

SAMPLING AND ANALYSIS FOR THE DETERMINATION OF
THE WATER CONTENT OF CRUDE OIL - AN OVERVIEW

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I) INTRODUCTION

Sampling for water in oil is not an exact science. Over the last few years there have been some major improvements in both the theory and practice of automatic sampling, but we still do not know all the answers. Any sampling operation has to be judged on a statistical basis and eventually has to be expressed as a percentage confidence that the result obtained is within a defined tolerance of the truth. Since by ISO 5168 definition, error is always unknown, it is usually best to work in terms of 'uncertainty' although other terms are often used.

This paper is a review of recent and current attempts to reduce the uncertainty of water-in-oil measurement. It deals with the recently approved draft of an International Standard and describes some practical and theoretical work that has been done or is near to completion. All of the currently available work is being collected together into a proposed new publication from the Institute of Petroleum, which will be called a 'Guide to Automatic Sampling'. Recent developments in the measurement of water in oil are also described with a brief glance at what might happen in the future.

II) INTERNATIONAL STANDARDS - ISO 3171

HISTORY

In December, 1975 the first edition of ISO 3171, an International Standard document dealing with Automatic Pipeline Sampling, was published by ISO in Geneva. It was known that this early edition was not complete, and in the UK it was decided that this edition would not be published by BSI as an identical, dual-numbered British Standard. It was considered that the methods described in it were not generally applicable to crude oil. Other countries were also doing work to improve the performance of automatic sampling equipment, and hence at the meeting of the ISO Technical Committee 28 Sub-Committee 3 in Mexico City, 1979, it was decided to set up a Working Group to prepare a new edition. The Secretariat of the Working Group was allocated to the UK, and was delegated via BSI to the Institute of Petroleum where most of the detailed work was done by the Panel PM-B-2, which is part of the Petroleum Measurement Committee PM. During the compilation of the new edition, major contributions were made from the UK, USA, France and Italy. After a lot of national and international discussion and many meetings, agreement was reached at the ISO TC28/SC3 meeting held in Rome, November, 1985 about what should be included in the new ISO 3171 (Ref 1). All the technical work has now been done; we now await formal publication.

As with almost all international documents the final result was an acceptable compromise. Not all of the contents were agreed unanimously (even within the UK delegation), but the recommendations made within the document were agreed to be the best available at that time and were agreed to be conservative rather than misleadingly optimistic. All the delegations recognised the need for early publication, even though new and better information was still emerging. Our understanding of the principles and practice of automatic sampling is still improving, and yet another edition of ISO 3171 is to be expected at some time in the future, maybe 10-12 years.

CONTENTS of ISO 3171

Some of the highlights of the new ISO 3171 are as follows:-

1) Definitions and Terminology

Some of the terms used in sampling (such as sample point, grab, profile testing, worst case conditions) have been defined more precisely than before and definitions of different types of water (ie., dissolved, suspended, free and total) have been brought into line with other international documents. Throughout ISO 3171, care has been taken to make sure that it does not conflict with other Standards, and in particular, some parts are identical to ISO 3170, a sister document dealing with Manual Sampling, which has recently been revised and which was also approved for publication at the Rome meeting.

2) Location of Sample Point

Recommendations are made about where to put the sample point. The preferred position is in the middle of a downward flowing pipe soon after the best available mixing device. Recognising that this ideal is not always practicable to achieve, other possible positions for the sampling point are discussed (Figure 1). A great deal of the Standard deals with the problems of sampling from a horizontal line.

3) Representative Sample

The definition of representative sample is the idealised case of the sample being identical to the pipeline average, but a practical limit is set of $\pm 5\%$ of reading (ie., 1 part in 20 of the water concentration) for the uncertainty that is likely to be achieved in a good sampling system. At water concentrations below 1% this limit is replaced by a fixed limit of .05% of water, so that impossibly fine limits are not called for at low levels of water concentration.

4) Sampler System

The Standard does emphasise the need for flow-proportional sampling and is also quite strongly in favour of iso-kinetic sampling (within a factor of two up or down).

