

CONFIDENTIAL

Report EP 92-0980  
October 1992**GUIDELINES FOR MANUAL SAMPLING  
AND ANALYSIS OF  
HYDROCARBON FLUIDS**

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SHELL INTERNATIONALE PETROLEUM MAATSCHAPPIJ B.V., THE HAGUE

Exploration and Production

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## 1. INTRODUCTION

### 1.1. SCOPE

The primary objective of this report is to provide engineers of all disciplines with a set of recommended specifications for the hydrocarbon samples and analyses they will require in order to obtain the data needed for optimum and economical development of a hydrocarbon accumulation.

This report extends and replaces report EP 05-0758 to cover the experience gained since 1979 in well stream (mainly gas) sampling and analysis. Parts of the earlier report have been included without significant alteration so as to give a complete coverage of the topic.

Emphasis has been placed on the sampling of gas and gas condensates because of the special problems associated with sampling these particular fluids. However, the sampling and analysis of (mainly) liquid hydrocarbon streams is also addressed.

Throughout this report sampling of "well stream fluids" is most often referred to. However comments can be applied to all fluid sampling anywhere in the process. In most cases the methods applied to well stream fluids are equally applicable to all streams. Where the handling of process or product streams requires different techniques these are described.

A detailed discussion of the methods and techniques associated with sampling and analysis of water streams is not included in the current report. The reader is referred to report EP 89.0150 for an in depth and up to date discussion of the problems peculiar to sampling and analysis of water hydrocarbon mixtures/emulsions in order to determine dehydration/deoiling properties.

This report covers only manual sampling and analysis techniques. Continuous, on-line sampling, recording or indicating devices are outside the scope of this report but are covered by DEP 32.31.50.10.-Gen, DEP 32.31.50.11.-Gen, DEP 32.31.50.12.-Gen and DEP 32.31.50.13.-Gen

This document does however attempt to cover manual sampling and analysis for monitoring of hydrocarbon production facilities and custody transfer although it is recognised that sampling and analysis for these purposes will frequently be carried out with automatic equipment and so would be beyond the current scope.

### 1.2. SUMMARY OF RECOMMENDATIONS

The recommendations made in this manual are summarised in tabular form in Appendix 1. The tables of appendix 1 list the data requirements, sampling methods and analytical methods recommended to be applied in any manual sampling of hydrocarbon fluids.

### 1.3. DISTRIBUTION AND INTENDED USE

Unless otherwise authorised by SIPM, the distribution of this report is confined to companies forming part of the Royal Dutch/Shell Group or managed by a Group company, and to contractors nominated by them.

This report is intended for use by all involved in the specification of samples and analyses

## 1.5. ABBREVIATIONS AND TERMS USED

**API** - American Petroleum Institute

**AMS** - Amsterdam Method Series (analytical methods developed and documented by KSLA)

**ASME** - American Society of Mechanical Engineers

**ASTM** - American Society for Testing and Materials

**BS&W** - Base Sediment and Water

**GC** - Gas Chromatography

**GCMS** - Gas chromatography Mass spectroscopy

**GLR** - Gas/liquid ratio

**GOR** - Gas/oil ratio

**GPA** - Gas Producers Association

**FTHP** - Flowing Tubing Head pressure

**FTHT** - Flowing Tubing Head Temperature

**FID** - Flame Ionisation Detection

**IATA** - International Air Transport Association

**IMDG** - International Marine Dangerous Goods

**IP** - Institute of Petroleum

**Iso-kinetic** - Refers to a sample taken such that the velocity of the fluid in the sample probe is the same as the velocity of the fluid flowing in the stream being sampled.

**ISO** - International Organisation for Standardization

**KSEPL** - Royal Dutch/Shell Exploration and Production laboratory

**KSLA** - Royal Dutch/Shell Laboratories Amsterdam

**LGR** - Liquid/gas ratio

**LNG** - Liquefied Natural Gas

**LPG** - Liquefied Petroleum Gas

**NGL** - Natural Gas Liquid

**PVT** - Pressure Volume Temperature

## 2. DATA REQUIREMENTS

### 2.1. GENERAL

Different disciplines in our organization have varying analytical interests in oil and gas samples and also require different levels of analytical detail. Usually a considerably more detailed hydrocarbon composition is required for the purposes of process and facilities design than is required for reservoir studies or other purposes.

Samples are collected for the following broad categories or reasons:

**Preliminary analysis:** To provide quick, preliminary information regarding the principal characteristics of the liquids or gases obtained, preferably by means of simple on site analysis (eg. density, BS&W).

**Evaluation analysis:** For general oil refining/processing information and to determine the economic value of crude or condensate for various refinery types and regions. The analyses are normally done at special crude oil evaluation centres associated with refineries.

**Custody Transfer:** To determine the properties of a gas or liquid stream or stored volume in order to establish a sales quantity and/or price. This is however most often carried out with the use of automatic samplers which are beyond the scope of this report.

**Process and Product Quality Monitoring:** Analysis required to ensure that a process is functioning correctly or that products remain on specification. This category could also be applied to gas samples taken in order to manually monitor properties of raw reservoir fluids or when analyses are required to validate process simulation models when only composition of light components (to C6) and a quantitative estimate of the heavy fraction is required. However process monitoring is most often carried out with the use of automatic sample and analysis systems which are outside the scope of this report.

**PVT analysis:** Used for reservoir engineering, well performance, pipeline, project and process design calculations. The analyses are carried out at specialized laboratories.

Traditionally the specification of well stream sampling and analysis requirements have been left to reservoir engineers alone. However the reservoir engineer may not always be fully aware of the analytical requirements of downstream interests. It is therefore strongly recommended that production chemistry and process engineering also provide input to the planning of the sampling campaign as representative of the more downstream interests. This should avoid the common complaint regarding a lack of sufficiently detailed data being available for facilities design.

It is recommended to combine the analytical requirements from well stream sampling for PVT and other reservoir engineering studies with those for downstream engineering work and, in all cases, obtain a suitably detailed well stream composition. Catering for the requirements of all parties in the one sampling campaign has many obvious advantages, including:

- The convenience and probable technical correctness of having all engineering studies using or being related to the same well stream samples and analyses.
- The strong possibility that the current test might provide the only opportunity to

sample the reservoir, so the analysis should be as good as possible.

The specific data requirements for the various disciplines are discussed in more detail in the following subsections and summarised in tabular form in Appendix 1.

## 2.2. DATA REQUIREMENTS FOR PRELIMINARY ANALYSIS

Generally only rudimentary analysis to determine fluid density, water content, water salinity and the presence of hydrogen sulphide and possibly carbon dioxide is required. Depending on the facilities available on site (eg. chromatograph in the rig mud lab. or service company portable analysis unit) an initial analysis of light hydrocarbons to C6 may also be possible.

Applied to rough samples taken during exploration drilling or during appraisal in order to confirm similarity with previous wells, this analysis is normally carried out on site.

## 2.3. DATA REQUIREMENTS FOR CUSTODY TRANSFER:

The properties of a gas or liquid stock which establish its sales price are explicitly stated in the relevant contracts. Typical analytical requirements are for crude density, water/salt content, TAN, sulphur content or vapour pressure. For gases, transfer price is frequently established according to calorific value and/or Wobbe Index. Contracts for custody transfer will frequently place restrictions on the level (maximum or minimum) of a specific fluid property rather than specifying a required range (eg. sulphur content, crude density).

