Active Creosote Extraction (ACE)

D1.1 Servicing, Calibration and Installation of Analytical Equipment

April 2022

Electricity Distribution

nationalgrid

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1. Identification and subsequent role of the analytical equipment

Overview of the extraction process

The basis of this trial is the extraction of creosote from end of life wooden poles using Supercritical Fluid Carbon Dioxide (SFCO2), carbon dioxide that is above its critical temperature (Tc) and pressure (Pc) (1078 psi and 31^{o}C). Critical temperature is the highest temperature a substance can remain liquid irrelevant of the pressure. Critical pressure, is where the point where a liquid and vapour can no longer co-exist. The Critical point (Cp) is the point on the liquid/gas equilibrium curve beyond which there is no distinction between these two phases. TP is the triple point for a substance and is the unique temperature and pressure where the three phases, solid, liquid and gas, all co-exist together.

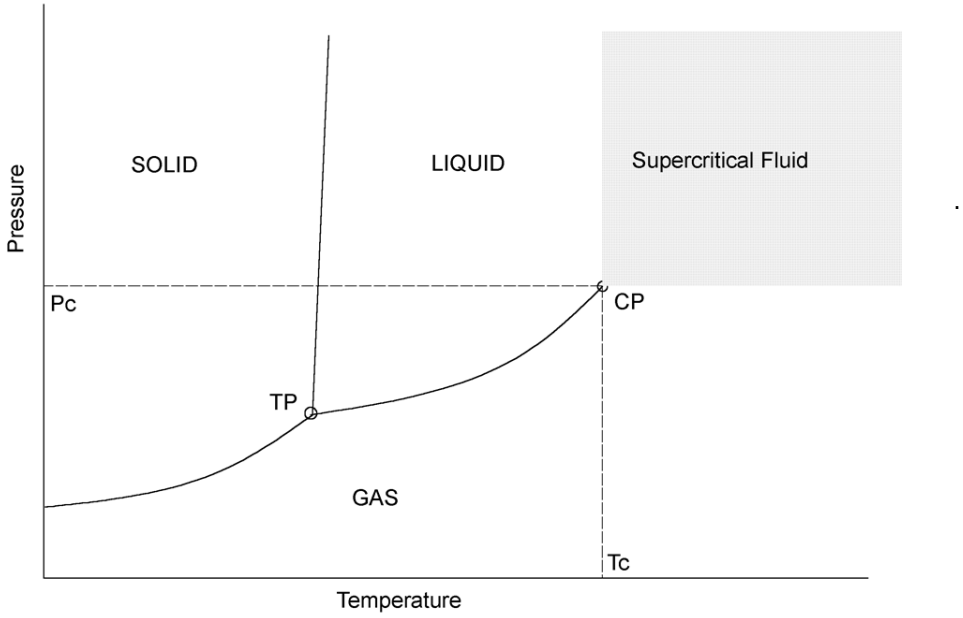


Fig. 1. Phase diagram showing Supercritical Fluid region

Under these conditions, it has a viscosity and diffusivity more like a gas, and a density more like a liquid. It is these characteristics have the potential to increase permeability into the wood and increase the mass transfer of the creosote out. (Viscosity is a fluids resistance to deformation. Diffusivity is the measure of the rate at which a fluid spreads. Density is mass per unit volume. Permeability is the rate of the diffusion through a porous material. Mass transfer is the movement of mass from one location to another.)

The basis of the extraction is the pressurisation of the wood under these conditions in a purpose-built temperature controlled high-pressure extraction vessel capable, in the first instance, of accepting poles, which are 2.5 m in length and 30 cm in diameter. The vessel will be pressurised to the required target conditions and when these conditions are attained, a low flow of carbon dioxide is continually flushed through to remove any extracted creosote. If success is achieved on this length, the extraction vessel can be increase to 5.0 m with the diameter remaining at 30 cm.

The conditions for the extraction will be 1200 psi and 32^{o}C.

