl,methoxyphenol	
417	142	142	71,115	methylnaphthalene	
430	142	142	71,115	methylnaphthalene	
490	204	94	119, 161	decahydro,tetramethyl,methenoazulene	43
497	154	154	76,152	biphenyl	
507	204	161	148,175	hexahydro,tetramethyl,methanonaphthalene	
522	204	161	147,189	decahydro,trimethyl,methylene methanoazulene	
552	152	152	76	acenaphthylene	100
593	168	153	127	diaromatic?	
608	204	105	153,161	hexahydro,dimethyl,methylethyl,naphthalene	
626	204	161	134,189	hexahydro,dimethyl,methylethyl,naphthalene	
667	166	166	83	fluorene	
820	178	178	89,151	phenanthrene	27
828	178	178	89,152	anthracene	
962	258	243	145,204	?	
973	256	241	159, 185, 213	?	
979	254	239		?	
998	256	241	159, 185, 213	?	
1025	252	237	179, 195	?	
1047	202?	202	101	fluoranthrene	
1091	286	257	123, 271	ethenyl, dodecahydro,phenanthrenecarbox- aldehyde	
1118	234	219		methyl,ethyl,phenanthrene	
1204	314	239	141, 299	octahydro,dimethyl,methylethyl phenanthrenecarboxylic acid?	50
1268	300	285	197,239	octahydro,dimethyl,methylethyl	43

phenanthrenecarboxylic acid?

Comments

The volatile terpenes are a noticeable fraction. N- and S- groups are not evident.

File: LC27829 #1-2138 Acq:27-AUG-1999 06:59:51 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-12 EAST ANGLIA