Custody transfer of natural gas will generally require the use of on-line process analysers. The choice and application of devices of this type are outside the scope of this report (see DEPs 32.31.50.10, 11, 12, & 13-Gen.). However manual samples must frequently (typically quarterly) be taken and analysed for the purpose of proving or validating on-line process analysers. In this case the data required is the same as that which the automatic system is providing and the analysis methods will be the same as described in section (4) below.

## 2.4. DATA REQUIREMENTS FOR OPERATIONAL CONTROL AND PROCESS MONITORING

### 2.4.1. Monitoring of Oil Processing and Transport Facilities

The main variables requiring monitoring in oil producing operations are crude BS&W, salt content, crude density, crude vapour pressure, hydrogen sulphide content (for protection of downstream facilities), TAN and possibly sand production. Because of the wide variation in circumstances it is not possible to specify minimum data requirements for monitoring liquid process streams.

Monitoring dehydration / de-oiling performance (eg performance of demulsifying chemicals) is also important but this is treated in detail in report EP 89-0150.

### 2.4.2. Monitoring of Gas Facilities

In most gas handling or treating operations it is necessary to check either plant

performance or product quality or both at regular intervals. In many instances either the nature of the operation or the stringency of contractual requirements make it a requirement to apply continuous, on-line sampling, recording or indicating devices for this purpose. These devices are beyond the scope of this report (see DEPs 32.31.50.10, 11, 12, & 13-Gen.) but as noted in (2.3) they will require validation by manual sampling and analysis.

In many cases where the operation is a relatively simple one or where plant upsets are unlikely infrequent or of less serious consequence, adequate control may be obtained by periodically sampling and suitably analyzing the appropriate streams. In these cases a simple chromatographic analysis to C8 or even a dew point measurement will generally suffice.

Calorific value, relative density, hydrocarbon and water dew points, concentrations of sulphur compounds or inerts are used in specific instances as key properties for monitoring performance or for quality control. These properties are used as key features in the quality specifications attached to gas sales agreements, and in that case a high degree of accuracy may be required.

Periodic monitoring of the condition of glycol in dehydration or hydrate protection systems will also be required. Data requirements for monitoring glycol condition must be according to DEP 20.04.10.10-Gen.)

#### 2.4.3. Product Allocation from shared facilities

Monitoring of plant outlet fluids is also important for product allocation from shared facilities. In offshore production areas it is common for different companies to transport their gas, crude or full production stream to shore through a shared pipeline and treatment facilities. Regular, periodic analysis of the different production streams, the mixed pipeline fluid and the plant products will be necessary to ensure equitable inter-company accounting.

For this purpose all gas samples, particularly at the inlet and outlet of the pipeline, should be analyzed routinely for hydrocarbons up to C8 and for water, inerts and individual aromatics and hydrogen sulphide. It may also be necessary to carry out routine measurements to determine the trace components in the gas.

Liquids should be routinely monitored for relative density, BS&W, salt, sulphur, TAN and RVP.

#### 2.5. DATA REQUIREMENTS FOR FLUID EVALUATION:

For general oil refining processing information and to determine the economic value of crude or condensate SIPM-MFSO/6 have established two different levels of required data.

A "simple" crude oil evaluation may be carried out on a crude from a production test of a promising well in a new area or on crude from a new field making a significant contribution to an existing facility.

A "standard" crude oil evaluation will be carried out on crude from a proven commercial, new discovery. Both the "standard" and the "simple" evaluation involve a standardized distillation of the crude and then varying levels of detailed analysis of the fractions.

The analytical requirements for the simple and the standard evaluations are summarized in Appendix 1. and are described in detail in report MF 81 0430.

## 2.6. DATA REQUIREMENTS FOR PROCESS SIMULATION AND PROCESS , PIPELINE OR WELL DESIGN

In all cases where the compositional and analytical data of hydrocarbon fluids are to be used as the basis for process design calculations, whether for new plants or facilities or for changes and additions to existing plants or facilities, the more extensive and detailed the data available the better. These data should at least include the following:

- Chromatographic analysis of hydrocarbons up to C16 including individual determination of light aromatics (benzene, toluene and xylene). C16 is chosen as the limit because analysis to this level is feasible using industry standard methods (ISO 6975) and standard columns.
- An accurate description of the properties of the individual carbon number fractions from C7 and above. The description of the individual carbon number fractions has a significant effect on the accuracy of computer simulations which are performed to simulate new or existing plants in order to size equipment and predict product yields. It is not adequate to assume that these fractions have the properties of the paraffins nor is it adequate to assume "standard" crude properties from published data. For typical EP applications (e.g. crude separation plant, LPG plant, gas refrigeration plant) a TBP analysis of the Cn+ fraction by distillation is required. This analysis should determine volume, average molar mass and average density for hydrocarbon fractions between specified boiling points. (usually equivalent to the paraffinic hydrocarbon components). This information defines the "character" of these fractions and process simulation programs can use this information to generate all other relevant properties for each fraction. The TBP analysis described in (4.13) should be carried out on a fresh sample (ie. not weathered).

Note that modern process simulation programs provide the facility to generate TBP or distillation curves from a compositional stream input. This is a useful calibration check against an experimentally determined TBP.

As an alternative to a TBP analysis, at least one service company is now offering GCMS analyses. The GCMS will provide normal boiling point (equivalent by chromatography) and average relative molar mass for the individual carbon number fractions from C7 and above. This information is then sufficient to characterise these fractions for use in process simulation packages. GCMS also allows greater possibilities to identify and quantify all components present in a hydrocarbon mixture (particularly for gas and condensate samples). The components identified may then be lumped into a usable number of fractions and the average properties (molar mass, relative density) of these fractions calculated.

- Experimental measurements (not computer simulated!) of phase behaviour (liquid/gas ratios and compositions, dew points) of the well stream at anticipated future processing pressures and temperatures so as to enable simulated phase behaviour to be accurately calibrated. The equation of state models used in process (and reservoir) simulators cannot be expected to be 100% accurate. Therefore it is essential to calibrate them with measured data (see report EP 88-2515).

For oils this should include a separation train experiment at likely process separation conditions culminating in a flash to stock tank conditions. The GOR should be reported at each separation and an analysis of the separator gas to C8 will also be required. Bubble point of the original reservoir fluid is also required.

For gases and condensates a similar separation train experiment is required along with the same gas analyses and stock tank fluid properties. In addition, 3 dewpoint temperatures across the likely process pressures are required to calibrate phase behaviour models near the phase boundary.

Other standard PVT experiments that will be required for reservoir engineering purposes also provide useful calibration data for phase behaviour models.

- standard non hydrocarbon analysis, including nitrogen, carbon dioxide and hydrogen sulphide.

Where a new field of unknown quality is being developed, where gas, with or without treatment is to be supplied to an NGL, LNG or chemical plant or where known downstream quality requirements make it desirable to do so, the following components should also be analyzed for :

- helium and hydrogen, to check whether there is a potential commercial yield, and
- trace components in gases: (eg. mercaptans, thiophenes, carbonyl sulphide, polyaromatics, mercury, radon 222 and polonium 210). Although the respective amounts of trace components are not usually included in process calculations, a fore knowledge of the presence or otherwise of any such components in the well stream is important because of the impact that this could have on downstream process facilities. **Sulphur** compounds are frequently toxic to humans and also poison catalysts in downstream processes. **Radon** tends to accumulate in those streams (product or otherwise) in which propane is concentrated, and in this way radon levels (and therefore associated radiation levels) in propane rich streams can be higher by a factor of 20-100 compared with the level in the feed. **Polonium** may become concentrated in the heavy ends of any condensate recovered from the gas and can become further concentrated through deposition in fractionating units. **Mercury** is not only highly toxic but also forms amalgams with aluminium and so causes effective corrosion of aluminium equipment such as low temperature heat exchangers. An analysis for **polyaromatic** compounds in crude may also be required as an input to an environmental impact study.