Measuring extraction success

There are 2 periods when quantitative chemical analysis will be required.

Firstly during the dynamic extraction period to follow the concentration of creosote being extracted from the wood. Dynamic analysis will be used to analyse the carbon dioxide, which contains the solubilised creosote, as it passes through the extraction vessel, and analysis is achieved by diverting a small representative sample into a purpose build high-pressure flow cell and monitoring its concentration using a Fourier Transform Infra Red spectrometer.

Secondly, post extraction, to determine the level of creosote remaining in the pole.

Here representative samples will be taken from different depths in the mid length of the pole, the furthest point from the open ends and the most difficult for the Supercritical fluid carbon dioxide to reach. These samples will be ground into sawdust, which gives the greatest surface area per mass. A solvent will then be added, in this analysis high purity Acetonitrile to ensure no contamination is added. After a period of 30 minutes of agitation, the solvent will be removed and a quantitative solution will be prepared by making the solution up to an accurately known volume. This is then analysed by GC/MS (Gas Chromatography / Mass Spectrometry) and HPLC (High Pressure/performance Liquid Chromatography.

Fourier Transform Infra Red spectroscopy

Infrared is widely used in society such as in heaters and heat detecting cameras, but in spectroscopy, it is used to qualitatively and quantitatively monitor the presence and concentration of organic compounds, such as creosote in this case.

Carbon dioxide consists of C=O bonds which absorbs Infra red energy at characteristic frequencies as seen in Fig. 2 below.

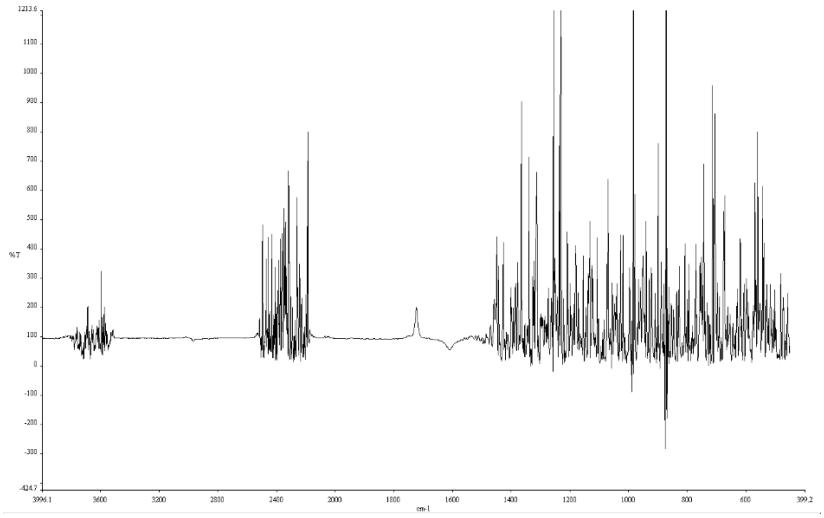


Fig.2. Characteristics of Infrared spectra of high-pressure carbon dioxide

Creosote is a mixture of hydrocarbons (C-H bonded together) and these bonds absorb infrared radiation at different characteristic frequencies, which allow them to be characterised and quantified as seen in Fig.3.