5) Sampler Performance

ISO 3171 offers two methods by which the performance of an automatic sampler can be assessed. The first is by carrying out a practical test in which a known quantity of water is injected into the pipeline at some location upstream of the automatic sampler. Details are given of the procedure to be followed in order to check if the sampler 'sees' this extra water within acceptable limits of accuracy. The second method shows how to calculate the overall uncertainty from a knowledge of the uncertainties of all the component parts or operations. In practice these component uncertainties are seldom known, but the method is useful to compare different options and to identify the most likely sources of major errors. Typical values are given.

6) Profile Testing

Before a sampler is installed (and afterwards if its performance is at all suspect) it is recommended that a profile of the water concentration across the vertical diameter where the sampler probe is to be installed, should be obtained by testing. The profile testing procedure (adapted from API) is described in detail and some typical results are shown.

7) Profile Calculation

Sometimes it is not possible to do a profile test, in which case ISO 3171 offers a method (developed in France) by means of which the shape of the profile can be predicted by calculation. This should be a major step forward in sampling system design and was welcomed by all the Working Group members. It was reckoned that the method is by no means perfect, but that it does provide some useful information and does allow valid comparisons to be made. It is believed that the method will not predict a better profile than that which will actually occur in practice.

DEFICIENCIES of ISO 3171

Even when the present ISO 3171 was agreed at the meeting in Rome, it was known that new and better information was still being published. Automatic sampling is still a matter for innovation and development. However, it was decided that there was sufficient new information in the agreed document to justify publication and to meet a recognised demand for international standardisation. To wait for the last word on the subject would be to wait forever.

Some ways in which ISO 3171 could be improved are as follows:

1) Definitions

The terminology to differentiate between the different types of automatic sampler (in-the-line, by-pass loop, cell) is not well defined and the term 'grab sampler' could mean different things to different people.

2) Accuracy

The "5% of actual concentration" criteria is used rather indiscriminantly throughout the document and in some parts an even poorer performance seems to be condoned. This ought to be put on to a more rational basis.

3) Minimum Sampling Frequency

The Standard does not give any really useful advice on this controversial matter.

4) Profile Testing

The method described for profile testing is labour intensive and not very practicable, although it can be done. The use of multiple continuous monitors to do this job should be advocated more strongly.

5) Profile Calculation

The method described in the Standard for predicting the profile is already quite complicated. Better methods involving more refined theory and a deeper understanding of

5) Cont'd

the physical principles involved are available. How much of this can be put into the Standard without making it too complicated for a design engineer to use, will be difficult to decide. There is however, a worldwide recognition that some improvements are needed which must be based on practical experience and feedback from users of these tentative proposals.

III) CURRENT INVESTIGATIONS

Concurrent with the preparation of ISO 3171 (and in some cases prompted by it) a number of research and development programmes concerned with automatic sampling have been set in progress. The results of some of these programmes are restricted by the need for commercial confidence, but in others the need for the conclusions to be widely understood and commonly accepted in all the oil industry (as a basis for fair trade between two parties) has been recognised. In most cases, all the important conclusions have been published for general use. In all cases at least one member of the Institute of Petroleum Panel on Automatic Sampling is aware of the results so that conflicting recommendations ought not to appear.

Three major programmes are worthy of note:-

1) BP at ROTTERDAM (Ref 2)

BP (Central Engineering Dept), who have always been pioneers in the design and construction of automatic sampling equipment, set out to test and compare the performance of some new designs of sampler. Facilities were set up at the BP Rotterdam refinery so that crude oil being unloaded from tankers and also being transferred between shore tanks could be sampled for water under realistic, but controlled, conditions. Tests were done with both in-the-line and cell samplers, which were checked both against each other and by means of the water injection test as described in ISO 3171. They also carried out profile testing as described in the standard. Additionally the opportunity was taken to test a new design of insertion flowmeter and the performance of a continuous water-in-oil monitor based on the large difference between the dielectric constants of the two components.