Because of the variety of circumstances, it is not practical to state maximum allowable levels for trace components. However a knowledge of the absolute levels of these components will allow the necessity for additional treatment (eg guard beds) prior to sales or further processing (eg. liquefaction) to be assessed.

- water/oil emulsion properties (see report EP 89-0150)
- total sulphur content of condensates and crudes.
- Kinematic viscosity of crudes and condensates at likely ranges of process and pipeline pressures and temperatures. Viscosity should always be determined at a minimum of at least two temperatures chosen to be representative of future (pipeline) transport conditions.
- Dynamic Viscosities of crude at a range of temperatures and shear rates. These should correspond with likely (pipeline) transport conditions.
- Minimum and maximum pour points (ASTM D 97).
- Total chlorides (as NaCl). It should be noted that salt content is not an intrinsic property of crude oil but is dependent on the salinity of water produced with the oil



and the effectiveness of the dehydration process prior to sampling. Knowledge of salt content in a crude sample will however be indicative of the requirement for further (better) dehydration or processing.

- Heavy metal content (eg. iron, vanadium or nickel) in the crude.
- TAN

## 2.7. DATA REQUIREMENTS FOR RESERVOIR STUDIES:

Analytical requirements for reservoir studies depend very much on the type of fluid and the anticipated recovery mechanism for the reservoir in question. All studies will require a (re-combined) reservoir fluid composition with hydrocarbon detail up to at least C7+ and including common non hydrocarbons (nitrogen, carbon dioxide, hydrogen sulphide, hydrogen). In view of the increasing use of compositional reservoir simulators and the fact that data requirements for reservoir studies should generally be combined with process engineering requirements, a more detailed analysis to C16 will normally be required (see 2.6 ). Most studies will also require a "constant composition expansion" ("flash") test to determine the phase behaviour of the fluid over a wide pressure range at reservoir temperature. All studies will also require one, two or even three stage separation tests at possible processing conditions and culminating at stock tank conditions to provide an experimental basis for recoverable fluid volumes and properties.

The following sections (2.7.1, 2.7.2, 2.7.3) attempt to categorise the reservoir engineering data requirements according to fluid GOR and density. However saturation pressure will also have a bearing on the requirements so that the following should be used as a guideline minimum only.

### 2.7.1. Medium and Heavy Oil Reservoirs

The recommended minimum data requirement for medium and heavy oil reservoirs (GOR up to  $150 \text{ m}^3/\text{m}^3$ ; 8 - 35 API) is:

- a constant composition expansion test at reservoir temperature from about 10% above bubble point pressure reducing pressure in stages until the total volume is about twice the bubble point volume. This will determine the bubble point, the under saturated oil compressibility and the oil density above bubble point.
- A differential liberation experiment at reservoir temperature to produce relative oil and gas volumes, oil and gas densities, solution gas oil ratios and compressibility factors at the various pressures.

**Note:** For very low GOR reservoirs (less than  $10 \text{ m}^3/\text{m}^3$ ) bubble point pressures may be so low that a differential liberation experiment could be meaningless since the reservoir will never see pressures below bubble point.

- At least one flash of bubble point fluid to separator conditions and then a flash of separator liquid to stock tank conditions to give separator shrinkage factors and the total gas oil ratio. This should report gas compositions and Molar Mass (Relative Molecular Mass - Molecular Weight), density and composition for the stock tank liquid.
- Oil viscosity determination over a range of pressure at reservoir temperature.

### 2.7.2. Light Oil Reservoirs

The recommended minimum data requirement for light oil reservoirs (GOR up to  $350 \text{ m}^3/\text{m}^3$ ; 35 - 45 API) is:

- Constant composition expansion as above
- a constant volume depletion with liquid volume and compositional analysis of the gas removed after each pressure reduction step .
- At least one flash from reservoir conditions to separator conditions with a subsequent flash of the separator liquid to stock tank conditions reporting gas composition and Molar Mass (Relative Molecular Mass - Molecular Weight), density and composition for the stock tank liquid.
- Viscosity determination as above.

### 2.7.3. Volatile Oil Reservoirs, Gas Condensate and Gas Reservoirs

The recommended minimum data requirement for volatile oil reservoirs (GOR >  $350 \text{ m}^3/\text{m}^3$ ; 50 API), gas condensate and gas reservoirs is:

- Constant composition expansion as above but usually will determine dew point at reservoir temperature.
- Constant volume depletion as above
- Separator tests as above
- Viscosity measurements as above

In certain special cases (eg. in the case of a gas injection project) measurement of gas/oil interfacial tensions at different pressure intervals together with experiments (eg "multiple contact", "rising bubble") determining miscibility between crude oil and injection gas may be needed. Report EP 91-0703 describes several more specialised experiments which have applicability in some circumstances.

### 3. SAMPLE COLLECTION

#### 3.1. LOCATION AND DESIGN OF SAMPLE POINTS.

DEP 31.38.01.11-Gen must be followed for the installation of sample points in process pipe work.

Sample points should be located close to a source of increased turbulence but must be located at least ten pipe diameters downstream from any bends. Sample points should be located in vertical pipe sections with upward flow.

Sample loops should be installed to allow purged fluids to be vented to the vent system or returned to the process. The sample vessel connection point should be as close as possible to the process line within the sample loop.

Sample points should be incorporated in production facilities during design. Installation of new sample points after the start of production will most often require a plant shut-down.

Likely sampling points in the process scheme where a knowledge of production stream composition will be useful include:

- at the well head
- Feed pipelines and inlet manifolds (but should be single phase flow or homogeneous two phase flow).
- Separator outlet gas lines (position sample point as close to separator as possible).
- Separator liquid outlet line. Samples should be taken at dedicated locations in piping leaving a vessel, not directly from a process vessel itself (to ensure maximum possible separation before sampling) however the sample point should be as close as practical to the vessel to minimise pressure drop and consequent flashing prior to sampling.
- Absorber and stabilizer inlet and outlet streams (gas and liquid).
- Compressor suction and interstage scrubbers.
- Metering runs for sales gas

note: the location of sample points must be carefully chosen not to interfere with the flow measurement taking into account the straight pipe length requirements of the primary flow elements).

- Custody transfer points

For streams which are *known* to be 100% single phase gas, samples can be taken from any convenient tapping at the well-head or in process flow lines (ie. without a sample "probe"). However it is generally difficult to guarantee that a stream will be 100% single phase and so such tappings will only rarely if ever be used. Wall tappings are also susceptible to plugging with produced debris.

Pipeline wall tappings should not be used when there is any possibility of two phases present since there is the possibility of segregation which will lead to non representative sampling.

For those gases which may be classified as 'dry' but in reality are produced with small amounts of condensate or water in the well stream, samples should be taken from a centre stream probe (see figure 1.) at a turbulent point to ensure thorough mixing of the flowing phases. An iso-kinetic upstream facing probe is recommended. Sample probe diameter should be such as to allow iso-kinetic sampling at design flow rates. The sample taken will be iso-kinetic when the probe entry dimension is sized such that the gas velocities in the flow line and probe entry do not differ by more than 30%. Figure 2. indicates the discrepancies in measured gas/liquid ratios that can occur for a homogeneous two phase (low LGR:  $\pm 100\text{m}^3/\text{std m}^3$ ) fluid if the sample is not taken iso-kinetically.

