WHAT'S HAPPENING ON THE SURFACE?

A combination of specialist commercial laboratories and the new generation of benchtop surface analysis instrumentation can bring sophisticated surface chemistry characterisation within the reach of any Petro industry laboratory.

Introduction

The analysis and understanding of the chemistry occurring on surfaces from the nano to the macro scale is of critical importance to many activities in the petroleum and petrochemical industries such as corrosion, deposit formation, surface cleanliness, protection and lubrication. This exists from exploration and production through refining and petrochemical manufacture to final products such as fuels, lubricants and chemical additives specifically designed to interact with surfaces. In this article we look at some of the options available to characterise surface chemistry including the development of benchtop surface analysis instrumentation. The article is not intended to cover all options for surface characterisation but to give a general overview of commonly applied approaches and techniques used by petro-based industries.

Sourcing Surface Analysis – External or In-House

Traditionally many of the techniques employed for the detailed analysis of surface chemistry and composition required a combination of large expensive instrumentation and subject matter experts which in the past was generally available in the central research facilities of many global oil and petrochemical companies. However, as the petro-based industries have matured and reduced overhead costs, many of the internal centres of expertise have either disappeared or been significantly reduced. As a result many companies have developed partnerships with universities to access their facilities but this can have drawbacks in terms of speed of access and sample turnaround as academic laboratories are generally not geared up for fast response industrial analysis and therefore these partnerships tend to be more suited to longer term research and development projects. It is also difficult to service the needs of companies which operate globally unless several university partnerships are established regionally.

Many companies have also turned to the use of specialist commercial laboratories which by servicing a wide range of industries can provide access to high end state of the art equipment and the relevant expertise to analyse samples and provide expert interpretation of the data. In addition, many of these labs now have regional facilities so can provide a service globally. One such provider is EAG who provide a plethora of techniques available in regional labs and have also produced the EAG SMART (Spectroscopy and Microscopy Analytical Resolution Tool) Chart offers a concise visual reference for comparing analytical techniques as shown in Figure 1. It allows an easy comparison of the detection limits and analytical capabilities of