The initial results from the tests indicated that the cell sampler in a 1" NB pumped bypass system did give good results under almost all test conditions, but that the in-the-

1) Cont'd

line sampler was not so consistent and usually gave low results. Further testing is being carried out under the supervision of NEL.

2) NEL JOINT INDUSTRY PROJECT (Ref 3)

For a number of years, NEL have organised a joint research programme to study and improve the use of automatic samplers in the petroleum industry. Phase 3 of this programme which was supported by 17 different organisations is now virtually complete. Phase 4 is about to start.

A lot of the work done by NEL for the consortium has been done on a laboratory test rig specially designed to check the performance of samplers and sampling probes. One of the conclusions drawn from recent work is to highlight the need to take care to minimise the effect of the 'dead volume' after the grab mechanism of in-the-line samplers. The shape of the inlet orifice to sampling probes has also been studied and the design with an internal taper is recommended. This confirms the shape shown in ISO 3171.

Another aspect of the NEL work has been concerned with the number of grabs required to give a representative sample. This has been done by computer simulation, and is described in another paper at this NEL Metering Workshop. (Ref 4)

An ongoing investigation by NEL on behalf of the joint project has been made possible by the generous co-operation of BP. The test facilities at the Rotterdam Refinery (mentioned earlier) have been made available for independently controlled tests, the results from which will be of use throughout the industry. The main objective of the current programme of tests is to find out how close to

2) Cont'd

iso-kinetic operation it is necessary to be, in order to get a representative sample of water in crude oil. The present recommendation within ISO 3171 for iso-kinetic sampling (within a factor of two either up or down) is based mainly on intuition and some qualitative test work. Better information is needed to clarify the position and to allow more positive guidance to be given.

3) CRAFIELD FLUID ENGINEERING RESEARCH (Ref 5)

Prompted and assisted by close collaboration with BP, the members of the Department of Fluid Engineering and Instrumentation at the Cranfield Institute of Technology have studied two aspects of automatic sampling.

A) Profile Calculation

The procedure described in ISO 3171 to calculate the water concentration profile in a horizontal pipe has been examined in detail. The validity of the formulae used and the basic assumptions and simplifications made, have all been challenged. Recently published work by Karabelas and Segev has been compared with the ISO method, and a computer programme has been developed so that all three methods can easily be applied to a given problem. The general conclusion is that none of the methods is strong enough to stand on its own as the sole judge as to whether representative sampling is or is not possible. The methods are useful for making comparisons and for identifying where improvements can be made.

All the methods should be backed up by practical tests. It has been confirmed that the ISO 3171 method is conservative and should not predict good sampling where it is impossible. The major source

A) Cont'd

of uncertainty in all these calculations is concerned with the water droplet size, which is difficult to calculate and almost impossible to measure. Further work is proceeding on this problem.

B) Number of Samples

As a supplement to and in some ways as a duplication of the work done at NEL, Cranfield have investigated the problem of deciding what is the minimum acceptable number of grabs required to get a representative sample. They have investigated both the influence of discontinuities in time (ie., slugs of water travelling down the pipe) and also discontinuities in space (ie., large drops evenly distributed). Broad agreement has been reached with the NEL work about which factors are most significant to this decision, but further reconciliation is still required.

IV) IP GUIDE TO AUTOMATIC SAMPLING

When the Institute of Petroleum Panel PM-B-2 had finished its work in helping to draft the ISO 3171 document, it considered what else was most required. It decided to produce a new document to be included in the IP Petroleum Measurement Manual series of publications, but which would be more of a guide or textbook rather than a standard. The Guide is intended to amplify and explain the recommendations in ISO 3171 and also to give more background information about the equipment available and the methods to be used. It also tries to deal with some of the problems left unsolved by ISO 3171.