Sampling from two phase flow systems (gas/oil or oil/water), whether from well streams, flow lines or other streams, is considerably more difficult than from single phase systems. If samples are to be representative then the two phases must be either homogenised or sampled separately (ie using a separator). Heterogeneous flow patterns such as annular, stratified or slug flow cannot be sampled directly using a centre stream probe (or any other kind of probe) without prior mixing of the two phases. Consideration must be given to the use of a mixing device although these flow regimes will still be difficult to mix properly. The representivity of samples taken from two phase lines must be considered to be significantly lower than that from single phase lines even with all precautions taken to ensure best possible sample point location and design. The reliability of such samples may be improved by taking multiple samples over a period of time.

For further suggestions on the location and design of sample points for the collection of samples from inhomogeneous mixtures in pipelines see ISO 3171.

Specific procedures for sampling of oil/water mixtures (primarily for the determination of emulsion properties) are dealt with in detail in section 3.3 of report EP 89-0150 and will not be repeated here. However sample points for oil/water mixtures should normally comprise centre probes located in turbulent areas in vertical pipe.

### 3.2. VOLUME AND NUMBER OF SAMPLES REQUIRED

The volume of sample required depends on the purpose of the analysis for which it was taken.

The volume of sample required for each of the sampling purposes described in (2.1) above is summarized in Table 1 below:

Table 1.

Minimum number of samples and sample volumes required for various analyses

Sampling Purpose	Minimum Number of Samples Required	Minimum Volume Required for Analyses (Litres - per sample)			
		Crude	Condensate	Gas	Water
Preliminary Analysis	2	1	1	10	1
Identification Analysis	2	2	2	10	5
Evaluation Analysis (Refinery)	2	30	30	-	-
PVT Analysis (down hole samples)	3	0.6	-	-	-
PVT Analysis (Surface Samples)	3 liquid & 3 gas	0.6	0.6	20 - 60	-

The number of samples and respective volumes quoted in the table above are minimum requirements for the indicated analysis. Samples for any other purposes, e.g. compatibility tests, re-startability and pumpability tests of waxy and viscous crudes and dehydration tests, are not included. For these and other more specialized analyses the laboratory to carry out the analysis should be consulted prior to sampling to determine the volume they require.

Several duplicate samples of gas and liquid are normally taken during each flow period in a well test. Following sample validation in the laboratory, the samples considered to be most representative can then be used for the subsequent PVT measurements. A minimum of 3 PVT samples from a well test is stipulated above so that at least 2 sets may be sent to the analysing laboratory while one set is retained at the OPCO in case of loss or damage during transport.

Local regulations also specify a certain number or minimum volume of samples to be taken in particular circumstances. Third parties may also be entitled to fluid samples.

With crude oils with high gas/oil ratios larger volumes of separator gas may be required in order to have sufficient gas to enable recombination according to the measured separator gas/oil ratio to the requisite volume for analysis.

It is generally advisable that a set of samples is retained in the Opco when samples are sent outside for analysis in case the originals are lost or damaged in transit. For this reason, transporting duplicate samples together should also be avoided.

If water is produced during a well test then at least 0.5L should be retained for production chemistry and petrophysical purposes.

### 3.3. TRANSPORT OF SAMPLES

Classified dangerous goods (eg hydrocarbon samples) can only be accepted for transport as air freight if they are packed in accordance with the Dangerous Goods Regulations as per IATA publications (current edition). Under these regulations only UN certified packaging must be used.

The IATA regulations will also prevent samples from being transported on certain aircraft. The current edition should be referred to for details.

Regulations for the transport of dangerous goods by road vary from location to location. However, suffice it to say that all local regulations must be adhered to and, at a minimum, sample containers must be packed (usually in wooden boxes) so that they, and any valves etc. attached to them, are adequately protected from physical damage. Sample bottles and packaging must be labelled with appropriate warnings on the hazardous nature of the contents according to local regulations. If no local regulations exist, the IATA regulations may be used as a guide-line.

Samples should not be transported in public transport.

If transported by road, samples must be in a separate compartment from the driver and may not be transported in the luggage compartment of a saloon car (leaking gas could enter the driver's compartment).

Samples transported by sea should be packed and labelled according to the latest IMDG instructions.

In many areas official documentation and labelling will need to be completed and transported with the samples (eg. "Transport of Dangerous Goods Declaration").

### 3.4. SAMPLING METHODS GENERAL

The method by which a sample is to be collected is dependent upon the fluid type (gas or oil) and the purpose for which the sample is to be collected. The following sections (3.5, 3.6, 3.7) are therefore partitioned accordingly. The sample collection methods recommended in these sections are summarised in Appendix 1.

During all sampling operations all local permit to work procedures and employee certification (hydrogen sulphide etc.) must be adhered to. All individuals involved must clearly understand the procedures and the potential risks involved prior to participating in the sampling exercise.

### 3.5. SAMPLING HYDROCARBON LIQUIDS

#### 3.5.1. Sampling Methods for Hydrocarbon Liquids for Preliminary Analysis, Evaluation Purposes, Process Monitoring or Custody transfer

Crude oils sampled (manually) for a preliminary analysis, for evaluation purposes, or custody transfer must be sampled according to ISO 3170. This international standard applies to the manual sampling of liquid petroleum products, crude oils or intermediate products which are stored in tanks at or near atmospheric pressure or transferred by pipelines and are handled as liquids at temperatures from near ambient up to 100 °C . It contains the specifications for suitable sample containers along with procedures for sampling from tanks and pipelines. It does not cover sampling of liquids with RVP greater than 180 kPa.

Sampling of glycols at low pressures must also apply ISO 3170.

ISO 3170 contains a section dealing with safety precautions, however the reader is referred to report EP 55000 section 32, particularly for reference to the dangers of hydrogen sulphide .

ISO 3170 refers to ISO 3171 for advice on sampling inhomogeneous mixtures (eg. flow line sampling). However refer to (3.1) for comments on reduced reliability when sampling multi-phase systems.

Because ISO 3170 does not seek to entirely prevent lighter fractions evaporating from the sample during the sampling process, it is not suitable to take samples for compositional analysis in aid of process design or reservoir modelling. Neither is it suitable for sampling liquefied petroleum gases (ie mixtures of propane and butanes - see (3.6)).

Sampling of crude/water mixtures at low pressures for dehydration and de-oiling performance monitoring can normally be carried out according to ISO 3170 if the testing is to be carried out on site (eg. emulsion settling tests for observing demulsifier performance). However if the sample is to be transported to the laboratory then it is better collected according to (3.5.2) in order to prevent oxidation of the crude. In any event every effort must be expended to ensure that contact of the sample with air is minimised. See report 89-0150 for a more detailed description of the practices and precautions when sampling

crude/water mixtures for dehydration/de-oiling tests.

### 3.5.2. Sampling Liquids for Process Design and PVT Analysis

Manual sampling of hydrocarbon liquids for compositional analysis should be carried out using only mercury free floating piston type samplers. Earlier methods used in Shell have involved displacing an inert liquid (usually mercury) from a sample bomb. However health hazards associated with mercury have led to the use of improved samplers (floating piston type) in Group operations. In some areas the displacement of aqueous fluids (eg. acidified brine, aqueous glycol) from sample bombs has also been employed. However recent experience with chloride stress cracking in sample bombs after using acidified brine has led to the current recommendation for the use of only floating piston type samplers.

Appendix 2 describes the sampling procedure.

### 3.6. SAMPLING LIQUEFIED PETROLEUM GASES

Liquefied petroleum gases should be sampled according to ISO 4257 which is suitable for obtaining representative samples for all standard specification tests (ASTM D 1835) on LPG's apart from compositional analysis.