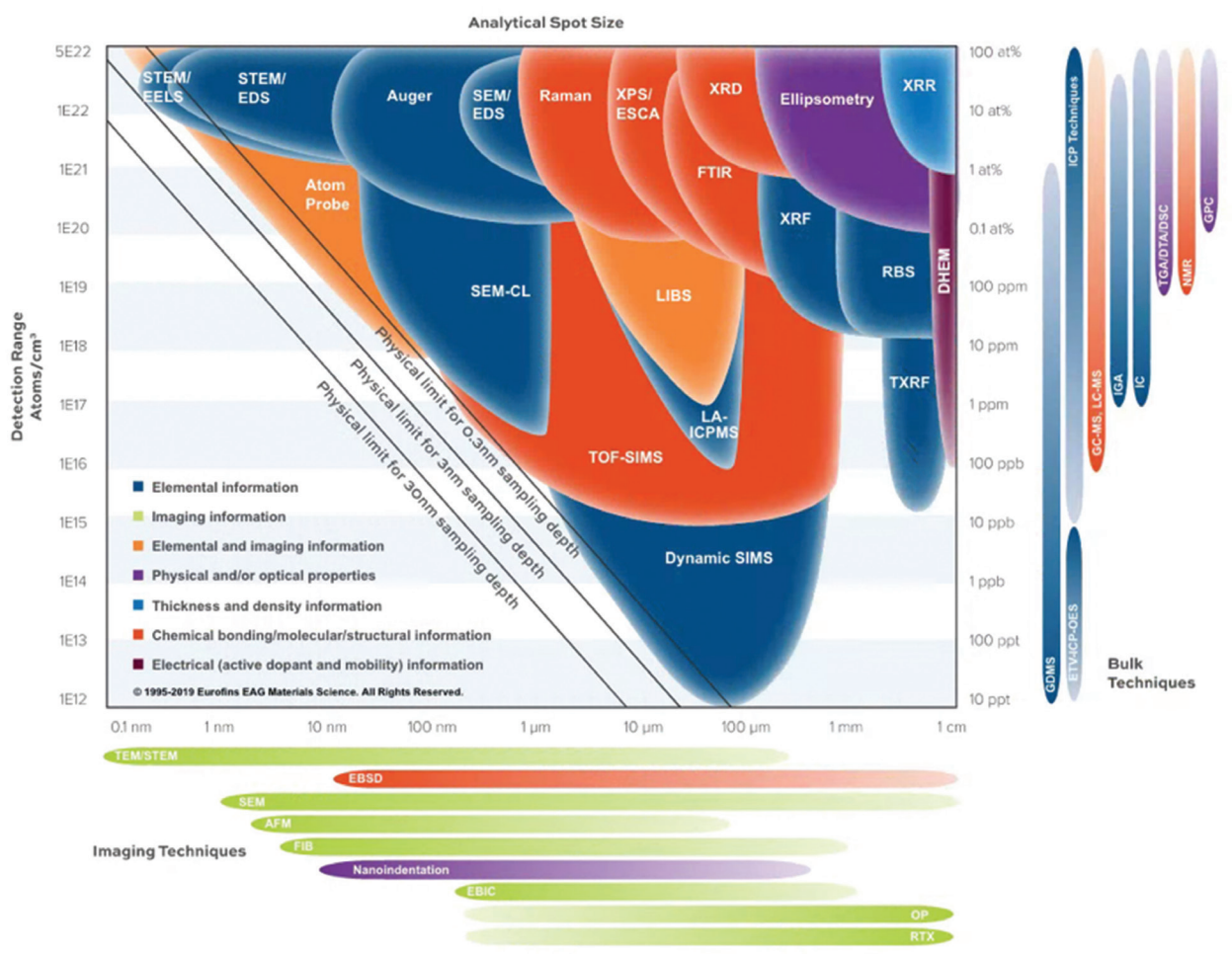

Figure 1 EAG Labs Spectroscopy and Microscopy Analytical Resolution Tool Chart (interactive chart available at . https://www.eag.com/techniques/.) Reproduced courtesy of EAG

techniques used for materials characterization, surface analysis and more. The online version of the chart is also interactive and links to detailed technical information, application areas and strengths and limitations of over 90 techniques and is a very useful reference tool for non experts to find the best analytical tools relevant to their requirements. https://www.eag.com/techniques/ .

Many areas of the industry, and especially those in B2B and B2C activities such as fuel and lubricants businesses, are expected to provide a specialist customer support facility and often have regional technology centres specifically for this purpose. These facilities are often very well equipped but cannot justify the expense and overhead of in- house high end surface analysis techniques and the expertise required to run them and this is a prime area where the latest range of bench top instrumentation has a role to play. The instrumentation we will describe here will in most cases not reach the sensitivity or spatial resolution levels of the high-end instrumentation but is significantly less expensive in terms of capital and revenue costs to run. Many of the instruments are highly automated with regularly used features such as chemical mapping and imaging embedded so for businesses with a high requirement for surface analysis, and by

Figure 2 The Thermo/Hitachi/Joel/ CoXem Benchtop SEM instruments

applying the ubiquitous 80:20 rule, if it can provide rapid in house solutions for 80% of your requirements then it is certainly worth considering.

Some basics for surface based analysis

There are many application areas for surface analysis including component wear and failure, unwanted deposits, lacquers and embedded debris, corrosion, coatings damage and to cope with such a variety of applications there are a wide range of techniques available which cannot be covered in an article like this. Readers who are unsure about the best approach for their needs are advised to consult relevant subject matter experts. The EAG SMART Chart on-line is also a valuable tool where technique capabilities, limitations and typical application areas can be easily accessed to scope possible techniques for your application areas.