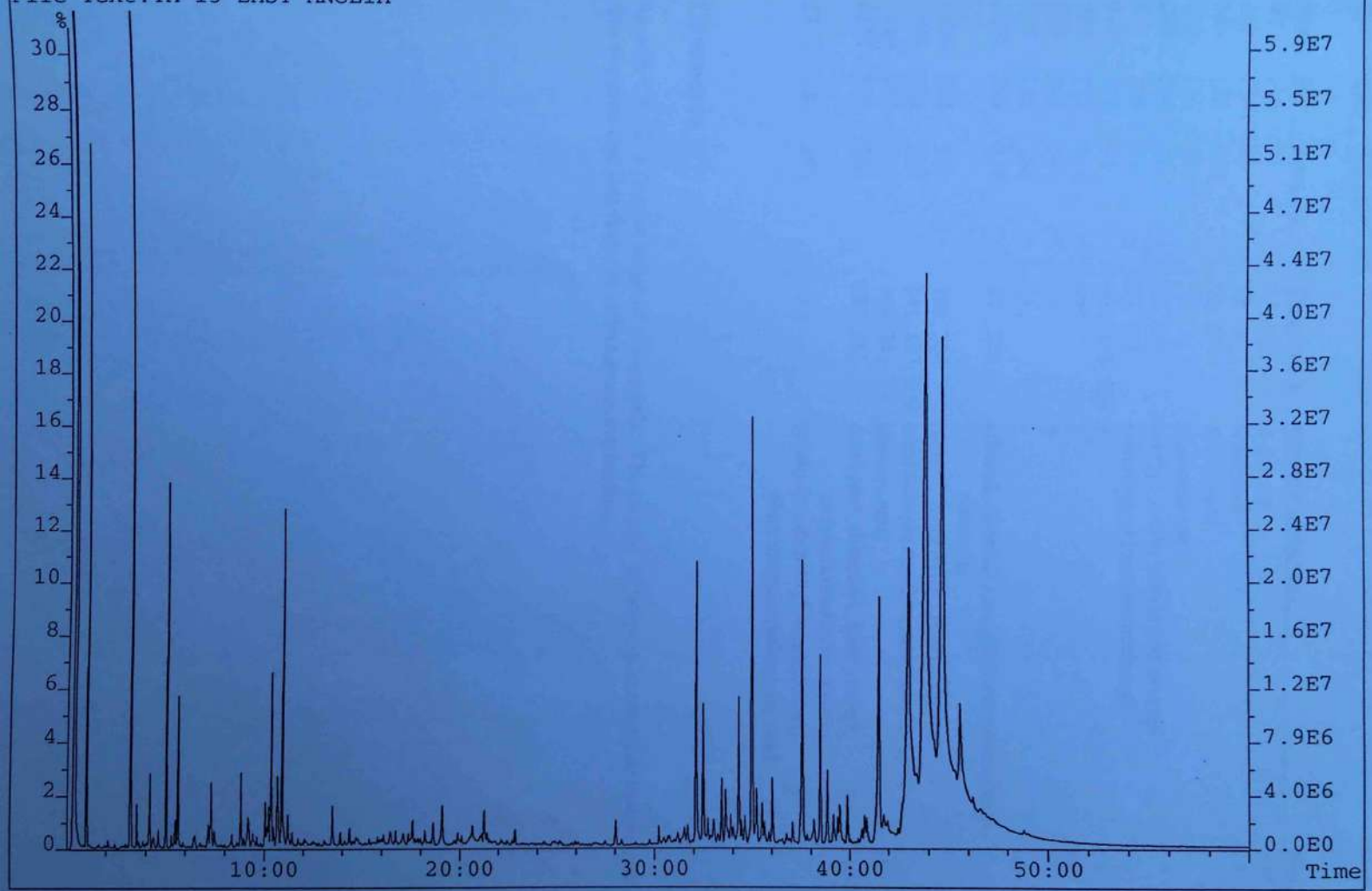
LC 27830 TA-13

Scan	M+	Base ion	Fragments	General structure	Height
91	136	93	77, 105, 121	carene	100
100	136	93	79, 107, 121	camphene	
142	136	93	77, 105, 121	carene	22
159	136	93	79, 121	methyl, methylethenyl, cyclohexene	
207	136	121	93, 109	methyl, methylethylidene, cyclohexene	
295	154	71	93, 111, 121	methyl, methylethyl, cyclohexenol	
304	150	132	59, 117	cymenol	
311	136	59	59, 93, 121	methyl, methylethenyl, cyclohexenol	21
915	272	93	161, 229	?	20
996	272	93	161, 229	?	28
1069	272	123	257	?	17
1182	314	239	141, 197, 299	octahydrophenanthrenecarboxylic acid	
1226	302	287		pimaric acid	
1250	300	285	239	octahydro, dimethyl, methylethyl, phenanthrenecarboxylic acid	36
1274	302	302	239, 285	abietic acid	33

Comments

Relatively few compounds. Those present, however, are not polycyclic aromatic hydrocarbons. This suggests that the limited compound range is source-related, and not a result of thermal alteration.

File:LC27830 #1-1903 Acq:27-AUG-1999 08:43:44 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-13 EAST ANGLIA