### 3.7. SAMPLING HYDROCARBON GASES

#### 3.7.1. Sampling Methods for Hydrocarbon Gases for Preliminary Analysis, Process Monitoring or Custody Transfer.

Hydrocarbon gases sampled for preliminary analysis, process monitoring or custody transfer must be sampled following GPA standard 2166 section 7.1 by the "Purge and Fill Method". By this procedure the sample container is repeatedly filled then emptied using the gas to be sampled. GPA 2166 details the required number of purge fill cycles depending on sampling pressure.

Care must be taken to ensure that sample depressurisation is sufficiently slow to avoid condensation and consequent build up of heavy ends in the sample container. The sampling line and cylinder must be kept at a temperature which is at least equal to but preferably slightly higher than the temperature of the gas being sampled while sampling is taking place. In order to avoid condensation forming in the cylinder or its connecting line, any pressure drop across the sampling system should be minimal. Note that GPA 2166 calls for the use of an extension tube between the final valve and the cylinder so that the pressure drop is taken some distance away from the cylinder. GPA 2166 also gives relevant precautions on the use of heat tracing on sample lines and cylinders.

GPA 2166 recommends the use of a "sample line separator" to remove any liquids from the sample upstream of the sample container. This recommendation is **only** supported if it is only the gas that is required to be collected (ie. no entrained liquid). If a representative sample of the **total** process stream is required then a sample line separator should **not** be used.

GPA 2166 is adequate for samples for which a simple analysis only is required (eg. density, hydrocarbon composition C1 - C8, Nitrogen, carbon dioxide) or for more detailed

analysis of gas streams that are *known* to be dry.

This method of sampling may also be used for custody transfer when the contract is based on light components in dry gas (ie C1 - C8).

The "evacuated container method" detailed in GPA 2166 may also be considered but is limited (by GPA) to sampling pressures below 7590 kPa(g) (1100 psig) . Samples collected by this method must be corrected for air contamination since containers will never be completely evacuated prior to sampling. This correction will involve separate analysis for oxygen. The evacuated cylinder method may be the only practical method of sampling if no safe means can be found to vent purge gas (eg. for high hydrogen sulphide content gases).

Additional points to note:

- Sample containers should be constructed to ASME section VIII division 2 in either AISI 316 or AISI 304 stainless steel and appropriately pressure rated for the planned sampling conditions. They must also have been tested to 1.5 times rated pressure or according to local regulations whichever the most stringent.
- Sample containers should be cleaned in advance according to the procedure described in Appendix 3.
- AISI 316 or AISI 304 stainless steel are still not completely inert so cannot be used when accurate determination of hydrogen sulphide in the laboratory is required. Coated cylinders (teflon) are available but these also absorb hydrogen sulphide to a certain extent.

Samples taken for trace sulphur analysis with hydrogen sulphide levels less than 50 mg/m<sup>3</sup> should be taken in salinized glass containers (with obvious regard for reduced pressure rating). However analysis for low levels of hydrogen sulphide should normally be carried out in the field (see 4.10.5.).

- The cylinder valves should be soft seated in preference to the metal seated variety.

It is possible to use single valve cylinders which have been evacuated prior to sampling but the recommended method is to use two valve cylinders.

- Care should be taken to ensure that the cylinder is held upright and the outlet valve is pointing downwards.
- The purged gas must be vented to a flare or to a well ventilated safe area. If the hydrogen sulphide concentration of the gas being sampled may be greater than 50mg/m<sup>3</sup>, then breathing apparatus must be worn and an observer acting as a safety standby must be in place a safe distance from the sampling operation. (see Shell standard EP 55000-32)
- The sampling temperature must always be recorded together with other relevant parameters. Then, when the sample is to be analyzed in the laboratory, the cylinder must be heated to 90 °C or at least 10 °C above the sampling temperature using a convective type oven and conditioned at this temperature for 24 hr prior to analysis (ref ISO 6975). Care should be taken that heating the cylinder will not cause over pressure of the vessel.



### 3.7.2. Sampling Methods for Hydrocarbon Gases for Evaluation, PVT Analysis, Process Design

#### 3.7.2.1. Conventional Sampling

The conventional gas sampling method (from GPA 2166) described in (3.7.1) can usually also be employed for evaluation, reservoir studies or process design if the chemical nature of the heavier hydrocarbons (C7+) in the gas is unlikely to influence the study for which the analysis is carried out (eg. gas sample from a low GOR oil well test where the chemical nature of the C7+ fraction in the gas can be inferred from the C7+ fraction in the oil). It is also acceptable for sampling of streams *known* to be above their dew points.

The quantity of heavier components in a gas sample taken according to (3.7.1) however will usually be insufficient to allow a full characterisation of these components. With chromatographic techniques the composition of the heavy fraction can be established, but these techniques cannot establish the physical properties (ie. molar mass, relative density) which are generally required as input for phase behaviour prediction computer programs. The nature of these heavy ends has a significant influence on the phase behaviour of the gas stream (see report EP 88-2515).

The use of GCMS techniques could potentially provide sufficient information for characterising the small quantities of heavy ends in a gas sample for use in phase behaviour prediction programs (mole fractions, relative molar masses and boiling point equivalents). However these techniques have yet to be widely applied in our operations.

#### 3.7.2.2. Split Phase Sampling

In order to be able to carry out a more detailed analysis of heavy ends in rich gas streams, Thornton Research Centre developed a split phase sampling method in the late 1970s. The method is based around the controlled phase separation and subsequent analysis of a representative side stream iso-kinetically removed from the stream being sampled. The principle advantages of the method lie in the fact that it does not rely on efficient separation and metering of streams in process separators and also that it allows phase separations to be made at reduced temperatures so as to provide sufficient liquid sample for subsequent analysis. Standard (well test) separators have been demonstrated to be highly inefficient when separating volatile oils and gas condensates at higher flow rates. These inefficiencies compound metering problems and lead to inaccurate recombination ratios being used to generate separator feed stream compositions. (see Appendix 4 for a detailed discussion of the split phase sampling method and its limitations)

Although the mixing device used in the TRC sampling manifold has recently been shown to be unreliable at lower flow rates, the TRC developed method (now marketed by PETROTECH AS of Norway) remains the best available method for sampling gas gas/condensate well or process streams. The technique is therefore recommended when the analyses from samples taken from such streams are to be used as the basis for reservoir studies and/or process design.

#### 3.7.2.3. Iso-Kinetic Separator Sampling

A method using iso-kinetic sampling of the gas out from the well test separator has recently been demonstrated to offer improvements over standard separator sampling in that it provides a means to correct for liquid carry over. The method has been applied to well test sampling but could also be applied to sampling around general process separators. See (3.8.4.2) for a more complete description of this method.

### 3.8. SAMPLING DURING WELL TEST OPERATIONS

For sampling purposes a well stream can often be looked upon in much the same way as any other stream in which case the appropriate rules in the various other parts of this section would apply.

However, some aspects of well stream sampling cause the subject to warrant special attention in this document. In some circumstances, the collection of fluid samples down hole is a viable alternative to collecting samples from surface flow lines or separators and therefore deserves discussion. Conditioning of the well prior to sampling and the production rate during sampling also have a major influence on how representative of the original reservoir fluid the samples taken will be. Planning well testing and the well conditioning operation are therefore highlighted as separate issues in the discussion that follows.

#### 3.8.1. Planning Well testing

Sampling is one of the more important reasons for carrying out a well test and, as such, should always be subject to appropriate planning prior to testing and should never be glossed over as being simply "routine".