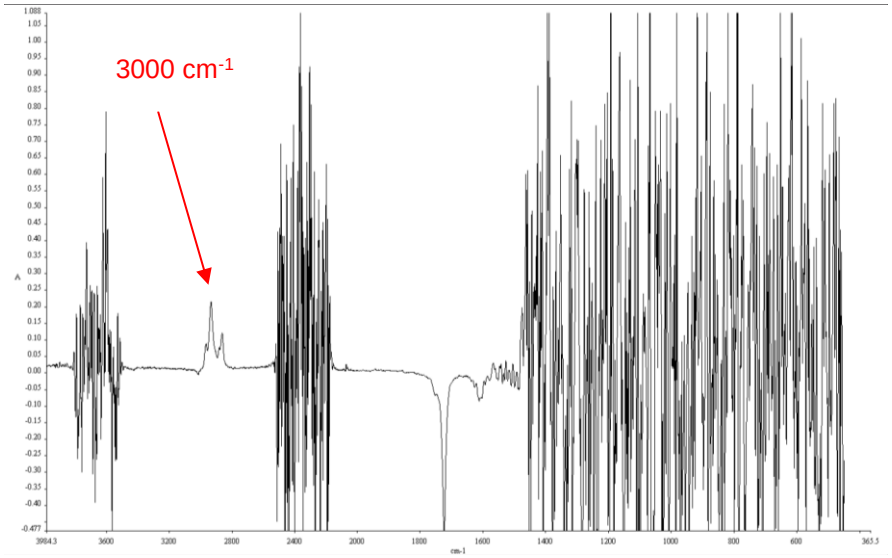


Fig.3. Infrared spectra of creosote (peaks at approximately 3000 cm^{-1})

Infrared radiation has an approximate wavelength range of 10^{-3} to 10^{-6} m. This corresponds, in this case, to the energy associated with bending and stretching the C-H bonds in hydrocarbons. These bonds interact with the incoming infrared radiation and stretch or bend.

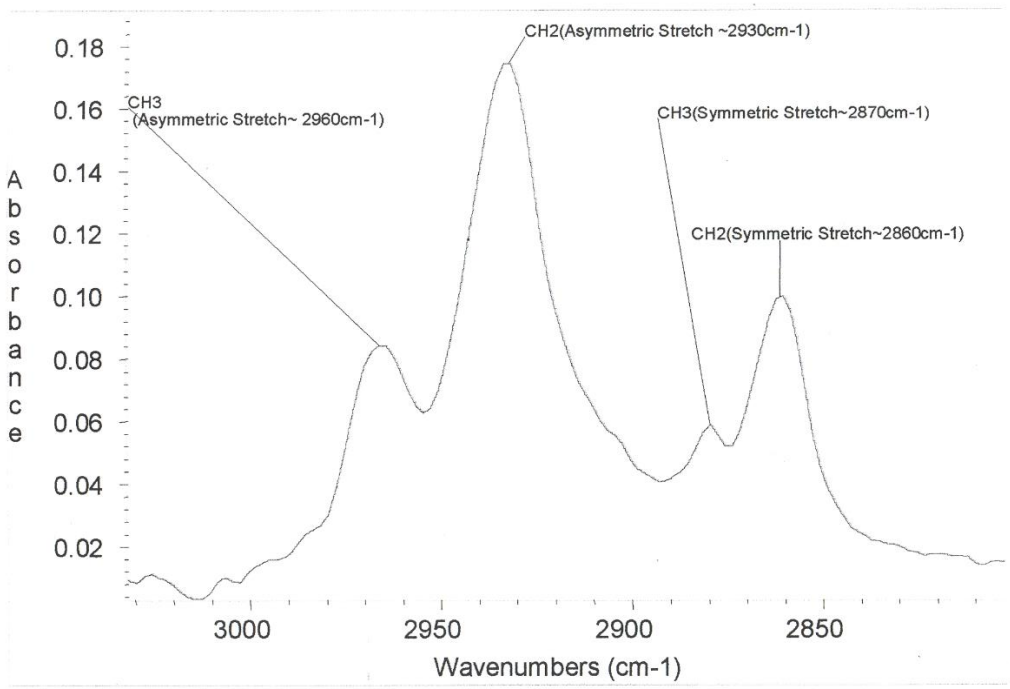
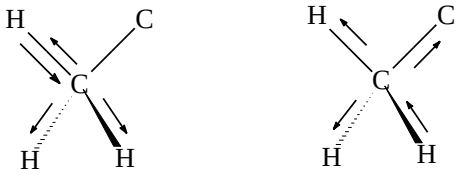
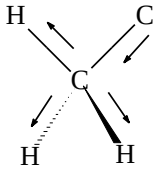


