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# CHEMICAL ANALYSIS AND MATERIALS CHARACTERISATION

We have developed use of a range of analytical techniques measuring the concentrations of specific volatiles generated during both laboratory studies and real fires.

The analysis of gases in fire effluents represents a specialized field due to the complexity and reactivity of the gas mixtures and accompanying particulates and the changes in concentration with time. This has led to adapting existing analytical methods or developing new ones for the analysis of gases evolved during combustion. BS ISO 19701 presents standard chemical methods for the determination of individual gases of toxicological importance. Typically, multiple methods are needed to determine all the species of interest for fire hazard analysis. Some of the most commonly used techniques in our laboratories are summarised below.

## Carbon, hydrogen, nitrogen and sulphur analyser (CHNS)

Carbon, hydrogen, nitrogen and sulphur analyser (CHNS) is an instrumental technique for composition of typical organic substances. Sample requirements are just a few milligrams of solid or liquid.

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# Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX)

SEM provides detailed high resolution images of the sample by passing a focussed electron beam across the surface and detecting either secondary or backscattered electrons. This also allows for imaging at very high magnifications, allowing sub micrometre features to be seen, well beyond the range of optical microscopes.

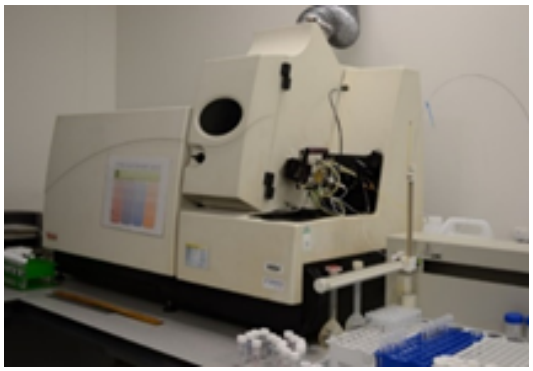
EDX can provide both qualitative and quantitative elemental analysis of larger atoms of particular features of the sample. However, the method cannot identify oxygen or nitrogen in organic matter as those ions are too small.


# Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is an elemental analysis technique capable of detecting most of the periodic table of elements at parts per million or parts per billion (µg/l) levels. It is used in a variety of fields including, but not limited to, environmental monitoring, chemical analysis, and clinical research.

The Inductively Coupled Plasma (ICP) is an ionization source that fully decomposes a sample into its constituent elements and transforms those elements into ions. Samples are fed through a plasma source where they become ionized. Then, these ions are sorted on account of their mass by mass spectrometer (MS).

ICP-MS systems are powerful analytical instruments. However to obtain the best quality of data from these instruments, sample preparation and introduction methods must be performed with care. In addition, data obtained needs to be scrutinised for the occurrence of spectral and non-spectral interferences.



Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

# Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS) has been regarded as a "gold standard" for volatile organic substance identification. The GC separates different molecules present in a volatile mixture, so they arrive at the MS analyser separately. The mS then identifies different molecules. Sometimes the high temperatures used in the GC-MS injection port and oven can also result in thermal degradation of injected molecules, thus resulting in the measurement of degradation products instead of the actual molecules of interest.

The typical GC-MS instrument is capable of performing either full scan (FI) or Selective Ion Monitoring (SIM) both functions run either individually or parallel, depending on the setup of the particular instrument.

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Full scan is useful in determining unknown compounds in a sample, and covers a broad range of mass fragments to monitor (typically m/z 50 to m/z 400) while SIM focuses only on certain mass fragments confirming the presence of specific volatile organic compounds in a sample.

Some common GC-MS applications include:

- clinical and medical studies
- fire investigation,
- forensic analysis
- environmental analysis,
- post-contamination
- explosives investigation,
- identification of unknown samples for volatile organic compounds presence


Gas Chromatography-Mass Spectrometry (GC-MS)

# Gas Chromatography- Mass Spectrometry Thermal Desorption (GC-MS TD)

Gas Chromatography- Mass Spectrometry Thermal Desorption (GC-MS TD) is a technique that involves collecting volatile and semi-volatile organic compounds onto a sorbent (thermal desorber/desorption tube, TD). This can be performed remotely and stored for subsequent analysis. Analysis involves heating the sorbent in a flow of the carrier gas to release the compounds and concentrate them into a smaller volume and then transfer them to the GC-MS.

