

The use of reference spectra of standard reference materials allow spectra of unknown ones to be compared manually or by computer using spectral library searches against databases containing spectra of different compounds such as pure chemicals, minerals and polymers. Identification of materials by infrared spectroscopy usually requires samples to be in a pure form and can require chemical clean-up and separation for good library search matches. Libraries of plastics, elastomers and other polymers are useful in classifying an unknown polymer. Elastomers can be identified by comparing the infrared spectrum of their pyrolysates (products of thermal degradation) against standard reference spectra.

Materials can be presented to the spectrometer in all physical states: gas, liquid or solid. Very small amounts of just a few milligrams of solid and liquid can be handled. Sample sizes down to 10 microns can easily be analysed and identified using an infrared microscope. A classic example of infrared microscopy is the identification of different fibres in forensic analysis. The individual layers of multi-layered polymers used in corrosion protection can be identified by infrared microscopic examination of microtome-thin cross-sectional slices. Some reflection accessories produce spectra that are essentially surface-sensitive and represent the first few microns of a surface. It is possible to identify layers on surfaces that are only several microns thick, e.g. varnish coatings, bloom finishes or surfaces contaminated with foreign substances.

#### Scanning electron microscopy - energy dispersive x-ray analysis (SEM/EDX)

This technique uses an electron microscope to examine bulk samples at low and high magnifications. Small particles or selected areas of interest can be examined. When samples are bombarded with an electron beam, the atoms emit X-rays that are characteristic of each element. An X-ray detector counts the X-rays and produces an X-ray spectrum. It is possible to obtain both topographical information such as details of a fracture surface, and chemical state information such as elemental composition. Elemental mapping and line scans allow spatial distribution of elements and compounds to be shown in a graphical format. Different colours can be assigned to differentiate different elements. Line scans can show sharp differences in chemical composition at interfaces/boundaries, layers, etc.

#### Gas chromatography - mass spectrometry (GC-MS)

The GC-MS technique uses chromatography to separate simple and complex mixtures. As little as 0.01 microlitres (~10 micrograms) of a mixture of organic compounds can be separated into individual compounds. The mass spectrometer detector (MS) generates a mass spectral fingerprint used to identify and quantitate each compound present. GC-MS is sensitive and can detect concentrations ranging from percent to parts per billion (ppb) - ideal for providing evidence of the presence of trace components. Small samples (milligram to microgram) can be pyrolysed at several hundred degrees Celsius.

The thermal degradation products are then separated to produce a GC-MS pyrogram, highly characteristic of a particular polymer. Adsorption tubes that contain adsorbent material such as Tenax, silica gel or charcoal are used to sample atmospheres such as air or gases. Trace components in air or in natural gas are trapped and concentrated on the adsorbent tube and subsequently thermally desorbed to produce a GC-MS analysis allowing compounds to be identified.

#### SEM/EDX ANALYSIS

**A domestic gas consumer's fire** exhibited a severe white soot-like powdery deposit on the glass front of the fire such that the flame couldn't be seen.

SEM/EDX analysis showed that the white deposits consisted of hydrated silica -  $\text{H}_2\text{SiO}_3$  caused by the combustion of the vapours of organic silicone compounds in the flame where the silica deposited out as a white fumed solid. There were **two potential sources of silicones**: the air and/or the gas supply. Air and gas samples were taken on adsorbent tubes and GC-MS analysis carried out. The presence of several silicones was confirmed in the house air but not in the gas supply.

#### DEPTH PROFILE

Infrared spectroscopic measurements through the wall of a 10-year-aged PE pipe showed the presence of oxidised surface which penetrated to a depth of approximately 2.5 millimetres.

In the oxidation of PE in the presence of sunlight, oxygen from the air attacks the polymer backbone of the PE hydrocarbon structure to produce hydroperoxides. These hydroperoxides decompose and further react with the formation of a mixture of carbonyl compounds such as esters, aldehydes, ketones and carboxylic acids. The carbonyl group ( $\text{C}=\text{O}$ ) absorbs infrared radiation at approximately  $1,700\text{ cm}^{-1}$  which can be **detected in the throughwall spectra**, the intensity of which gives an indication of the penetration with distance through the wall.

