

LABOATORY ANALYSIS TECHNIQUES

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LABORATORY ANALYSIS TECHNIQUES & WATER CONTENT OF CRUDE OILS.

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The title of the paper being "Laboratory Analysis Techniques", begs the question that before receipt at the laboratory the sample is representative of the whole shipment or transfer.

The best method of ensuring this, is to have automatic sampling devices installed in order to produce a representative sample. As this is a subject in itself I intend to begin the chosen subject at the point where the sample is received at the laboratory.

In the first instance it could be that the laboratory is responsible for sampling direct from the automatic sample container which is commonly a can of the order of 11 litres.

The laboratory should then possess equipment suitable for the homogenisation of the sample, as outlined in papers given by Ken Underhill of Esso Research and Bob Mackison of B.P. Sunbury at Maidstone November 1981. The sample is then subjected to the homogenisation procedure which ensures representative subsampling.

Whilst it is realised that such massive disturbance of the sample reduces the representivity of the sample for such properties as light ends and density, it has been shown that the alteration in these properties once the sample has once more settled oil from water is relatively minor.

It is customary to obtain a 500 ml sample for testing for water by the laboratory.

Secondly the laboratory could receive a sample of oil for direct analysis. In this case it would have to be assumed that an approved procedure had been used to obtain the representative sample.

Finally, the sample could have been obtained manually, by a series of "Spot" samples.

The commonest of these are "J,M & B" samples out of shore tanks. It is here that representivity leaves much to be desired and that agreement is necessary to ascertain the suitability of such samples.

Thus the laboratory now has a sample which it has to check for water.

There are several ways this can be attempted, involving either physical or chemical methods and we can now examine such methods individually from a critical viewpoint to determine which is the best technique for each laboratory's purpose.

One step however, which has to be carried out immediately before any testing of crude oil, is to re-homogenise the sample.

It has been found that in order to obtain reproducible results an homogenisation procedure such as that given in IP 356 has to be used. Mere shaking the can by mechanical shaking is not sufficient to obtain a representative sample.

After this procedure a sample may be taken with relative confidence of its representivity.

The long serving standards have been by physical means of separation of oil and water.

Firstly, centrifugation has been seemingly the test employed as long as the oil industry has been established. It has evolved from hand centrifuging in the field to heated laboratory centrifuges whirling round at a mathematically correct speed to apply a particular quantity of 'g' at the centrifuge tube tip.

This letter is the basis of the present day standard specifications. - See Fig 1.

It is commonly used world wide but has been proved to give low results. (At Esso Abingdon an exercise on a series of North Sea crudes outlined this problem some three years ago.)

Also it combines water at the bottom of the centrifuge tube with any other extraneous matter in the sample, particularly sand and possibly wax if the test is improperly carried out.

Thus erroneous results with this method are common.

In order to carry out such a test it is necessary to have a laboratory equipped with accurate balances and a heated centrifuge.

The centrifuge tubes although reasonably robust have a tendency to break during cleaning.

It is both time consuming and labour intensive but probably its main drawback is that with many crudes, provided the homogenisation procedure has been correctly followed, the centrifuge is not capable of breaking down the fine emulsion, consequently separate layers of water and oil do not form correctly.

Thus a critical examination of this method shows that it is costly to perform and yields obtained are generally below the true value. If transfers using this method for water are carried out it can result in large monetary losses along the way.

One should not however decry its value in the examination of particular products for water and it has its value in the laboratory but not in examination of crude oils.

Continuing attempts at improving the method for crude oils are being attempted but it is considered that effort on improvement would be more fruitfully directed elsewhere.

The alternative standard physical method of estimation of water in oil is by distillation, using a suitable solvent and this has been applied with modifications to crude oils and products ranging from gas oil fractions to bitumen. It is not so successful at water determination of the lighter fractions, but usually these contain so little water that this is a relatively unimportant property.

The standard methods given in Fig 1 are all technically equivalent and to date it is the only reliable method of determination of water which is internationally accepted.

The advantages of this method is that it is simple and reliable to operate. It is cheap and does not require many man hours of operation. Also this method may be carried out using a bank of apparatus with six or more determinations being carried out simultaneously.

Its principal drawback it that the determination takes approximately three to four hours minimum and care must be taken to ensure that water retained in the condensor and the trap is carried to the bottom of the trap by mechanical means.

A laboratory environment is more or less obligatory for this test as both electricity and running cold water are a necessity plus the apparatus and a balance.

With ASTM D4006/IP358 standard size 5ml and 10ml traps are quoted but it is common to use alternative sizes such as 2ml traps when examining product samples.

It is known that the results with this method has a low bias and seemingly there should be a fall off in precision when using the larger volume traps, although it is not shown in the repeatability and reproducibility figures for crude oils.