The majority of TD applications use sorbent tubes and a two-stage desorption process to focus the analytes into a narrow band of gas, and so achieve the maximum sensitivity enhancement. TD is applicable to a wide range of sample types – solids (using dynamic headspace, or direct desorption), liquids and gases (passive sampling, on-line sampling or Tedlar bags).

Applications of thermal desorption cover a very broad range applications. Some of those important to our work include:

- Workplace/occupational health monitoring
- Outdoor environmental monitoring
- Residual volatiles emitted from building products and materials
- Breath analysis for disease diagnosis
- Defence/homeland security (detection of chemical agents)


Gas Chromatography- Mass Spectrometry
Thermal Desorption (GC-MS TD)

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# Gas Chromatography Tandem Mass Spectrometry (GC-MS/MS)

Gas Chromatography Tandem Mass Spectrometry (GC-MS/MS) volatile organic compounds are separated in a gaseous state based on their various physical and chemical properties and their interaction with the analytical column's stationary phase. Once separated, they enter the tandem mass spectrometer (MS/MS).

MS/MS is a technique where two or more mass analysers are coupled together, using an additional reaction step, to increase the analytical sensitivity. The analytes of interest are quantified through comparison to external or internal standards. In addition GC-MS/MS is well-suited to the identification of unknown volatile components using the mass fragmentation patterns and mass transitions associated with the unknown analyte.

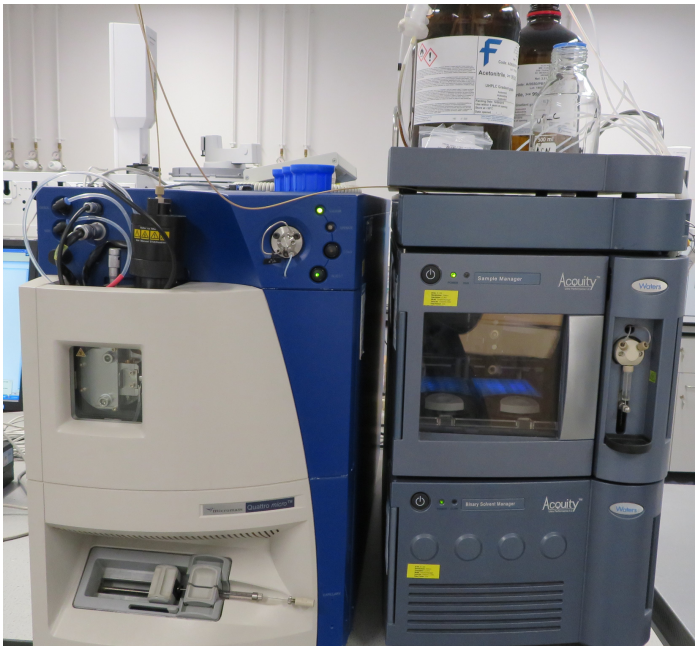
GC-MS/MS analysis can be performed on liquids, gases or volatile solids. For liquids, the sample is directly injected into the GC. For gases, gastight syringes are used to transfer the gaseous components directly into the GC.  For solids, the analysis involves solvent extraction pre-treatment.

Some common GC-MS/MS applications are:

- Analysis of liquid mixtures
- Toxicological screening (analysis of small molecules in serum or urine).
- Identification of organic pollutants.

## Ultra Performance Liquid Chromatography - Tandem Mass Spectrometer (UPLC-MS/MS)

Ultra Performance Liquid Chromatography - Tandem Mass Spectrometer (UPLC-MS/MS) is an analytical technique that combines the physical separation capabilities of liquid chromatography (LC) with high precision mass analysis capabilities (MS/MS).




Its application is oriented towards the general detection and potential identification of volatile, semi-volatile and non-volatile organic compounds in a complex mixture. The technique has both qualitative and quantitative uses. These include identifying unknown compounds, and determining the structure of a compound by observing its fragmentation or simply quantifying the amount of a compound in a sample.

