Oil in water analysis

What is being measured?

The determination of the oil content of refinery effluent water has long been a subject of studies. CONCAWE first published a report on oil in water analysis in 1972. Although we all know what 'oil' is, it cannot be defined scientifically as it may contain millions of compounds ranging from gases to tars. We therefore have to measure some surrogate property, and the value we obtain for oil therefore depends upon the analytical method.

CONCAWE published an additional report in 1984 (1/84) which considered the methods used by refineries at that time for the determination of oil in their effluents. It concluded that the most suitable method consisted of acidification of the sample before extraction with carbon tetrachloride, treatment of the extract with a sorbent and analysis of the extract by infra-red (IR) spectroscopy at three wavelengths. The absorbance was then to be compared with that of a known standard. This method became known in many quarters as the 'CONCAWE method' although it was really more of a recommendation to adopt one of a number of national standard methods which used this technique.

Since that time, most of the refineries in Europe have used variations on this method, although a few refineries have used methods based on different principles such as gravimetry (the standard method in the USA) or ultraviolet (UV) spectrometry. The use of carbon tetrachloride being discouraged on health grounds, it was, in most cases, replaced by Freon 113 which has similar (although not identical) properties. This solvent was later found to be an ozone depleter and therefore its use was also banned for most purposes under the Montreal Protocol[1]. A special derogation, now withdrawn, allowed its use in this particular test for several years.

A few years ago the UK Institute of Petroleum developed a new test which was similar to the old 'CONCAWE' method but with tetrachloroethylene (TTCE) as solvent. This test has been adopted by the refineries in the United Kingdom but by few others. Other refineries have recently changed to a gas chromatographic method (GC). CONCAWE's Water Quality Management Group has recently carried out a limited survey of European refineries which revealed that that a range of methods and therefore of solvents and physical properties for determining oil are in currently use. What does this mean in respect of the reporting and comparison of measurements of oil in refinery effluents?

Oil in water analysis contains a number of steps, namely:

- sampling;
- sample pre-treatment;
- extraction;
- treatment of extract; and
- analysis.

Even before analysis starts, sampling and subsequent handling is very important. Samples should be taken in an area of high turbulence so that the effluent is well mixed. Also, the whole sample, including the container, has to be extracted to achieve an accurate result, otherwise oil may have stuck to the walls of the container. The sample is then usually treated with acid which stabilises the sample and makes separation during the extraction phase easier. Acid can, however, catalyse chemical reactions and thus alter the result.

The solvent used for extraction has a large effect on the amount and types of compounds extracted. Treating the extract with an adsorbent such as Florisil removes polar compounds from the extract, which are certainly not oil but would otherwise be recorded as such. The different types of analysis also all measure different things. For example, IR determines the number of carbon–hydrogen bonds. As the level of adsorption is

[1] *Agreement on substances that deplete the ozone layer, September 1987*

not the same for all such bonds, the absorption is normally compared with a standard, either synthetic, or made from the type of oil likely to be present. If the composition of the oil in the sample is very different from the standard, systematic errors will creep in.

With a gravimetric analysis, the low-boiling solvent is evaporated and the remaining oil weighed. During this process, low-boiling material is lost. A similar limitation applies to the new GC method which also uses a low boiling hydrocarbons solvent.

Thus, every method measures something different and the result it gives will be different from other methods, sometimes very different. Comparative tests have shown that changing the solvent from Freon to TTCE does not affect the results significantly. However, comparative tests carried out in The Netherlands showed that the GC and IR methods did not consistently give similar results.

Do these differences matter? It cannot be said that any of the methods gives the 'correct' answer but it must be realised that the result obtained depends on the method. If the method is changed, any standards based upon it should also be changed. This needs to be stressed to the regulatory Authorities.

Finally it is important to consider why oil is being measured in the first place. If it is a concern that oil in effluents could form a slick in a river or the sea, then it is the heavier oil which is of concern. The gravimetric or GC methods will give a good prediction of this tendency as the lighter ends would evaporate. This was the situation when the first CONCAWE refinery effluent survey was conducted in 1969. Today, however, when refinery effluents contain less than 1% of the oil reported in that first survey and nearly all European refineries apply biological treatment, floating oil is no longer likely and so the IR method could be the appropriate one.

Given that measuring oil is difficult, particularly at very low concentrations, there seems to be little point in analysing for oil at all, or in setting oil effluent standards. Other measurements routinely carried out, such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), give a better indication of what is being discharged. Indeed, the European Polluting Emissions Register (EPER) regulation which requires all IPPC[2] sites (including refineries) to report their emissions does not include oil in the list of pollutants to be reported.

Although CONCAWE has no current plans to research this issue, it will evaluate any new method through its Water Quality Management Group and keep refineries informed so that they can choose the optimum solution in their local context.

[2] *Integrated Pollution Prevention and Control*