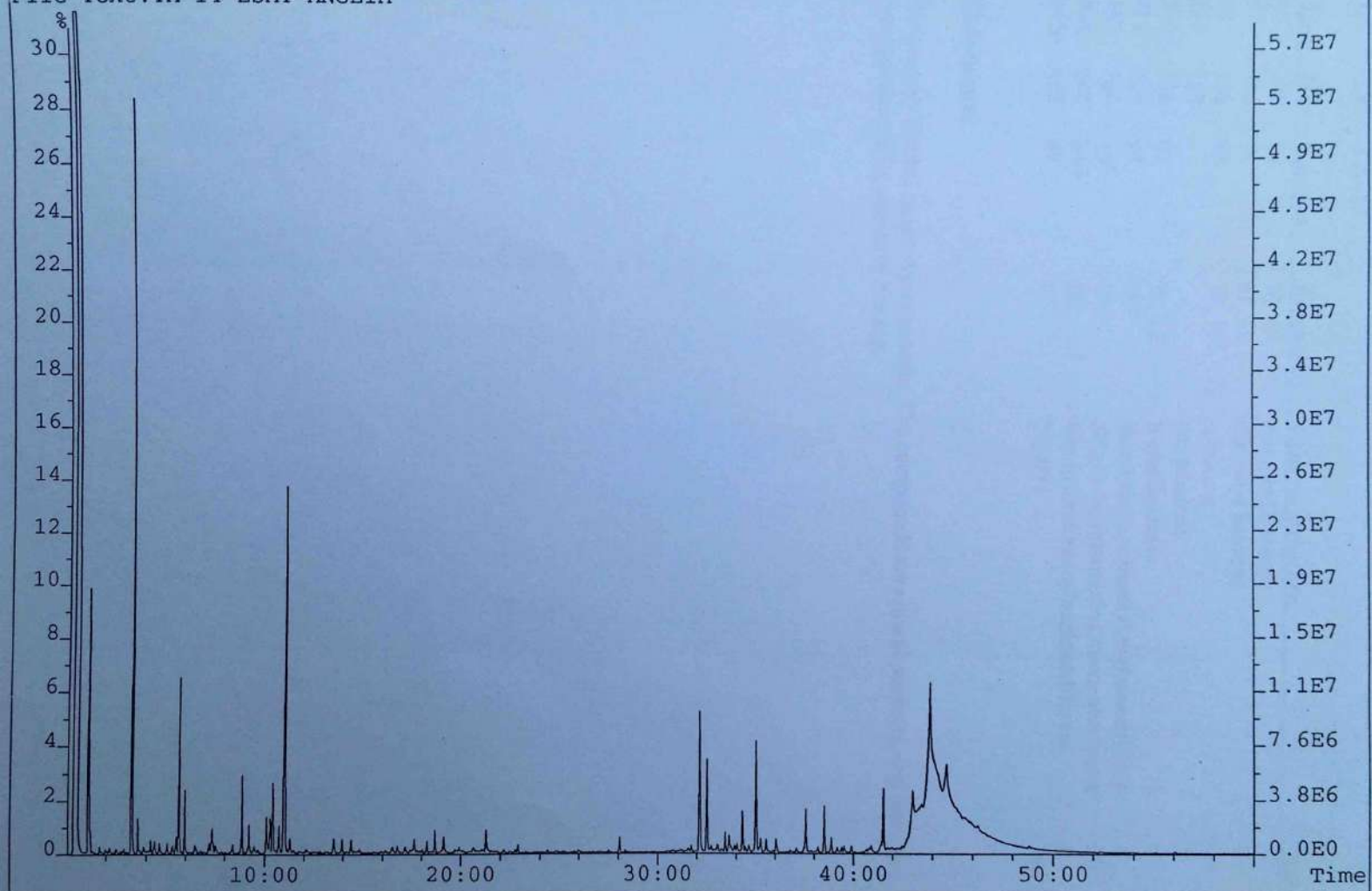
LC 27831 TA-14

Scan	M+	Base ion	Fragments	General structure	Height
93	136	93	77, 105, 119	α -pinene	100
161	136	68	93	limonene	24
169	135	133	73, 116	N-aromatic	
252	136	121	79,	phellandrene	
296	154	71	93, 111	methyl, methylethylcyclohexenol	
313	136	59	93, 121	trimethylcyclohexenmethanol	36
916	272	93	161, 189, 229	?	17
927	272	161	229	?	14
978	254	241	159	?	
998	272	161	229	?	10
1071	286	257	123, 271	ethenyl, dodecahydro,phenanthrenecarbox- aldehyde	
1098	234	219	190, 204	methyl, methylethyl,phenanthrene	
1183	314	239	141, 197, 299	octahydrophenanthrenecarboxylic acid	
1246	302	287	149, 241	pimaric acid	
1251	300	285	197, 285	octahydro, dimethyl, methylethyl, phenanthrenecarboxylic acid	
1274	300	285	239	octahydro, dimethyl, methylethyl, phenanthrenecarboxylic acid	

Comments

As with TA-13, a limited range of compounds. The paucity of polycyclic aromatic hydrocarbons also suggests that this does not reflect excessive heating.

File:LC27831 #1-2138 Acq:27-AUG-1999 13:33:54 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-14 ESAT ANGLIA