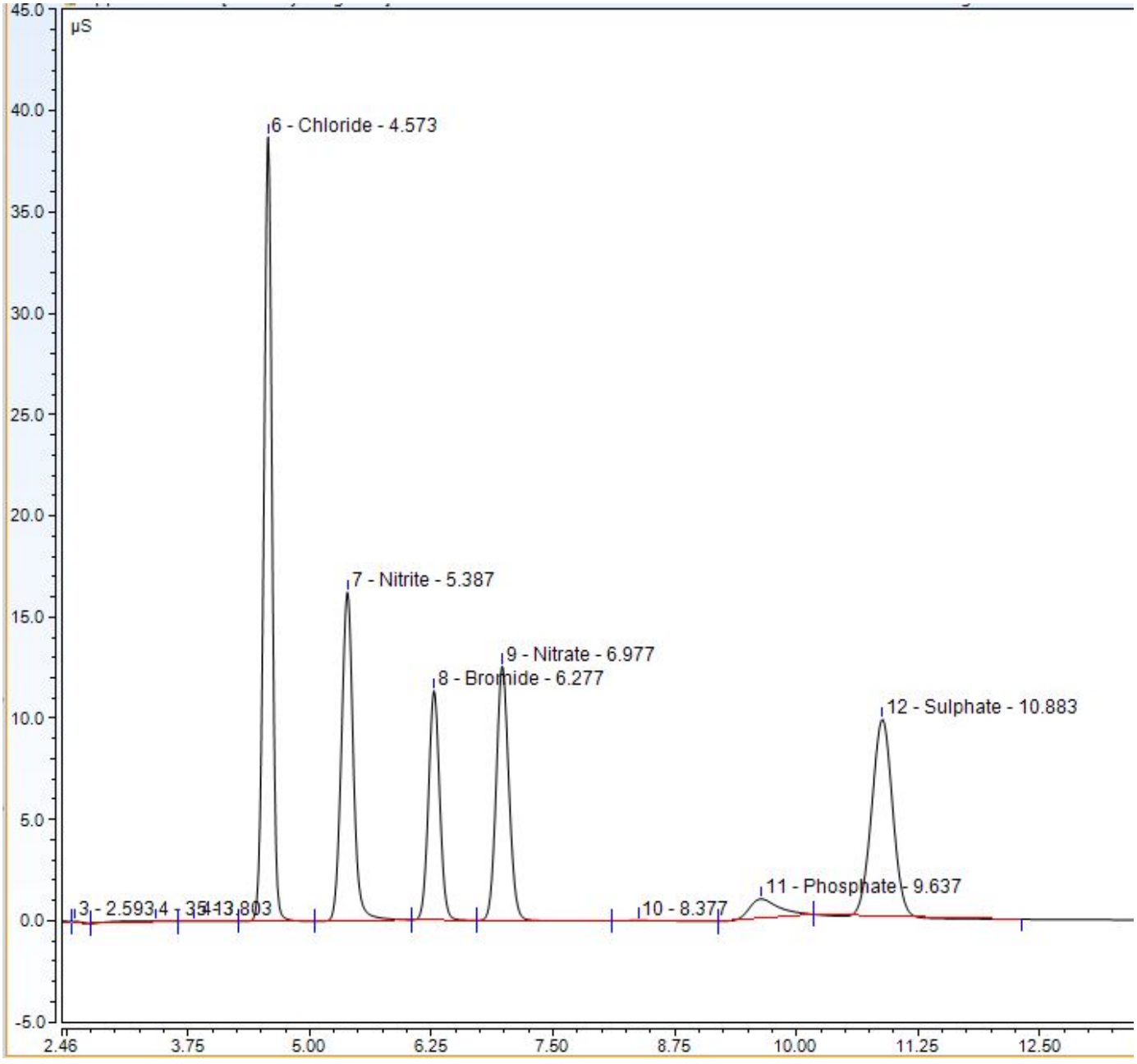
Some common UPLC-MS/MS applications include:

- Toxicology screening and confirmation
- Forensic research
- Environmental analysis

## High Performance Ion Chromatography (HPIC)

High Performance Ion Chromatography (HPIC) measures concentrations of ionic species by separating them based on their interactions with a resin (inside of the column). There are two types of ion chromatography: cation-exchange (the desired molecules to separate are cations) and anion exchange (to separate anions). The most common ions analysed in the fire field are: cyanide, fluoride, chloride, bromide, nitrate, nitrite, phosphate, and sulphate, in the parts-per-million (ppm) range.

An example for the chromatogram containing anions from the sample solution is presented below. The concentration of ions moving through the column at a particular time is represented by the height and the breadth of the peaks and can be then correlated to the concentration of a particular species in the sample solution.