In order to obtain a representative data on the initial reservoir fluid it is important to take an adequate quantity of good samples during the exploration and appraisal stages of the life of a field before significant production has occurred. Samples taken after the field has been producing may be misleading as a result of possible phase changes through pressure depletion throughout the reservoir and, especially, around the well bore. There will never be a better opportunity for taking representative samples than in the initial exploration/appraisal wells. Indeed, this may be the only opportunity.

Incorporating sample requirements into an overall test design can generate conflicts. The resolution of such conflicts will depend on the main objectives of the test. The main areas of conflict are related to the length of perforation interval and to tubing size.

From the point of view of sampling, account must be taken of the possibility that, with long hydrocarbon fluid columns, there may be significant variations in reservoir fluid properties and composition with depth. This may dictate that only limited intervals are perforated, and in addition may require several discrete intervals to be tested. However, if productivity testing is the prime concern, a restriction on the length of the perforated interval may not always be feasible in low permeability reservoirs. A productivity test may also require more complete perforation to avoid complications in reservoir analysis as a result of partial penetration of the reservoir thickness.

High flow rates are often required to determine, for example, non Darcy effects (although this is not critical as long as the multi rate test includes a significant variation in flow rates). High flow rates will in general require large tubing diameters. However large tubing at the low flow rates required for sampling may induce unstable flow as a result of slip of produced liquids. From the sampling viewpoint the tubing diameter should be as small as practicable.

It is recommended that the conditions that are likely to provide stable tubing flow are calculated before the test takes place. This can be estimated roughly for a range of possible well conditions, using in house computer programmes such as WIPCO/WIPCOG or the new ICEPE well performance simulator to generate a set of curves of well-head pressure against flow rate for the main parameters of GOR, water cut, inflow performance

etc. This will necessitate using whatever prior information is available on the properties of the well stream or by making assumptions of these properties (covering a suitable range). The predicted results can be checked during the actual test and can be corrected if and when more reliable data on the well stream's properties are available.

A large draw-down may be desirable to help clean up mechanical skin so as to give a satisfactory indication of well productivity. However, for sampling purposes, draw-down should be kept to a minimum to limit the possibility of phase changes in reservoir fluids near the bore hole (ie. if possible do not produce with bottom hole pressures below saturation pressure prior to sampling). It therefore may be desirable to carry out two clean ups; one for sampling and a second to remove mechanical damage.

Ideally both sampling operations and well flow rate tests should be carried out before any significant volume of fluid has been produced from the well. The analysis of fixed rate or multi-rate flow tests is complicated by prior production while production of well bore fluids (particularly with high draw-downs) may result in phase changes in the reservoir near the well bore which could result in non representative samples being collected or at least extended well conditioning periods being required.

In general the effect of prior production on reservoir analysis from well tests can be compensated for (as long as production details are known) so that sampling should take priority and should be carried out before any other tests in the well test programme. A typical test program should therefore consist of a short high rate clean up period followed by a shut in period so that pressures go back to original and then low rate well conditioning (see 3.8.2) and sampling.

### 3.8.2. Well conditioning

**API RP 44** contains a thorough description of well conditioning operations and should be followed in detail. The most pertinent aspects of the API practice are summarized below in order to improve the readers understanding of good well conditioning practices and the need for well conditioning.

The following paragraphs have been written to specifically refer to sampling during production testing of a new well. Well conditioning to produce original reservoir fluid from a well that has been in production below saturation pressure for some time is not possible.

Well clean up should be as short as possible. Mud, sea-water and spent acid, if any, must be produced out of the well bore before sampling but the well should be sampled before any significant production of reservoir fluids has occurred. The volume of production prior to sampling is always a compromise between minimising hydrocarbon withdrawal and ensuring that any fluid which may contaminate the sample has been removed.

The objective of well conditioning is to replace the non representative fluid (created as a result of phase changes through pressure reduction during clean-up) located around the well bore by displacing with original fluid from more distant parts of the reservoir. Simply shutting in the well to restore the pressure around the well bore will not return the fluid in the affected area to its original condition or composition. It will be necessary to flow the well at its minimum stable rate (determined by a series of step wise flow reductions) to allow the altered fluid to be displaced by unaffected fluid.

It is essential that production is stable prior to and during sampling. Unstable production will result when the rate is too low to lift all liquids continuously to the surface. Liquid hold up results in the well slugging and can only be eliminated by either increasing the production rate or reducing the tubing size.

Some criteria by which to judge whether a well may be producing at constant composition are as follows :

- Stabilization of FTHT and FTHP at constant flow rate may go parallel with the stabilizing of the composition.
- Stabilization of the fraction of the light hydrocarbon components of the gas at a fixed temperature and pressure (portable analytical equipment is required at the well site).
- Stabilization of the GLR measured at the test separator may give an indication of well stream stability. However it should be remembered that such a separation is a bulk process and small changes in well stream composition which may be significant from an analytical viewpoint, may not be readily apparent at the separator. Sufficient time must elapse for condensate levels, etc. to build up and be recorded. If separator GOR is to be used as a stability indicator, then it should be used in conjunction with one of other criteria described above.
- Stabilisation of hydrogen sulphide or carbon dioxide content
- Stabilisation of water composition

Considerable time (days!) is sometimes required to accomplish acceptable well conditioning. Sufficient time should be allowed in the test program to ensure that the well is stable and producing as representative fluid as possible. Little advantage would be gained if, in order to save a few hours of testing time, the sampling operations were carried out on an unstable well and the data obtained as the basis for project design or reservoir modelling were either faulty or inadequate. **Sub optimum reservoir development or the installation of inappropriate production facilities will always be more expensive than a few hours rig time.**

### 3.8.3. Subsurface sampling

#### 3.8.3.1. Open Hole Samplers

Open hole sampling tools (eg Schlumberger's Repeat Formation Tester - RFT) can be useful for obtaining a sample for preliminary analysis (eg confirming the presence and type of movable hydrocarbons). However these tools cannot be relied upon to provide samples for more detailed analysis. Samples are almost always contaminated with drilling fluids and are limited in volume. Most often a high draw-down will be required to flow through formations damaged by drilling. The high draw-down will result in flashing of the sample during sampling (ie gas break out in the reservoir) and produce an unrepresentative sample.

Schlumberger have attempted to overcome these limitations somewhat with the introduction of their Modular Formation Dynamics Tester (MDT) which allows controlled draw-down sampling and permits multiple sample chambers in the same tool string. The MDT also allows continuous flushing of the reservoir fluid through the tool which permits clean-up prior to capturing the sample. However experience to date with the MDT in Group operations is insufficient to base a general recommendation on its reliability and usefulness. Initial use has shown teething troubles.. In addition, well control implications of flowing reservoir fluid into the well-bore through a wire-line tool warrant careful consideration.

Schlumberger are also developing techniques (density and optical) for determining the

nature (oil/water/gas) of the sample during the sampling operation with the MDT down hole.

Other service companies are also introducing controlled draw-down samplers of different descriptions.

### 3.8.3.2. Cased Hole samplers

Cased hole subsurface PVT sampling has had the reputation of being somewhat unreliable because sampling tools were prone to failure and to leakage. However sampling tools are now more reliable and, in certain circumstances can be used more cheaply and efficiently than surface sampling in order to collect what may be a more representative sample.