In the mid 1970's it was realised that alternative procedures must be examined for water determination in crude oils as the physical methods were no longer suited to large and rapid transfers both by VLCC and pipeline.

In this country and elsewhere chemical methods of determination were considered and originally two were singled out as promising.

The French petroleum industry required a rapid evaluation of water in the field which was simple to operate and gave consistent, accurate results.

An apparatus designed originally for marine engine oil purposes was adapted for use with crude oil and it was shown that results better than those obtained by centrifuge could be obtained using the 'Fina Aquatest' apparatus.

It has been found simple to operate and is both cheap and rapid, but its biggest asset or "defect" is in its "take anywhere" value.

The apparatus is light, easy to carry and because it involves no electricity, can be taken into areas where other methods of test cannot be performed.

Its defect of course is that if used in a hazardous area, it is a near impossibility to obtain an homogeneous sample. The argument being that, as homogeneity is crucial to good water determinations it follows that a laboratory is required.

With the "field check" argument however, the use of a gas evolution method is probably the best method at present of obtaining a water determination.

It is a simple apparatus where a suitable quantity of crude oil is placed in a special receiver and a capsule of calcium hydride added. The gas evolved is measured in a cylinder, calibrated to read in percentage of water present.

The answer given is in a volume to volume manner which is useful in a field situation.

Its use is generally restricted to stabilised crudes as it does not perform well with light or gassy type crudes. Similarly heavy crudes or crudes with above 2% water require dilution with a dry solvent in order to give results on the scale of the apparatus, with consequent alteration to the direct reading ability of the apparatus.

Only one result can be obtained at each operation and a fairly comprehensive cleaning is necessary to ensure gas-tightness for each successive test.

In the U.K. we took a close look at the Karl Fischer titration method for water in North Sea crude oils. The technique had always been seen as unsuitable for crude oils, but with a better designed apparatus, a "scaling down" of sample size and a fresh look at the solvents used we were eventually in a position to use the method in North Sea crudes. Whilst this development proceeded we also examined other crudes and concluded that the method could be seriously looked at with a view to becoming internationally accepted. Internationally, four difficult crudes were tested and statistically examined, the results, which were studied by both ASTM and IP in early 1984, has resulted in a draft for a joint method which we hope will be published in 1985.

For those not familiar with the Karl Fischer titration it is based on a complex chemical reaction between the water molecule and the reagent (A solution of iodine and sulphur dioxide in pyridine).

The water present being equivalent to the amount of iodine liberated. When excess Karl Fischer reagent is present a change in colour from violet to straw is noticed. The colour change is now however irrelevant as the end point is measured electrically.

The use of the Karl Fischer titration technique has led to an increase in accuracy of water determination. Together with its relatively simple operation and its speed, we feel it will become the prime laboratory method for water determination in crude oils.

The method is being examined internationally with the proposal that it will eventually become an ISO method.

Development using Karl Fischer technique as a basis for testing is continuing.

The original reagent had what can mildly be described as a pungent odour. Non pyridine type reagents have now been marketed which in many cases are suitable for use with crude oils and are much more sociably acceptable.

Another development which has been in parallel with the development of our standard method is the use of coulometric apparatus using a modified reagent.

These are considerably more expensive than the normal Karl Fischer apparatus but however, are usually automated so that results are printed out in a matter of seconds.

Although only moderate skill is required to operate these pieces of equipment and the operation is simple, great care must be taken over the homogenisation step, the sample weighing and injection into the tester.

The sample is only of the order of 0.1 - 0.5g so one can see that any slight error will magnify or reduce the water result considerably.

Where a high throughput of samples is required on a permanent basis such a method can be highly commended, provided suitably accurate balances are available together with careful operators.

The high cost of the apparatus tends to disqualify their use for intermittent or varied work.

The coulometric method of Karl Fischer titration is at present being examined by a working group so that it may be included as a standard method for both ASTM and IP as soon as possible.

The necessity for sampling homogenisation, sub-sampling re-homogenisation and laboratory testing seems to be a cumbersome approach to water determination in crude oils. The obvious solution would be to measure the water "in situ" as oil passes down a pipeline.

Many approaches have been made to this such as density measurement, conductivity etc.

To date however no break through has occurred and it is still entrusted to the laboratory to obtain results on which millions of pounds a year hang upon the accuracy of the determination.

CRUDE OIL

ISO 3733 API 10:2 IP 358 ASTM D4006 DIN 51582

ISO 3734 API 10:3 IP 359 ASTM D4007 DIN 51793

IP 356

PRODUCTS

IP74 ASTM D95

IP75 ASTM D1796

FIG. 1.

References

[1] Paper presented at the North Sea Flow Measurement Workshop, a workshop arranged by NFOGM & TUV-NEL

Note that this reference was not part of the original paper, but has been added subsequently to make the paper searchable in Google Scholar.