#### Summary

Chemical analysis is an essential science applied to the gas, oil, water and electricity sectors for various purposes including quality control, corrosion control, evaluation of kinetic and thermodynamic properties of materials and their interactions with each other within transportation, distribution and storage systems, and in utilisation. A large range of chemical analysis techniques are available that include both on-site and laboratory-based methods. Depending on the techniques and methods used, it is possible to obtain compositional analyses from percentage levels down to part per trillion concentrations. Without chemical analysis and its ability to study materials at a macroscopic, microscopic and atomic level, data critical for failure and forensic investigations would not be available.

For further information, please contact Martin J. Maple, Materials group leader, [martin.maple@dnvgl.com](mailto:martin.maple@dnvgl.com)

# THE CONTRIBUTION OF CHEMICAL ANALYSIS TO INCIDENT INVESTIGATIONS

The analytical expertise of DNV GL's chemistry specialists is indispensable in investigations of material defects and component failures in oil and gas assets, from offshore drilling rigs to processing plants and distribution networks.

DNV GL applies chemical analysis to many important areas in the oil and gas sector, such as health and safety at work, environmental protection, investigation of incidents, identification of materials, studies of polymer degradation/oxidation, phase equilibria, thermodynamic and kinetic reactions, and quality control.

**Investigation begins with inspections at the operator's premises and various symptomatic observations are recorded. Some tests are carried out on site and samples may be collected for analysis in the laboratory.**

Failures or non-compliances with specifications may result from failing materials, a chemical process fault, or contamination of the manufacturing equipment or the raw materials used. Gas pipelines may deposit liquids and/or solids in addition to the fluid they are designed to carry. Filters may block up with debris from an upstream process or due to chemical or physical reactions in the pipeline or storage vessel. Contaminants may be hazardous with respect to handling, replacement and disposal. Symptoms are generally reported when a component stops working or behaves differently due to blockage, corrosion, leakage, sticking of seized parts, etc. Metals and alloys used in the construction, fabrication and components of pipelines and appliances may corrode or fail for various reasons.



Optical microscopy is an essential tool at the start of most investigations.

Surface coatings may fail due to photochemical oxidative degradation, thermal degradation, moisture absorption causing blistering or disbonding, or chemical reaction of gas components with those in the coating composition.

Understanding the question

When carrying out investigations or obtaining evidence to answer a specific question, it is important for the client and the analytical chemist to understand the original question and the significance of what a particular chemical analysis test result could achieve. This helps to avoid costly “blanket analysis” requests where endless amounts of testing could provide little or no value in answering the original question. Tests and results aimed at providing a definitive conclusion should be considered prior to chemical analysis. This might involve looking for evidence of the presence of “a pin in the haystack” or “markers” providing the crucial evidence of trace amounts of a substance in a complex mixture. Alternatively, the question could focus on one or more major components. Examples include:

- Part per million concentrations of a specific antioxidant in a lubricating oil could help identify one of several potential lubricating oils that could have entered a section of an asset due to error, a breakdown, etc
- Traces of mercury in debris could indicate a filtration system was not working correctly. Absence of mercury in process water could indicate compliance with the discharge consent of a water treatment plant
- Presence of a certain dye could uniquely identify a substance and confirm its origin
- A specific substance (e.g. soil, clay, seawater salts, rock) that should definitely not be present may indicate “carry-over” due to unwanted ingress
- Presence of specific compounds or other materials can help establish a thermal history, e.g. presence, extent and depth or penetration of thermal degradation of polymer coatings or char compounds on a pipeline
- Presence of elemental sulfur in blocked valves and orifices in fuel jets of natural gas turbines can indicate specific circumstances that should be avoided
- The presence of corrosion products helps to determine corrosion-causing mechanisms, which may implicate excursions or non-compliance with gas specifications on moisture, carbon dioxide, hydrogen sulfide content, etc
- In gas leak investigations, the ratios of alkane hydrocarbons can be used to differentiate different types of gases, such as transmission/distribution gas, sewer gas, biologically generated gases, mine gas, landfill gas, petrol or solvent spillages in drains and sewers
- Presence of odorant compounds added to commercial natural gas can be used to differentiate the gas from other gas sources. Presence of naturally occurring odoriferous substances can aid identification of biological gas sources such as bacterial, animal and plant metabolism
- Ratios of alkali and alkaline earth metals in salts can be used to differentiate (or identify) a particular seawater, groundwater or potable water source.