Bottom hole sampling has the advantage of avoiding the necessity to separately meter then re-combine separator fluids with all the potential errors involved in that process. If the sample is kept at reservoir pressure then asphaltic or other heavy compounds which may precipitate with pressure reduction can often be kept in solution (Due to temperature reduction as the sampler is recovered the pressure in a standard bottom hole sampler decreases. However there are a number of samplers now available that have a pre-pressurized chamber that maintains reservoir pressure as the tool is removed ). Subsurface sampling will also make it easier to determine the presence or significance of compositional gradients. The technique however also has a number of serious disadvantages:

- The technique can only be used for sampling fluids that are single phase liquids at the sampling depth. It is not possible to gather a representative sample from a two phase fluid.

For gas samples, temperature changes in bringing the sample to surface may result in phase separation and so careful conditioning by heating, pressuring and agitation will be necessary before transferring into the transport container. This process can take several hours and there is always the risk that if the sample has not been completely reconditioned to single phase it will no longer be representative after the transfer.

- Most sampling tools rely on differential pressure from high sample pressures for sealing. Experience in high GOR gas/condensate wells has shown that loss of pressure differential in the tool as a result of cooling while coming to surface has sometimes resulted in the loss of sample.
- Problems have also been experienced due to the presence of solids (fines) being trapped between the valve and the seat in the sampling tool resulting in a loss of sample. Damage to sealing "O" rings due to corrosive fluids (hydrogen sulphide, carbon dioxide) is also a cause of leakage.
- Subsurface samples are generally limited to a volume of 0.6 L which is often insufficient for performing the required PVT experiments. This can be overcome to a certain extent by taking several samples however subsurface sampling a gas reservoir is unlikely to result in sufficient "heavy ends" to enable a satisfactory analysis for process design purposes.
- The contents of a subsurface sample may depend on the precise depth and time at which it was taken. Small variations in the producing composition are averaged out when sampling from a surface separator but are not when taking a 0.6 L sample at depth. This can have benefits as well as disadvantages since it allows selective sampling from different depths to be used to gauge composition variation with depth.

Bottom hole samplers can be run on electric wire line or on slick line. Frequently the sampling tool will be the same in either case with only the activating mechanisms differing. The slick line tools are most often controlled via a clock mechanism which activates the sampler to take a sample at a pre-programmed time. Electric line tools allow the time of sampling to be determined by the operator from surface.

The waiting time associated with clock controlled slick line tools is usually balanced by the extra time involved with rigging up electric wire line operations. Choice of method could then determined by tool rentals or by the operations preceding the sampling operation which may allow rigging down and rigging up for the different type of wire line operation to be avoided. However electric line sampling operations are generally considered to be more successful than slick line sampling. Electric line operations also offer more flexibility in terms of when the sample is taken thus allowing optimum conditions to be chosen.

Modern bottom hole samplers also utilise a positive displacement mechanism which allows a sample to be taken at a closely control rate thus eliminating the possibility of flashing as the sample is taken.

A bottom hole pressure gauge should be run with any sampling tool to record the exact sampling pressure at the time of sampling. Electric samplers can be run in conjunction with tools giving surface read out of pressure, temperature and density for monitoring sampling conditions. At least a survey of pressure and temperature is required during sampling operations.

Report EP 87-1006 must be followed for detailed procedures and policies related to wire line operations.

A minimum of three bottom hole samples should always be obtained so that duplicate samples can be shipped to the laboratory for validation purposes so as to provide one good sample if one container leaks during transit. The third sample should be retained in the Opc. While sampling tools can be run in tandem, duplicate samples should not be taken from the same run since both samples could easily be taken from the wrong depth (for example). It is also not recommended to transport duplicate samples together if at all practical.

Samples should always be checked for consistency at the well site by demonstrating a reproducible bubble point in successive samples (see Appendix 5. for procedures for determining bubble point at the well site). The samples are usually considered to be duplicates if the saturation pressures agree to within 2%. The agreement in pressure is generally accepted as reasonable proof that the samples are representative. The data collected prior to and during sampling will often permit the saturation pressure of the sample to be estimated. If the samples exhibit bubble point pressures substantially different from the estimated pressure, the sampling operation should be reviewed and additional samples taken.

#### 3.8.4. Surface Sampling

The surface sampling method is generally the preferred approach for nearly all types of reservoir fluids with the exception of under saturated oils.

##### 3.8.4.1. Single Phase Surface Sampling

If the fluid at the well head is *known* to be single phase then surface sampling can often be simplified and a gas or liquid sample can be taken from any convenient sample point at the well-head. The procedures for sampling single phase *well* streams are then the same as

those described in (3.5.2) for liquids or (3.7.2) for gases.

The single phase sampling procedure may be applied for gases when the gas is *known* to be very lean (i.e. containing only traces of hydrocarbons heavier than C6, the nature of which is not significant for the purpose for which the sample is taken). Alternatively, it may be applied for gases that, while not necessarily very lean, are known to be flowing in virtually single-phase and for which a rapid and not too accurate analysis of the C1 to C8 components is required (eg. for well production monitoring)

Single phase techniques for well-head sampling of hydrocarbon *liquids* should only be used if the liquid is well above bubble point pressure or for hydrocarbon streams which are mainly liquid and for which there is no interest in the very minor quantities of gas that may be present.

#### 3.8.4.2. Surface Sampling of Two Phase Well Streams

If the well-head fluid is not single phase then, conventionally, samples are taken from the gas and liquid outlets of a well-head separator (test separator) and re-combined. No reliable means has yet been demonstrated for sampling high liquid to gas ratio two phase fluids without separation.

#### *Conventional Separator (Recombination) Sampling*

The conventional two phase sampling technique (ie. recombination of gas and liquid samples from a separator) should be applied:

- for sampling low to moderate GOR oil streams (as long as the separator is operating well within its design range - see (3.8.4.3)).
- for sampling higher GOR oils or gas condensates where only a quick analysis is required (eg for production monitoring). These samples may be unsuitable for process design if very careful attention is not paid to metering around the separator and the separator is not well within its efficient operating range.

#### *Split Phase Sampling*

The alternative, less conventional, Thornton sampling method (described in (3.7.2) and Appendix 4) avoids problems associated with operation of a well test separator (carry over, metering etc) but should only be used for relatively low LGR fluids flowing at high velocities. It should be applied for sampling very high GOR oils or gas condensates for process design or detailed reservoir simulation or for sampling rich gas streams for which an accurate analysis is required.

#### *Iso-kinetic Sampling in the Well Test Separator Gas*

A method using iso-kinetic sampling of the gas out from the well test separator has recently been demonstrated to offer improvements over standard separator sampling. The method involves collecting two iso-kinetic samples. The first is collected with an upstream facing sample probe and the second with the sample probe facing down stream. It is assumed that the first sample will be representative of the entire stream (all liquid carry over is assumed to be evenly distributed as a fine mist) while the second sample will not contain any liquids so will be representative of the gas stream alone. Comparison of the two samples allows the liquid carry over to be estimated and the well stream GOR, and

therefore recombined fluid composition, corrected accordingly. This method has been demonstrated by PETROTECH to give consistent results to those obtained with the Thornton manifold. However, while it overcomes the problem of liquid carry over in the well test separator, it does not eliminate errors associated with metering around the separator(3.8.4.3, 3.8.4.4). The Thornton method therefore remains the preferred method for sampling gas or gas/condensate systems for process design or reservoir engineering data. The iso-kinetic method may however be used in conjunction with the Thornton method for verification purposes.

#### 3.8.4.3. Preparation of the Well Test Separator

The discussion below refers particularly to well test separators but can be applied to any separator, whether used for an exploration well test or in a existing facility.

Conventional surface sampling of two phase streams is only possible if reliable flow, pressure and temperature measurements of the separator inlet and outlet streams can be made.