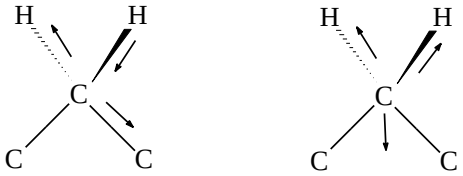
Fig.4. Individual peaks and their associated stretching configurations



CH_3 Asymmetric Stretch



CH_3 Symmetric Stretch



CH_2 Asymmetric Stretch CH_2 Symmetric Stretc

Fig.5. Detailed stretching configurations, arrows showing direction of stretching

The functional groups, the groups of atoms that give the compound its chemistry, absorb the infrared radiation at different wavelengths and depends on the energy required to stretch or bend the bonds. Some examples are given below. In this case, Wavenumber is used as a more convenient unit and is 1/wavelength in cm, and is defined as the number of waves in 1 cm.

Table 1 Functional Groups

Functional group	Approximate wavenumber at which they absorb (cm^{-1})
C-H	3000
O-H	3300-3600
C=O	1700
N-H	3400
C=C	1600

In our case, we have C-H bonds. By going by table 1, we would expect there to be absorbance in the 3000 cm^{-1} region which is what we observe.

In addition, the height or area, of the peak(s) is directly proportional to its concentration (within limits) and by monitoring the characteristic peak height/area, we can determine its concentration, this is the method used for the dynamic extraction period. According to the “Waste classification, Technical guidance WM3”, all components of the creosote must be at or below 0.1% to classify the waste as non-hazardous.

GC/MS Gas Chromatography/ Mass Spectrometry

Gas Chromatography / Mass Spectrometry is an analytical technique that will be used post extraction to determine the concentration of the creosote remaining in the wood. This analytical procedure involves several stages.

Firstly sampling the wood to take a homogenously representative sample for analysis. This is done by sampling the wood at the centre point of the pole at different depths to determine the efficiency of the Supercritical extraction and its ability to penetrate into the pole. In addition, samples from the whole width of the pole will be taken and blended before analysis to achieve an overall creosote concentration for the wood.

Secondly extraction of the creosote using a suitable solvent. The solvent used must be capable of dissolving the contaminant, in our case Acetonitrile.

Thirdly prepare a quantitative sample.

Quantitatively injecting the solution into the GC/MS system, using a accurately graduated glass syringe.

The creosote consists of numerous hydrocarbon components; those represented in the standard method of creosote quantitation are included in appendix A. The standard solution consists of accurately measured individual compounds dissolved in a known volume of solvent, the solvent being Acetonitrile.

Gas chromatography is a separative technique and involves passing the injected solution through a long thin coated glass tube, known as a column (coating known as the stationary phase) (Column used in this analysis is 30m in length by 0.25 mm in diameter), using high purity Helium gas (99.9999%) (carrier gas or mobile phase) to carry the components through without interaction.

Each of the components will interact differently with the column coating as they travel along, (due to boiling points and chemical structure) and the greater the interaction the more the column retards and slows the component’s passage. This results in the complex mixture being separated and arriving at the exit of the column at different times (retention time). Under given conditions this time becomes representative of the component.