Chemical analysis and how is it carried out

Chemical analysis looks at the chemical composition of any material such as a metal/metal alloy, simple or polymeric inorganic or organic solid, liquid or gas. Materials can exist as pure elements (e.g. iron) and pure compounds of a number of

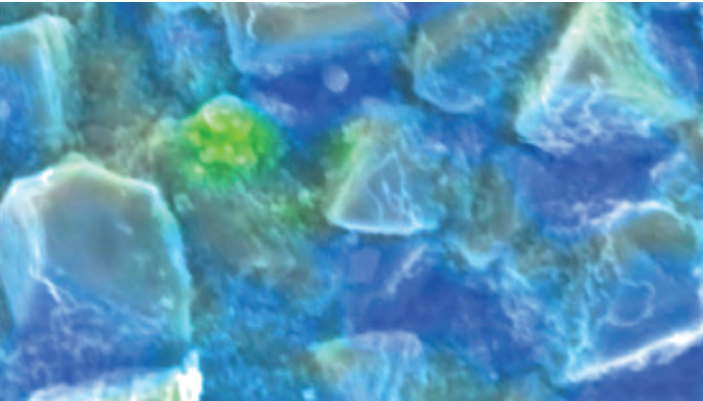
elements (e.g. iron carbonate, ethyl alcohol, benzoic acid, etc), and also as simple or complex mixtures.

THE JIGSAW PUZZLE OF CHEMICAL ANALYSIS

Many **scientific and technical investigations** can be seen as jigsaw puzzles that describe a hidden or unknown story or picture. The analytical chemist uses chemical analysis as one of several tools to provide pieces of the puzzle. Eventually, when several pieces are collated, **a picture may start to emerge**; once sufficient pieces exist to complete the puzzle, the original question can be answered.

Further pieces of the puzzle may or may not add value and the investigation could stop **without additional cost**. In some cases, one piece of the puzzle may be all that is necessary to address a specific question. In other cases, several pieces combine to strengthen conclusions.

Chemical analyses can be simple or complex, depending on the original question that needs to be answered and the number of substances present. Consider a mixture of water, rust, rock, salt, oil, glycol, iron sulfide, iron oxide and iron carbonate. The original question may be: “Is there any salt present, and if so, how much?” Analysing for salt only would answer this question. But if the original question required a breakdown of all major and minor components, the mixture would first need to be separated into suitable fractions for subsequent analysis by appropriate techniques.



SEM/EDX analysis of 5 micron mercury sulfide particle in an iron oxide matrix found in gas filter units. Elemental mapping at high magnifications revealed the presence of trace quantities of mercury sulfide, which could not be detected by other techniques.

The techniques used for separating mixtures can be as simple as manual separation with tweezers and examining the sample under a stereomicroscope at low magnification. Magnets are useful in separating magnetic particles from non-magnetic particles. Particles with different densities can be separated by adding them to inert liquids of different density; dense particles sink while less dense particles float. More complex separation methods are filtration, distillation, dissolution in acid or alkali and extraction with suitable solvents. A mixture of rock and salt can easily be separated by adding water to dissolve the soluble salt and filtering off the insoluble rock. The salt is isolated by evaporation of the water extract. Suitable chemical analysis techniques are then used to determine the mineral compositions and identity of the rock type as well as the composition of the salt, which may be a mixture of chlorides and sulfates of sodium, magnesium, potassium and calcium, or

pure sodium chloride. If the mixture was a dirty sludge due to the presence of oil, another solvent such as cyclohexane would be needed to clean the rock and extract the oil for analysis by another technique. In a quantitative separation process the percentage weight of each fraction is recorded. Following chemical analysis of the individual fractions, a more detailed quantitative analysis of all fractions is possible.

Chemical analysis can be routine or non-routine and a range of tests may be needed to provide sufficient information. Even development and validation of a new test, highly specific to identify a particular substance, can be explored if it will provide a confident answer. Chemical analysis results alone may provide sufficient information or they may contribute to a larger pool of evidence from several other disciplines such as engineering, metallurgy and physics.