Some interesting features of the Guide are as follows:-

A) Sampler Types

The Guide describes many of the different types of sampler that are in use. It divides them up into three (3) main categories:-

i) In-the-line Samplers

where the grab isolation point is inside the pipeline itself, usually on the end of a long probe.

ii) External-Loop Samplers

where the grab isolation point is outside the pipe and is taken from a subsidiary system (often known as the fast loop).

iii) Cell Samplers

which are a combination of the other two, so that an in-the-line sampler in a moderately sized by-pass loop takes samples from a manageable sub-division of the main pipeline flow.

The Guide does not recommend any one type above the others.

B) **Mixing**

The Guide describes some of the various mixing devices that are available to help provide suitable conditions in a pipeline, so that a representative sample can be obtained. It describes the jet mixer and how it can conveniently be combined with a cell sampler to form an integrated system. However for design details of all such systems, it is necessary to refer to the manufacturers. In the future, it is expected that there will be a growing emphasis on the need for more deliberate mixing prior to sampling. The need for mixing after sampling (ie., homogenisation before analysis) continues to be emphasised.

C) **Sampler Location**

The recommendations in ISO 3171 about sampler location have been expanded and explained in more detail in the Guide. A vertical section of pipe with downward flow is still the ideal location, but other locations can still produce acceptable results. The ISO method of calculating the concentration profile in a horizontal pipe is explained in detail and the other methods are introduced with references. It is hoped that some clear-cut advice about iso-kinetic sampling will be available in time for publication.

D) **Minimum Acceptable Number of Grabs**

The Guide attempts to bring together all the recommendations currently available to give advice on the number of grabs that need to be taken to ensure that the total sample is representative of the whole. By combining a basic theoretical approach to the problem with the statistical and computer modelling work done by Exxon, NEL and CIT a simple formula has been proposed by means of which the minimum acceptable number of grabs can be calculated. (Fig 2) A lot of discussion will be required before we have a widely accepted solution to this contentious problem.

E) **Practical Testing**

Based on practical experience in using the two test procedures described in ISO 3171 (ie., profile testing and water injection testing), the Guide gives more detailed advice about the difficulties to be overcome. It also gives more information about how to interpret the results once they have been obtained. It emphasises that an overall accuracy of one part in twenty is not really very good and that we ought to be able to do better.

V) AUTOMATIC KARL FISCHER ANALYSIS

HISTORY

For many years the only recognised method for measuring water in crude oil was by means of centrifuge tests. The terminology 'BS + W', which is still very widely used, implies that the result is obtained by centrifuging. It takes the oil industry a very long time to change its terminology and to accept logical precision in its use of words, but it has not taken very long for the centrifuge to fall out of favour and to be replaced by an analytical procedure based on the Karl Fischer reaction.

The first method to be approved by the Institute of Petroleum IP 356/82 was designated for use with North Sea Crude Oil. The revision in 1984 (IP 356/84) removed the specific reference to 'North Sea' and implied a much wider field of use. However, the method described in those documents is to use a titration apparatus with the end point determined by an electrical potential difference method. The reagents used include pyridine which is not a very nice chemical to deal with, and moreover the reagents are not very stable and they need to be made up fresh and to be standardised daily. This is not the sort of job normally given to offshore operators more traditionally accustomed to the use of centrifuges.

COULOMETRIC ANALYSIS

A new version of the Karl Fischer method is now available that is much easier to use. It has become so popular that it is now in widespread use by North Sea operators, even before an official IP method has been published. In the new method the important reagent (iodine) that reacts with the water is produced electro-chemically by electrolysis of the anode solution. Only enough iodine is produced to react with all the water present, and by measuring the quantity of d.c. electricity (coulombs) required to liberate that iodine, a direct measurement of the quantity of water present is obtained. The end-point is still detected electrically, but in this case it is usually an a.c. potential measurement.

These new instruments are usually micro-processor controlled and apart from weighing the sample and injecting it from the syringe into the stirred measuring cell, the analysis is fully automatic. The cell is kept in operation for 24 hours per day so that any moisture that seeps into it is eliminated before the next set of samples are injected. Each refill of reagents can last several days depending on how much water is in the sample that is injected and how much seepage of water into the cell takes place.