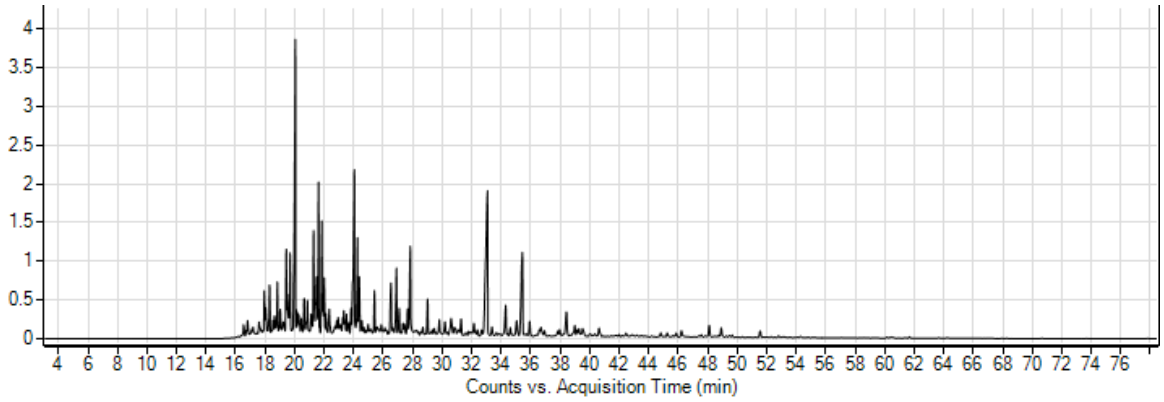


Fig.6. Gas chromatogram of Creosote, each peak represents an individual component

On exiting the column each component enters the mass spectrometer where each individual component are subjected to fragmentation and this pattern can be regarded as a “fingerprint” for that component, and allow identification

Once again, as with Infra Red spectrometry, the peak height/area of the separated components is representative of their concentration. With reference to Fig.6, it is important that the supercritical fluid is able to dissolve and extract all the individual components in the creosote, selective extraction would leave certain components behind. To ascertain whether selective extraction is taking place, the extract is compared to the standard reference solution.

HPLC - High Pressure / Performance Liquid Chromatography

HPLC works on a similar principle to GC, a solution mixture travels through a column where the mobile phase is a liquid. This is used in conjunction to GC and can separate out components, which prove problematic to separate in GC, and so give a complimentary analysis. Problematic components tend to have high boiling points or functional groups (those groups of atoms within the molecule that give the chemistry) which interact very strongly with the stationary phase and therefore have very long retention times (time it takes to come off the column), or in some cases remain bound to the column.

2. Servicing, installation and calibration of the analytical equipment

The analytical equipment has been in storage and after moving to the new location required servicing and reinstallation.

New columns specifically for this analysis were required for both GC and HPLC, all the seals in the high pressure liquid pumps have to be replaced.

Servicing has required the software to be upgraded to allow support by Agilent and the current version of Windows.

Agilent are the makers of the chromatography systems and are the leaders in this field.

The infrared spectrometer requires an upgraded Laser to be fitted along with an infrared source and software. The infrared spectrometer requires an infrared source, this consists of a glowing ceramic lamp, to generate infrared radiation, and also a laser to monitor the movement and position of the optics which generate the spectra. Both of these have a limited lifespan and require replacing by an engineer.

Fig.7 GC/MS system (MS on left, GC on right)