However in simple terms there are 3 basics capabilities which can provide valuable insight into a wide range of applications:-

1. The ability to get high resolution images of surfaces with a suitable degree of magnification
2. The ability to detect, measure and map elemental compositions over the area of interest
3. The ability to detect and map molecular species over the area of interest

If addition to these basic capabilities there are some other nice to haves including the ability to depth profile species of interest and true surface 3D profiling but these generally fall into the higher end instrumentation category so this article will concentrate on benchtop instruments which can provide a good basic coverage.

Benchtop Scanning Electron Microscopy with Energy Dispersive X-Ray Detection

Since the introduction of electron microscopes in the 1930s, scanning electron microscopy (SEM) has developed into a critical tool and as soon as microscopic information about the surface or near-surface region of a specimen is needed. Traditional SEM instrumentation was typically costly, required a specialized room and highly skilled operators and therefore was effectively not an option for many laboratories. However, rapid progress in electronics and computer hardware and software have facilitated the development of "Desktop/Tabletop SEM" instruments which are cheaper, robust, boast enhanced ease of use with many common analytical protocols automated via software, and a reduced frame size allowing siting on a normal lab bench. In addition to their SEM capability most also have digital optical capabilities which can effectively replace the need for conventional optical microscopes in the lab. Such instruments are available from several instrument manufacturers and can easily meet our first basic need to get high resolution images of surfaces with a suitable degree of magnification.

But, the benefits of SEM don't end there as during the SEM analysis the impact of the electron beam on the sample produces x-rays that are characteristic of the elements present on the surface of the sample. EDS detection in SEM can be semi quantitative and can detect most elements (detection limits typically 0.1 -1%) in a depth range of 0.1 to 5 microns of the sample surface depending on the energy of the electron beam. Therefore by adding an Energy Dispersive X-Ray Spectroscopy (EDS) detection system to the benchtop SEM we can effectively also cover our second basic capability to detect, measure and map elemental compositions over the area of interest with the same instrument. Many companies including Thermo, Joel, Hitachi and CoXem have benchtop SEM offerings with EDS detection and often with a wider range of optional configurations in terms of sample stage size, electron source type and achievable resolution/ magnification depending on the application area. For example the Thermo website features 8 off the shelf variations of their Phenom benchtop SEM which can also be customised further depending on the customers' requirements.

A selection of benchtop SEM Instruments are shown in Figure 2. SEM with EDS does have some drawbacks in that at best it is semi -quantitative, samples generally have to be relatively flat and only relatively small areas can be analysed but even with these limitations it does offer a very powerful tool the characterisation of surfaces commonly encountered in the petro based industries.

Fourier Transfer Infrared Spectroscopy (FTIR)

FTIR spectroscopy is a powerful technique for molecular characterisation and especially for the types of organic molecules commonly encountered in surface analysis applications in the petro industries. Many laboratories have an FTIR spectrometer which with the addition of a special attenuated total reflectance (ATR) accessory can give a limited ability to study species on the surface of solids with minimal or no sample preparation. An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. The infrared source beam from the spectrometer is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with it. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum. Most FTIR manufacturers can supply ATR accessories optimised for their instruments and there are also specialist accessory manufacturers such as SPECAC who can supply a range of accessories depending on the application.

However, FTIR with ATR is useful for many applications it is limited in its application for surfaces to the spot on the sample which is in contact with the ATR crystal and if spatial resolution and mapping of components across the surface is required then infra-red microscopes provide a better solution.

FTIR Microscopy

Most FTIR Spectrometer manufacturers have customised microscopy accessories which can convert their spectrometers into an FTIR microscope with varying capabilities. In recent years the development of stand-alone FTIR microscopes, such as the Bruker Lumos II and the Nicolet iN10 (Figure 4) with automated scanning and surface mapping capabilities, has expanded the application area for surface analysis and visualisation. These instruments can operate in either transmission, reflectance or ATR modes, have a small footprint, are highly automated for ease of use and are well suited to the industrial lab environment.

It is not possible in an article such as this to compare and contrast all the features in these instruments and readers are advised to consult the individual manufacturers regarding the instrument capabilities and its usefulness to their specific application areas.