On an offshore platform weighing the sample syringe (before and after injection) could be a problem, but modern electronically controlled weighing machines can average a large number of instantaneous readings to get an accurate result even if the platform is moving. This is often known as the 'animal weighing program'.

OPERATION

There are a number of features of the new Karl Fischer method that need to be watched:

1) Homogenisation

To get a water-in-oil mixture into a sufficiently finely-divided homogeneous state so that a representative sample can be drawn into syringe through a small bore needle requires vigorous agitation. The best high speed homogenisers must be used and the mixing time required must be determined by a rigorous series of tests. Homogenisation for Karl Fischer needs to be much better than for centrifuges.

2) Calibration

The calibration of an automatic coulometric Karl Fischer method is usually checked when first installed by testing it with made up samples. Thereafter the electrical-to-chemical conversion is assumed to remain constant. This will only be true if the fundamental design is right and there is rigid quality control of the reagents used. An IP standard method of test is currently being prepared.

3) Salt Correction Factor (Ref 6)

The Karl Fischer method measures the mass of pure water in a weighed sample that usually consists of salt water in crude oil. If it is required to use the Karl Fischer analysis result to calculate how much salt water was in the original bulk transfer then a Salt Correction Factor must be applied. In order to avoid the possible error of applying the SCF twice, it is recommended that it is never applied to Karl Fischer percentage figures, but is only used when calculating an absolute mass of salt water.

4) Interference Reactions

Hydrogen sulphide will react with the Karl Fischer reagents in the same way as water and will appear in the result. This is the only interfering material that is likely to occur in crude oil and will usually only be present in concentrations much less than the known uncertainty of water measurement, and hence can be ignored.

Care must be taken not to introduce any other interfering agents, particularly with any solvents used for cleaning. Acetone should not be used.

5) Sediment

The old centrifuge method included any sediment in with the water measurement. The Karl Fischer method ignores any sediment. If sediment is present, it can be measured by the IP 53/70 method, but this is very much a laboratory procedure. Samples taken specifically for water measurement may not be truly representative of sediment concentration.

VI) FUTURE TRENDS

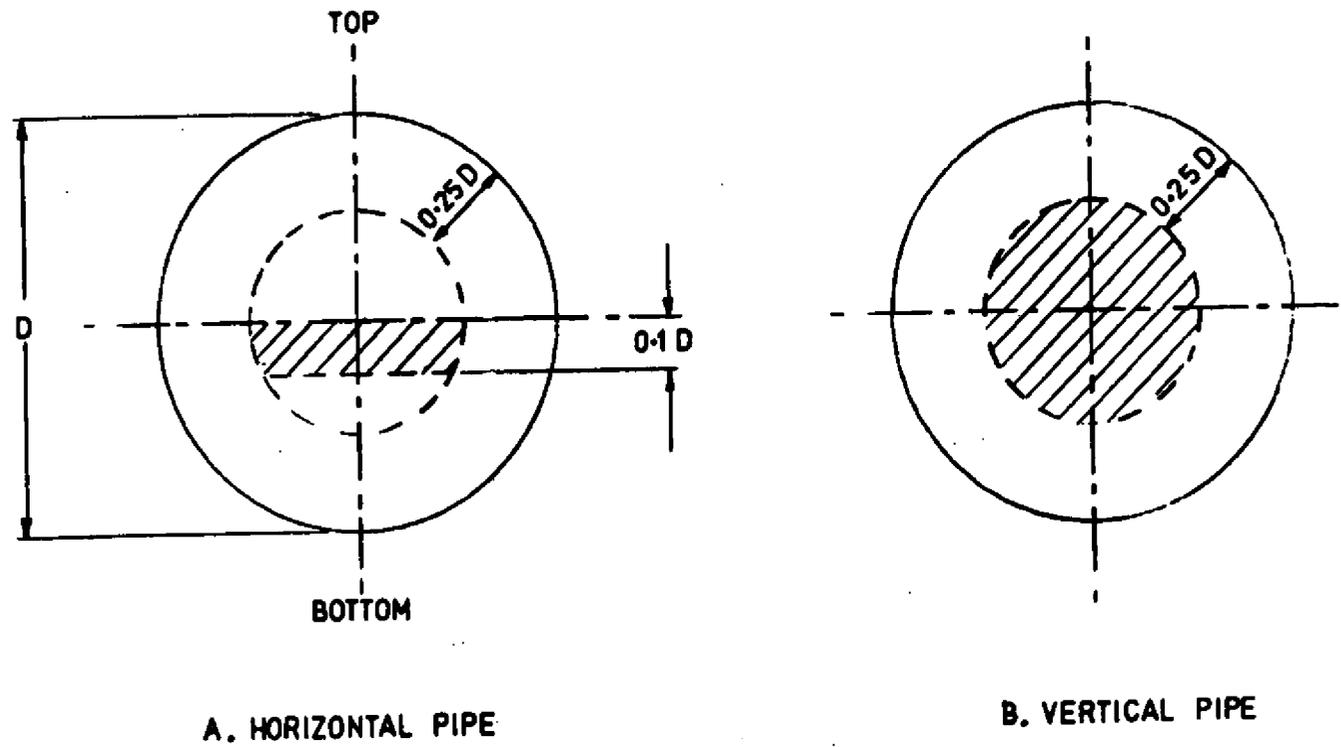
As we begin to understand the problems of automatic sampling, it becomes more and more obvious that proper mixing is vital before it is possible to obtain an accurate result. Emphasis will concentrate on the theory and practice of mixing non-homogeneous liquids in pipelines so that sampling devices can have some chance of grabbing good samples. The cell sampler with a moderately - large pumped by-pass flow loop may be the answer to this problem.

