Sulphur speciation analysis and treatment of sampling equipment for reduced sulphur species

Sulphur is present in various forms and concentrations in crude oils. Of all the sulphur containing-compounds found, the volatile components such as sulphides, thiols (mercaptans) and thiophenes are of most interest.

Hydrogen sulphide (H_2S) is the predominant volatile species most commonly found in crude oil whilst typically, thiols, are the next most prevalent species. These sulphur species are toxic; they can be corrosive to plants and can poison catalysts. Many processing facilities have units specifically aimed at removing these sulphur species. Hence it is often important to establish which species are present and at what concentration.

Sampling pressurised oils and gases for subsequent determination of these sulphur species can be problematic since reduced sulphur species tend to have an affinity for the surfaces of steel sampling vessels. An untreated steel sample vessel may adsorb sulphur species (in particular H_2S) from the sample during transit and storage. When the sample is then analysed in the laboratory, erroneously low values for the volatile sulphur compounds may be obtained.

For this reason, vessels used in service for the determination of volatile sulphur species must be either coated to prevent absorption of sulphur species or 'conditioned' prior to sampling. Conditioning may be achieved by repeated use of a vessel to sample a particular well or pipeline. In time, contact with the sample neutralises the active sites on the internal surfaces of the vessel, so that it no longer adsorbs reduced sulphur species. However, this takes time and until equilibrium has been reached the analytical data obtained will almost certainly be erroneously low.

A faster method of conditioning can be carried out which involves pacifying the metal surfaces of sampling equipment under carefully controlled conditions in the laboratory. The process, which takes several days, brings the active surfaces to the point of neutrality where they no longer adsorb reduced sulphur species from a sample. This has the advantage of being quicker than conditioning through sampling and ensures that the sample need only be sampled once before reliable data is obtained.

The alternative to conditioning is to use sample vessels that are manufactured with an inert coating on the internal surface, e.g. sulfinert. However, it is important to verify the integrity of the coating prior to sampling using calibration gases to ensure no losses are occurring.

Which types of vessels can be used?

Sample vessels and sampling tools can be of any physical type. The conditioning technique is ideal for stainless steel surfaces, which is most commonly used, but other materials such as titanium and aluminium can also be treated successfully.

What needs to be treated?

Ideally, anything which comes in contact with the sample needs to be treated: cylinders, valves, cylinder heads, pistons, agitation balls/rings, etc. In the case of bottom hole samplers, the sampling tool will need to treated plus the sample bottle and the transfer adapter, unless they are constructed of an alloy that does not absorb sulphur species (consult tool manufacturer for this information), Equipment can only be treated if it is clean and dry; all traces of previous sample and grease or displacement fluid must be removed first. Some pieces of equipment are best treated in a dismantled state.

How long does the conditioning treatment last?

The surface treatment is certified for 60 days, provided that equipment is stored so as to maintain its integrity. Exposure to atmospheric oxygen or moisture will reduce the time over which the treatment remains effective. Dismantled tools must be assembled as soon as is practical to protect the coating, but touching and handling of the treated surfaces should be avoided as far as possible.

Which sample vessels should I use?

Expro's analytical data services maintain several sets of cylinders dedicated for sulphur species sampling. These are either conditioned or coated. Cylinders are loaned out on a first-come, first-served basis to customers who do not have their own sample bottles, or wish to use dedicated, clean vessels. Please ask in advance if you may need these; as availability at short notice can not be guaranteed. Alternatively we can treat the customer's own equipment, and will advise on its suitability.

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What types of sample can be analysed?

Expro's analytical data services can carry out sulphur speciation analysis on hydrocarbon liquids, hydrocarbon gases and aqueous liquids. By the nature of multiphase hydrocarbons, these are typically pressurised samples. Typically these samples are de-gassed down to room temperature and atmospheric pressure and analysis is carried out on the gas and oil fractions separately (and water fraction if present and required). If required, de-gassing can be carried out at a specified temperature to mimic plant conditions.

How are the sulphur species determined?

All sulphur species are determined using Gas Chromatography with Sulphur Chemiluminescence Detection (GC-SCD). Gaseous samples and clean condensates can be injected directly whilst "black" oils and aqueous samples are introduced using a headspace analyser. For sulphur species that are gaseous at room temperature, calibration is carried out using certified gas calibration standards. For sulphur species that are liquid at room temperature, calibration is carried out using standards prepared from the pure compounds.

What sulphur species are included in the analysis?

Any of the following species can be determined individually or as a suite.

Sulphides	Thiols (mercaptans)	Thiophenes
Hydrogen Sulphide	Methanethiol	Thiophene (and/or 1-Methyl-1-Propanethiol)
Carbonyl Sulphide	Ethanethiol	2-Methylthiophene
Dimethyl Sulphide	Propane-2-Thiol	3-Methylthiophene
Carbon Disulphide	Propanethiol	Tetrahydrothiophene
Ethylmethyl Sulphide	Butanethiol	2-Ethylthiophene
Diethyl Sulphide	Pentanethiol	2-Propylthiophene
t-Butylmethyl Sulphide	Hexanethiol	2-Butylthiophene
Dimethyl Disulphide	Heptanethiol	3-Butylthiophene
t-Butylethyl Sulphide	Octanethiol	1-Benzothiophene
Dipropyl Sulphide	Nonanethiol	
Diethyl Disulphide	2-Methyl-2-Propanethiol	
	2-Methyl-1-Propanethiol	
	3-Methyl-1-Butanethiol	
	2-Methyl-1-Butanethiol	
	1-Methyl-1-Propanethiol (and/or thiophene)	

NB: Co-elution of Thiophene with 1-Methyl-1-Propanethiol means these species have to be reported as the total of both

What concentrations of sulphur species can be determined?

For most species detection limits of 0.1 mg/kg (ppm w/w) can be obtained in the gas and liquid fractions (some of the heavier species e.g. nonanethiol will have a higher limit of detection of approximately 0.4 mg/kg in the liquid fractions). Concentrations of H2S at the percentage level concentration can easily be measured. The uncertainty about the measurements is typically between 5% and 10% relative or the limit of detection, whichever is the greater.

Who uses this service?

Several major oil companies and offshore service companies use this service on a regular basis. Analysis can be carried out on individual samples in the laboratory, or if required an onsite service can be provided. This may be monitoring of individual process streams, assessment of the efficiency of sulphur removal beds or could be a full sulphur survey whereby all sulphur species are determined in several processing streams. This can provide detailed information on the separation of individual sulphur species and provide a mass balance across the plant process.

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