Figure 3 The Horiba XGT-9000 X-Ray Microscope and the Bruker M4 Tornado 2D Micro XRF

However, there is another option for the quantitative analysis of larger irregularly shaped samples using micro XRF instruments such as the Horiba XGT-9000 X-Ray or the Bruker M4 Tornado 2-D Micro XRF shown in Figure 3. Both instruments offer quantitative, high resolution elemental mapping, line scanning and spot analysis of large samples but have different performance specifications in terms of spot resolution, max sample size and weight, mapping area etc and full performance specifications can be obtained from the manufacturers.

So benchtop SEM/EDS and Micro XRF instrumentation can provide our first 2 basic capabilities but what options do we have to detect, measure and map molecular species over the area of interest? In most cases it is organic species we are interested in and FTIR spectroscopy is the ideal technique.

What about Depth Profiling?

The depth penetration into the surface of the techniques we have discussed so far is varied and depends on many factors including the sample substrate, and in some cases dependent on the instrumental modes and settings used, and users must always be aware that the results obtained will often be specific to a certain layer thickness which may in itself compose many sub layers. Again the previously mentioned EAG SMART Chart also provides a comparison of different techniques and their typical analysis depths. Secondary Ion Mass Spectrometry (SIMS) is one of the most commonly applied techniques for depth profiling analysis and can provide elemental depth profiles over a wide depth range from a few angstroms to tens of microns. The sample surface is sputtered/etched with a beam of primary ions and secondary ions formed during the sputtering process are extracted and analyzed using a mass spectrometer. The secondary ions can range in

Figure 4

concentration from matrix levels down to sub-ppm trace levels. There are many high end instrumentation options for SIMS and EAG Labs claim to have the largest range of Secondary Ion Mass Spectrometry instruments worldwide (more than 40) staffed by exceptionally qualified scientists.

If SIMS is a proven technique for your requirements and you do not need the highest performance instruments then there are a choice of 2 benchtop MiniSIMS instrument available from SAI https://www.saiman.co.uk/sims.

The first is the entry level MiniSIMS Alpha (Figure 5) with a quadrupole mass analyser and liquid metal ion source capable of operating in all 3 SIMS modes and is aimed at routine monitoring of low numbers of elemental and organic surface species and industrial QA applications. The MiniSIMS-TOF which employs a time of flight mass spectrometer to give superior detection performance characteristics in terms of mass range, mass resolution, acquisition efficiency and also allows retrospective analysis implying no "a priori" assumptions are needed about sample composition before undertaking imaging and profiling experiments. These extra capabilities widen the application area to R&D and problem solving applications.

Summary

The analysis and understanding of the chemistry occurring on surfaces from the nano to the macro scale is of critical importance to many activities in the petroleum and petrochemical industries such as corrosion, deposit formation, surface cleanliness, protection and lubrication and there are a wide range of techniques available to provide insight into surface chemistry.

Many of these techniques require high end instrumentation and specialist expertise and as such are not now routinely available in-house for many companies but they can still be accessed via many university centres of excellence or specialist commercial laboratories who achieve cost effectiveness through servicing the needs of a wide range of industrial sectors and customers. A high proportion of surface characterisation applications in the Petro based industries can be covered by the three basic capabilities, namely high resolution imaging of topography combined with the ability to detect, measure and map elemental and molecular compositions over the area of interest. For many applications the ultimate performance of high-end instrumentation is not required and the recent developments in benchtop instrumentation have meant that options are now available to develop in-house capabilities to cover many application areas.

Therefore by utilising a combination of specialist commercial laboratories and the new generation of benchtop surface analysis instrumentation sophisticated surface chemistry characterisation can be tailored to need the needs of any Petro-industry laboratory from fundamental R&D through to Customer Support and routine QC operations.

Disclaimer: The information shared in this article does not relate to a recommendation of any particular instruments, manufacturers or suppliers and is included to provide background information for readers on some of the instruments available on the market at the time of writing.

Figure 5 The SAI MiniSIMS benchtop instrument

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