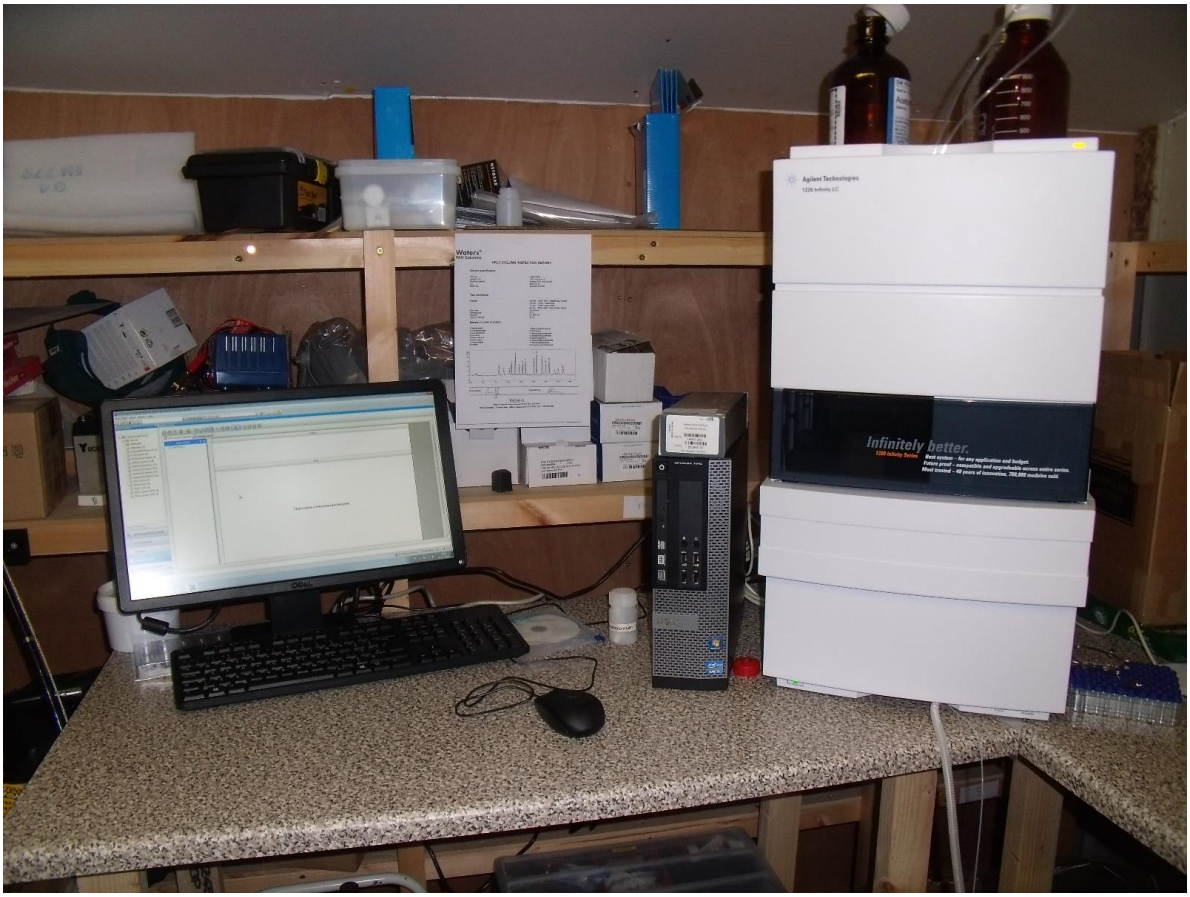


Fig.8 HPLC system

3. Monitoring and quantitation of the extraction process

As stated, there will be two periods when analysis will be required; during dynamic extraction and post extraction.

Analysis of the dynamic extraction phase will be completed by Infrared spectroscopy using a high pressure flow cell specifically designed for SFCO2. This analysis will be able to determine the extraction efficiency of each of the phases of this trial.

Post extraction, to examine extraction efficiency and remaining creosote concentrations. These results will also be analysed independently by Minton, Treharne Davies based in Cardiff, and these results will be supplied to Natural Resources Wales. As already stated, we will need to reduce each of the components to, or below, 0.1% of the total for the waste to be classed as non-hazardous.

The extraction is followed by monitoring intensity of the CH peaks, using the Infrared spectrometer and shows that the intensity decreases with time showing the concentration of the hydrocarbon decreases (i.e. creosote) as it is extracted and flushed away. Fig 9 shows a past extraction profile and shows the how the intensity of the hydrocarbons decreases over time.