Types of chemical analysis

Chemical analysis can be divided into two main classifications: wet chemical analysis and instrumental analysis.

Wet chemical analysis

This involves classical wet chemistry procedures that include spot tests, which are often carried out in test-tubes, volumetric titrations, gravimetric and colorimetric analyses. The substance under investigation can be tested for physical properties such as colour, odour, hardness, consistency, melting and boiling points, refractive index, density; and for chemical properties such as effect on heating or burning, pH, solubility in water, acid, alkali or any number of inorganic and organic solvents. Flame tests for specific elements can be quick, simple and conclusive. For example, where only two possibilities existed a chlorinated rubber O-ring can be quickly differentiated from a natural rubber O-ring by burning a few milligrams in a Bunsen burner flame and allowing the combustion gases to impinge on red hot copper metal. A blue-green flame would indicate the presence of chlorine in the chlorinated rubber and the analysis and differential identity of the rubber would be complete. There would be no further need for any other analysis unless the question had additional requirements, such as filler content and identity. Thousands of qualitative and quantitative test tube and paper strip dip tests exist for the analysis of different substances or classes of substances. Wet chemical analysis generally requires large samples (several grams/millilitres) but many micro-analytical tests are applied to small sample sizes (milligrams) including tests under a microscope when the sample is limited. Some wet chemical analysis is destructive; if the sample is limited, careful decisions need to be made which destructive tests would maximise the information gained.

Some types of instrumental analyses can be used to analyse extremely small amounts of substance (e.g. a few milligrams to micrograms). Even if the technique/test is destructive, there is often sufficient material left for further tests for examination by third parties for reproducibility. Some instrumental techniques are non-destructive so the sample can be preserved if it is important not to destroy evidence.

Instrumental chemical analysis

This uses instruments designed to look at physical, chemical, electrical, magnetic and spectroscopic properties of the atoms in molecules in pure substances and mixtures. A range of chemical analysis techniques exist, each with its own instrumentation, usually connected to a computer for operation, data acquisition, processing and reporting.

Differential scanning calorimetry (DSC)

DSC measures energy changes that occur when materials are heated. Small samples (~10 milligrams) are heated from liquid nitrogen temperatures (-197°C) to several hundred degrees Celsius in an atmosphere of flowing gas (air, nitrogen, oxygen). Materials that undergo changes in physical or chemical state will either absorb (endothermic) or emit (exothermic) energy. A plot of energy flow against temperature is known as a thermogram. Melting range, melt enthalpy, percent crystallinity, degree of cure, glass transition temperature (T<sub>g</sub>), thermal degradation or oxidative characteristics are useful diagnostic parameters when comparing different polymers that may be the subject of a failure or incident investigation.

Standard reference materials are used for DSC comparison. A reference material could be an elastomeric or plastic component, e.g. an O-ring, diaphragm or seal from an appliance such as a gas meter that has not failed in service. Comparison could reveal that the failed component has different DSC properties to the non-failed component (e.g. a different T<sub>g</sub>). This evidence, together with other, complementary evidence from further chemical and physical tests is used to identify causes of failure such as a faulty batch, incorrect or accidental selection of material not fit for purpose, thermal or oxidative degradation, contamination, etc.



Historical yellow polyethylene (PE) gas service pipe with black outer layer of lead and lead sulfide. Due to the black discoloration, the live gas pipe was misidentified as a water pipe and was cut open causing a gas leak. Lead pigments are no longer used in modern polyethylene pipes.

Infrared spectroscopy

Infrared spectroscopy studies the vibrational energies absorbed by the bonds between atoms in the molecules of compounds. A plot of amount of energy absorbed against wavelength is referred to as an infrared spectrum. Groups of specific atoms called functional groups such as OH, COOH, COOR, NH<sub>2</sub>, NO<sub>2</sub>, etc., absorb at unique infrared wavelengths and are diagnostic spectral features in the spectrum identifying the presence of a particular functional group. The fingerprint region of the spectrum ~1,500-500 cm<sup>-1</sup> is uniquely different for each compound and helps to differentiate compounds.