An alternative device that has been around for a long time, but looks to be making some progress, is the dielectric constant type water monitor. Potentially this can solve both the sampling and the analysis problems all in one unit. It has not yet made the same dramatic impact that the coulometric Karl Fischer method has achieved, but it may do so one day.

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REFERENCES

- 1) Final Draft - December, 1985
International Standard ISO 3171
Petroleum Liquids - Automatic Pipeline Sampling
- 2) A Comparison of the Performance of In-Line and By-Pass type
Sampling Devices in the BP Rotterdam Tests.
R C Gold and J S S Miller.
North Sea Flow Metering Workshop, Stavanger, November 1985.
- 3) The Study and Improvement of the Design and Operation of
Automatic Samplers used in the Petroleum Industry.
National Engineering Laboratory. Joint Industrial Contract
- 4) Computer Simulations to determine the Optimumm Sampling
Frequency during Custody Transfers.
N W King. NEL
- 5) Sampling Water-In-Oil
Prof. Roger C Baker
Cranfield Press
- 6) Measurement Errors in North Sea Exploration and Production
Systems resulting from ignoring the properties of Water.
T J Hollett.
North Sea Flow Metering Workshop. NEL, 1984



A. HORIZONTAL PIPE

B. VERTICAL PIPE

THE INLET ORIFICE SHOULD BE LOCATED WITHIN THE SHADED AREA

FIGURE 1 LOCATION OF WITHDRAWAL POINT (INLET ORIFICE).

$$\begin{array}{l} \text{MINIMUM ACCEPTABLE} \\ \text{NUMBER OF GRABS} \\ \text{(MANG)} \end{array} = \frac{300 \times P}{E \times A}$$

Where P is the Peak concentration (percentage) that is expected during the transfer. This can be obtained from experience with similar operations and systems elsewhere.

Where A is the Average concentration (percentage) of the whole transfer. This can be estimated in advance, but should not be set too low without some consideration of the appropriate associated values of E and P.

Where E is the Error limit (as a percentage of A) that is being aimed at with 95% confidence. E is usually 5%, but may need to be more if A is less than 1%.

FIG 2 PROPOSED FORMULA FOR SAMPLING FREQUENCY