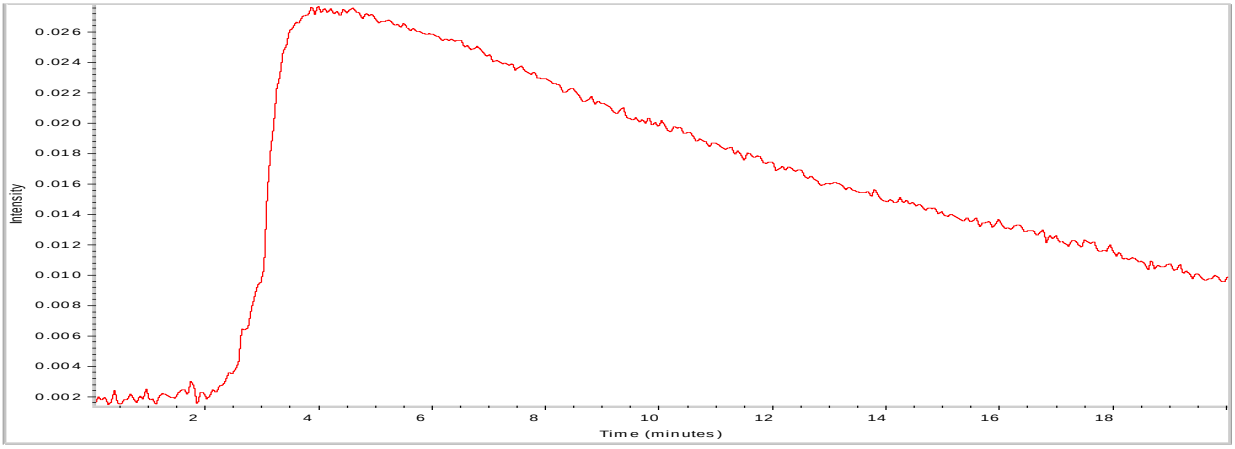


Fig.9 The extraction profile from past extraction, the graph shows the height of the peaks at approximately 3000 cm-1

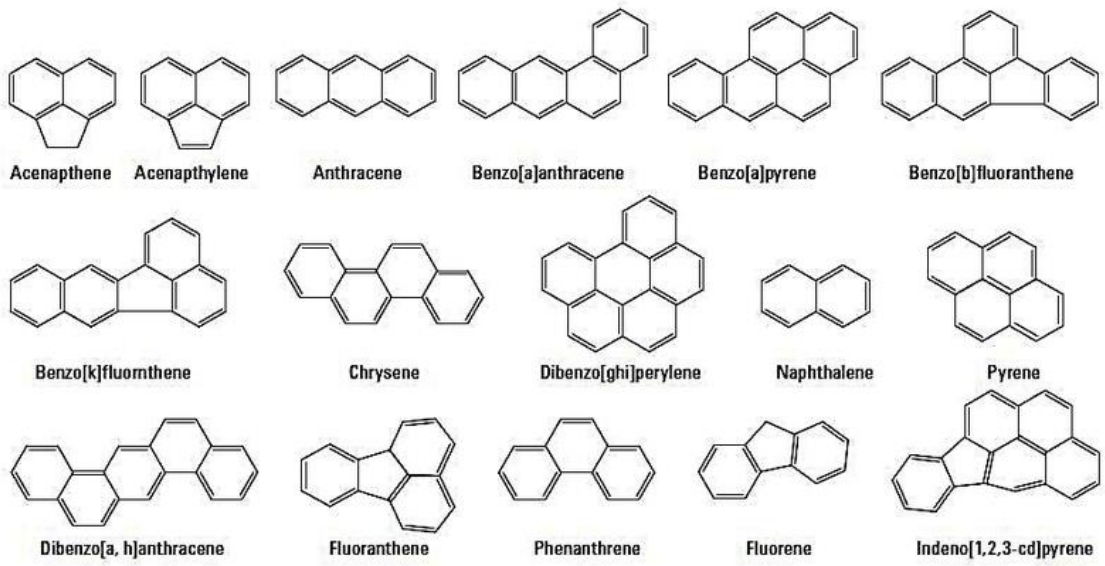
Fig. 10 Infrared spectrometer

Fig. 11 High pressure cell situated in infrared spectrometer

Appendix A

Table 2 Test compounds for Creosote

Test Compounds
Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo[a]anthracene
Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Indeno(1,2,3-c,d)Pyrene
Dibenz(a,h)Anthracene
Benzo[g,h,i]perylene



The chemical structures can be seen above and consists of multiple rings of carbon atoms.

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