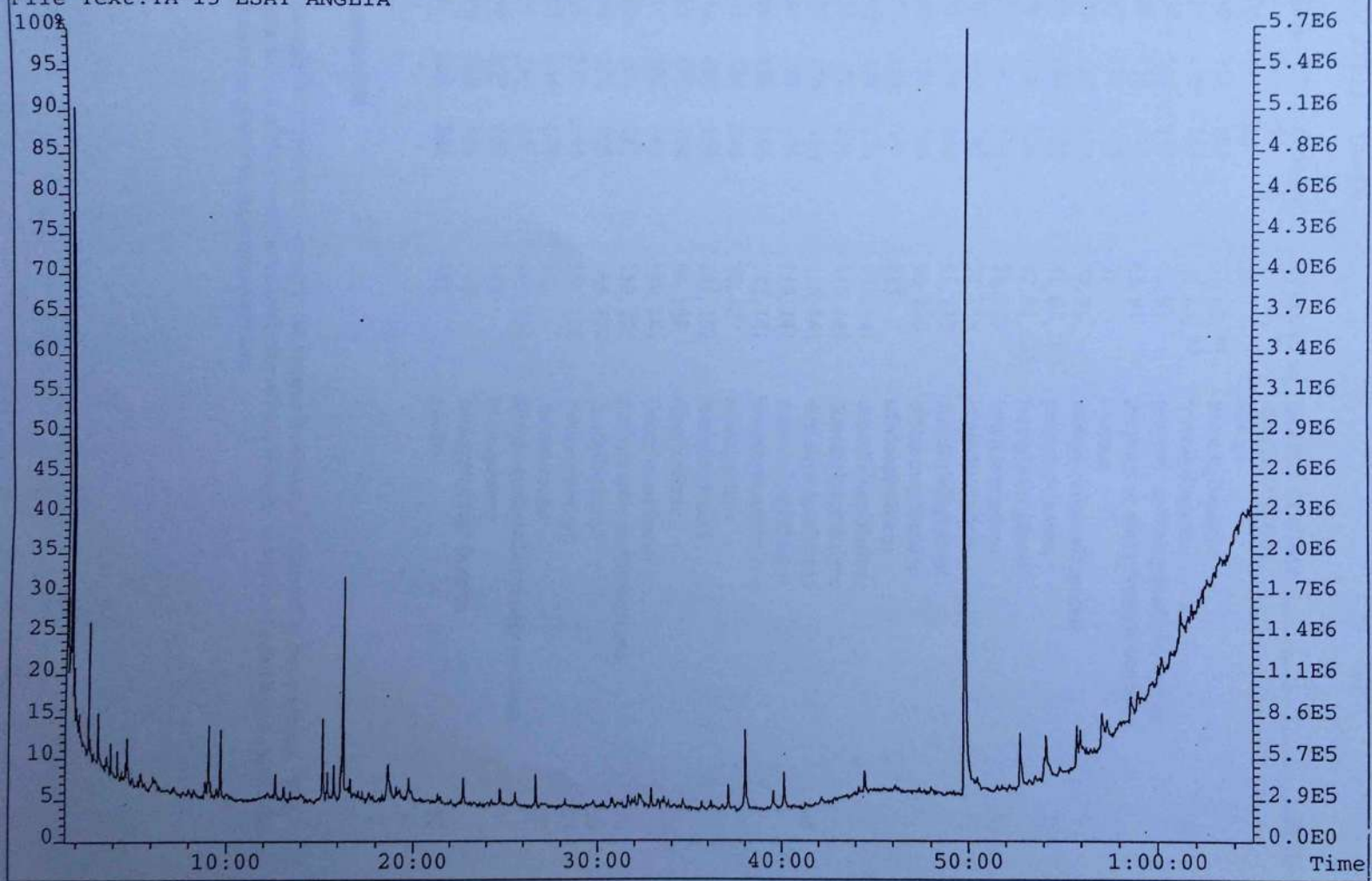
LC 27832 TA-15

Scan	M+	Base ion	Fragments	General structure	Height
46	106	91	51, 65, 77	dimethyl benzene	
49	106	91	51, 65, 77	dimethyl benzene	
75	136	93	77, 105, 119	α -pinene	15
257	128			naphthalene	7
275	136	93	79, 121	β -phellandrene	7
431	204	94	189	decahydro,tetramethyl,methenoazulene	8
462	204	161	189	decahydro,tetramethyl,methenoazulene	30
1083	240	240	152, 165	tetrahydrodimethylnaphthodifuran	8
1420	412	69	177, 191	hopanol	100

Comments

Extremely limited range of compounds. The compounds are natural products, and have not been aromatised by excessive heating.

File:LC27832 #1-2138 Acq:28-AUG-1999 08:12:22 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-15 ESAT ANGLIA



LC 27833 TA-16

Scan	M+	Base ion	Fragments	General structure	Height
50	106	91	51, 65, 77	dimethyl benzene	
105	94	66	55	phenol	
110	120	105	51, 65, 77	trimethylbenzene	
115	120	105	51, 65, 77	trimethylbenzene	70
137	118	115	63, 91	propenyl or ethenylmethyl-benzene	
140	118	115	63, 91	propenyl or ethenylmethyl-benzene	
157	134	119	91	cymene	
223	132	117	77, 91	methyl, propenylbenzene	
261	128	128	51, 63, 102	methyleneindene	100
286	136	121	77, 91, 103	methyl,ethylphenol	
363	142	141	71, 115	ethylideneindene	66
375	142	141	71, 115	ethylideneindene	53
431	178	163	91, 117	dimethylethylphenol	
440	154	154	76, 128	ethenyl-naphthalene	
451	156	141	115	ethylnaphthalene	
462	156	156	115, 141	dimethylnaphthalene	
473	156	156	115, 141	dimethylnaphthalene	
477	156	156	115, 141	dimethylnaphthalene	45
490	156	156	115, 141	dimethylnaphthalene	
501	156	156	115, 141	dimethylnaphthalene	
525	154	154	76, 127	acenaphthene	
535	168	168	141, 152	methylbiphenyl	
555	168	168	84, 139	dibenzofuran	
611	196	165	139, 181	fluorene, methanol	
629	196	181	153, 165	methylenebis, methylbenzene	70
695	210	195	165, 178	diethylbiphenyl	93
721	210	195	165, 178	diethylbiphenyl	33
763	178	178	152	phenanthrene	50
807	210	57	165, 195	dihydromethylethenyl, naphthofuran	
827	222	207	115	hydroquinone	
877	208	193	102	tetramethylnaphthacene	
57	202	202	101	pyrene	20

Comments

Although there are some O-groups, the sample is noticeably depleted in heteroatoms. The concentration of polycyclic aromatic hydrocarbons is high. A series of substituted naphthalenes is present in unusually high concentrations.

File:LC27832A #1-2137 Acq:31-AUG-1999 10:22:02 Septum EI+ Magnet 70SE
TIC (+RP) Exp:DEFAULT
File Text:TA-15 EAST ANGLIA