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# X-Ray fluorescence analyser (XRF)

The presence of an element is identified by the element's characteristic X-Ray emission wavelength or energy. Each specific element has a characteristic X-Ray energy that is emitted. The peak height of each element can be then converted to a percentage of that element via a calibration method. However, there are common interferences that can influence the analysis of the elements of interests. They are well-known and documented and must be corrected or compensated for in order to achieve adequate analytical results.

A handheld, portable XRF unit is also available. It offers ease of use, rapid analysis time, and substantially lower long-term maintenance costs. However data obtained can be presented only qualitatively.

Some common XRF applications, primarily used for elemental and chemical analysis, cover:

- Investigation of metals in the building materials,
- Forensic science,
- Environmental analysis,
- Post-contamination,
- Analysis of pigments used in cave paintings.

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# Cascade Impactor - Aerosol measurement in fire effluents

Aerosol particles are a major hazard, both from diesel exhausts and from other fires.  The smaller particles, known as PM 2.5 and 10s (2.5 and 10 µm diameter) are capable of penetrating deep into the lung, where they can cause pulmonary oedema (flooding of the lung) and other problems. In addition, they can act as vehicles allowing other toxicants to evade the body's normal defences.

The characterisation of particles (aerosols) by mass size distribution and particle number concentration can be made by using accumulative methods such as a low pressure cascade impactor. It separates the aerosol particles according to their aerodynamic diameter. The low-pressure cascade impactor consists of several successive impactor stages, each one specific to a particle size. This is achieved by gradually decreasing the nozzle diameter.

Our ELPI+ instrument is a modified cascade impactor that measures the particle size distribution and number concentration of aerosols in real-time. It is separated into three main parts: the electrical charging of particles; size differentation by the cascade impactor; and detection of the charged particles by sensitive electrodes.

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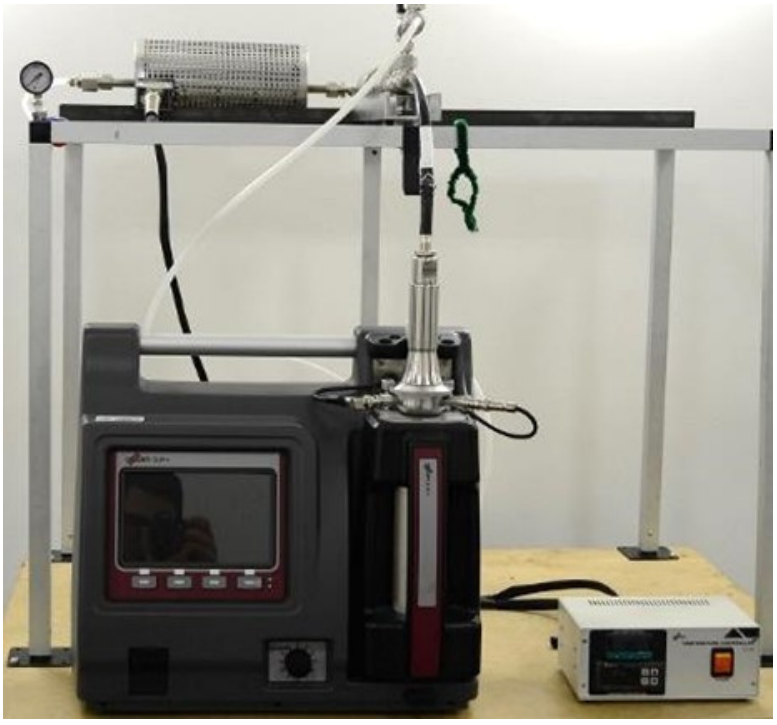

Cascade Impactor - Aerosol measurement in fire effluents

As the particles enter the instrument they are charged by a corona prior to the cascade impactor. The particles are then separated according to their aerodynamic diameter as described above. The sensitive electrodes can detect the number of charged particles that impact on each plate.

The measured current signal is directly proportional to particle number concentration and size.

The ELPI+ system can quantify particles of size range 10µm – 6nm and has attributes that enable its application in a broad range of aerosol measurements. The instrument has a robust build that allows the operational measurement use in harsh conditions such as automotive exhausts or from fires. The particles collected can also be analysed gravimetrically and chemically post-measurement.

# Gas Phase Fourier Transform Infrared (FTIR) Analysis for Fire Gases

In this technique, a beam of infrared with wave numbers from 400 to 4000cm-1 is passed through a sample of fire gas in a heated cell. The various structural groups of fire gas molecules will absorb different amounts of energy in different parts of the infrared spectrum.


The components of the gas mixture can be identified by the overall shape of the intensity of the absorption at different wavenumbers while their concentration of the gases can be determined by the intensity of the absorption.

This technique can identify and quantify most of the important fire gases in a single operation. The infrared absorption spectra can be recorded and re-analysed at a future date for gases not included in the original analysis.  The technique can be applied to a gas flow which enables gas concentration / time curves to be obtained.

FTIR measures the infrared absorption data over a range of wave numbers. There is a unique absorption band for nearly every gas and the absorption spectrum of a fire effluent consists of the summation of all the overlapping absorptions. The analysis of the fire gas spectrum for specific gases needs to consider interferences from the other gases present and requires the use of complex data analysis, experience and common sense as well as multiple gas calibrations at different concentrations. The absorption of minor amounts of gas onto the filters, sampling lines, etc. and the necessity to remove soot from the gas stream can results in some errors. However FTIR is a very powerful tool for fire gas analysis and complements the other techniques including GC-MS.

## Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuated total reflectance (ATR) is a special accessory unit which can be used together with Fourier Transform Infrared (FTIR) spectrometers.

It is a sampling technique which enables samples to be examined directly in the solid or liquid state, without any preparation, by pressing the sample towards an ATR crystal (e.g. diamond).

An ATR accessory operates by measuring the changes that occur in an internally reflected IR beam when the beam comes into contact with a sample. Based on the sample's composition, a small part of the infrared light is absorbed when the evanescent wave interacts with the sample, resulting in a slightly attenuated total reflection.


Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy (ATR-FTIR)

It is ideal for strongly absorbing or thick samples which often produce intense peaks.

# Optical Microscopy with Digital Imaging

**Microscopic photography** allows us to view objects that cannot be seen within the resolution range of the normal eye. A digital microscope provides a digital image taken through a microscope to show a magnified image of an object.

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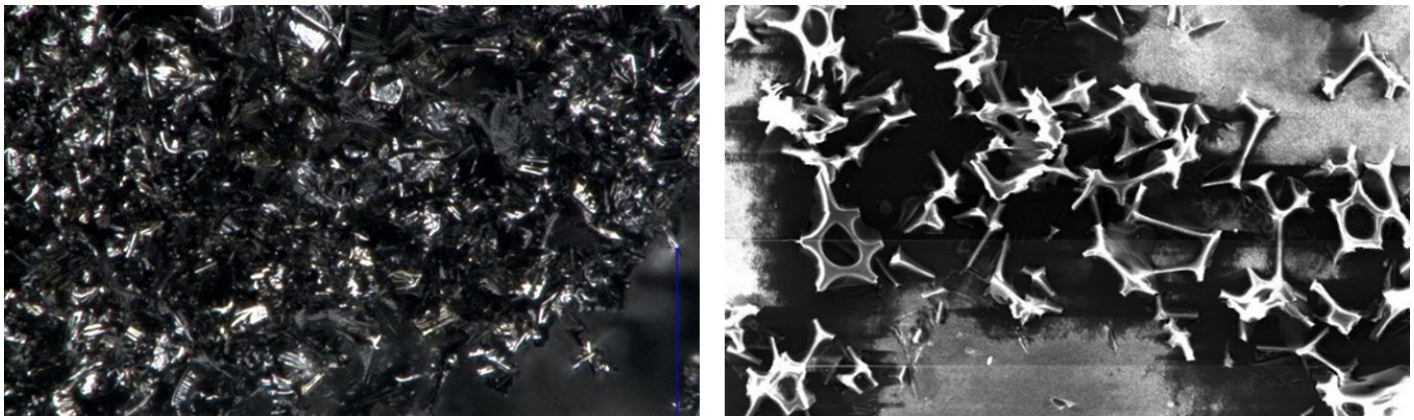
Optical Microscopy with Digital Imaging

The Keyence VHX-2000 digital microscope was designed to improve the shortcomings of traditional, optical light microscopes - shallow depth-of-field, short working distance, etc. It offers a magnification range from 0.1 to 5000 times and up to a 20,000×20,000-pixel image that expands the viewing area by up to 200 times. This, for example, allows objects with large variations in surface topography to be focused and accurately observed in a single image, something that is impossible with conventional microscope optics.



Microscopic photography