The main causes of unreliable samples for recombination are as follows:

- liquid carry over into the gas stream, caused by
  - flow rates too high
  - inefficient separation
  - foaming
  - high separator levels
  - Blocked or holes in demister pads
- gas carry under into the liquid stream, caused by
  - flow rates too high
  - liquid level in separator too low or not correctly controlled
  - inefficient separation
- faulty gas metering, caused by
  - wrong range of meter
  - badly calibrated meter, pressure gauges and thermometers
  - carry over as above
  - use of wrong correlations for determining gas densities
- faulty liquid metering, caused by
  - wrong range of meter
  - badly calibrated meter and thermometers
  - carry under as above
- gas breakout downstream of the separator but upstream of the liquid meter through pressure reduction
- dirty sampling lines
- dirty sample containers

The most common type of separator used by the service companies for well testing is a



horizontal three phase vessel with internals, such as demisters pads, to minimize carry over of liquids entrained in the gas. Each separator will have a design capacity for liquid and for gas. The liquid capacity is largely dependent on the gas/liquid or liquid/liquid interfacial area whilst the gas capacity is largely dependent on pressure and, vessel cross sectional area available for gas flow and, of course, the vessel internals (see DEP 31.22.05.11-Gen and report EP 89-0150 for design rules for two and three phase separators). Service company estimates of separator capacity are frequently optimistic. A "typical" 42" ID portable well test separator operated at 10,000 kPa with "typical" gas and condensate densities will have a gas demisting capacity of less than 800,000 std m<sup>3</sup>/d. At lower operating pressures the gas capacity expressed in std m<sup>3</sup>/d will be significantly less. The same "typical" vessel with the same "typical" fluids separated at 500 kPa would have a capacity less than 200,000 m<sup>3</sup>/D.

The engineer responsible for the well test should obtain information from the service company on the dimensions and geometry of the separator and ensure that this information is used to calculate allowable flow rates over a range of operating pressures and gas/oil ratios. It should be kept in mind that both liquid and gas capacity need to be considered. If the well test separator is a 3 phase separator as most are, then it's capacity for free water knockout should also be checked (see report EP 89 0150).

It is recommended that the separator be operated at well below its maximum capacity to avoid carry over or carry under as discussed below. The process engineer can contribute to ensuring that separators used are appropriately designed for the flow rates expected during sampling and testing. The well test supervisor should also check to ensure that the separator has been adequately maintained and its internals and controls are in working order.

#### 3.8.4.4. Metering Around the Separator

The validity of most samples taken, and in particular gas and liquid samples taken for later recombination, are clearly dependent on good metering. The discussion below again refers particularly to metering around an exploration or appraisal well test separator but the statements made apply equally to metering of any streams to be sampled and re-combined or used in some other material balance in an existing facility.

Liquid hydrocarbon flows are nearly always measured by positive displacement meters or turbine meters. Both types of meters have a limited range for a specific size. Most testing companies can supply a range of different sizes of meters. The engineer responsible for the well test design should specify that the meters have a sufficient range to cover the flow rates that are likely to be encountered. The ranges for the meters supplied by the testing contractor should overlap. The meters should be calibrated before and after the test using a fluid with physical properties as close as practical to those of the fluid to be measured. Calibration records should be supplied to the operator. If a hydrocarbon fluid calibration is not available, at least a water calibration must be supplied by the contractor.

The separator liquid level should be high enough above the meter to ensure that no vaporization occurs in the meter. This is of course dependent on the length, size and configuration of the piping connecting the separator to the meter and upon the flow rate to the meter. It should be noted that usually only the liquid rate at the test separator conditions is measured but stock tank rates are often reported. Standard correlations are usually used for "shrinkage" in order to convert separator rates to stock tank. It is important that the actual rate measured at the test separator is reported along with the separator temperature, pressure and any "meter factors".

Accurate metering of very low liquid rates is difficult. In some cases better results can be obtained by measuring the liquid build up in the separator or in an atmospheric collection tank. In the latter case, it is necessary to flash a sample of the separator liquid to tank conditions in the laboratory in order to determine the shrinkage factor, i.e. the relationship between tank and separator liquid volumes. Further inaccuracies are therefore introduced by this method.

The difficulty in accurately measuring low liquid flows also applies to water meters, although an error in metering water will not usually have as serious a consequence as an error in metering the hydrocarbon liquids. For testing well streams with a low liquid content, it is important that the liquid levels for both water and hydrocarbon remain constant throughout the metering period. The liquid levels should be noted at the beginning and end of the sampling period and corrections made to the liquid throughput if the levels have changed.

Gas metering is potentially more straightforward than liquid metering though usually subject to at least as much error. Gas flow rates are almost always measured with orifice type meters. The meter instrumentation should be calibrated before the test. The orifice plate should be of the correct size to cover the expected range of gas flow and should be checked to ensure that it is clean, flat and free of nicks and burrs. Orifice plates can usually be easily removed for inspection with the system remaining under pressure in portable well test set-ups. There should be adequate straight runs of pipe upstream and downstream of the orifice. ISO 5167 should be followed for proper gas metering.

The gas gravity and compressibility factor affect gas measurement and are usually calculated from the observed gas specific gravity. After obtaining the gas analysis, the on site assumptions must be verified and a check made on the standard correlations used by the service companies in their flow calculations to ensure that they are suitable. Liquid carry over will obviously seriously disrupt the density component of the meter calibration.

It is a common fallacy that the accuracy of a measured GOR can be assessed by using a process simulation program to re-flash the re-combined feed composition at the separator conditions and then compare the predicted GOR with that used for the recombination. If a gas and liquid are in equilibrium at a certain pressure and temperature, then re-combining their compositions in **any** ratio and re-flashing at the equilibrium conditions should reproduce the same ratio at which they were re-combined. Thus simulated re-flashing a re-combined sample is no check on the recombination ratio.

Temperature and pressure measurements during well test sampling are also important. Firstly for the effect that they have upon the corrections for both liquid and gas measurement, but also because the correct temperature and pressure must be known to determine molar ratios for recombination of the gas and liquid samples in the laboratory. Pressure gauges should be calibrated before and after the test by using either a calibrated deadweight tester or master gauge. The thermometers and/or temperature recording devices should be likewise calibrated before and after the test.

### 3.9. SAMPLING FOR SAND

Sampling well effluent for sand may be required to monitor the sand production level of suspected sand producing wells. In many cases a threshold level is specified and remedial action will be taken if a well exceeds this critical level. In oil fields sampling for sand is frequently carried out in conjunction with water cut determination but techniques for quantitatively representative sampling for sand are not well developed. A critical aspect of this operation is to ensure that a representative sample of the flow is taken, especially in view of the very low concentrations that are looked for (5-15 pounds sand per thousand

barrels) and the fact that sand production may not be continuous.

In practice, samples taken for sand sampling are rarely representative. The samples are mostly taken from a tap off the flow line without taking precautions to ensure a representative sample. Hence sand cut measurements by sampling can only give a broad indication of the level of sand production. A possible exception to this involves sampling of low GOR, heavy, viscous crudes for sand where experience has indicated that representative samples can sometimes be taken from well head tapplings.

On line sand detection using intrusive or clamp on acoustic probes has been demonstrated to be feasible (e.g. Flopetrol Sandec) but, although the tools are commercially available, their true capabilities have not yet been fully established. The acoustic technique is only really valid for single phase streams and tools require continuous calibration. Only qualitative indications of sand production can be obtained so far.

Electrical resistance techniques are also currently being tested by number of Shell OPCO's. The basis of this method is the change in resistance of a probe inserted into the flow line as fine metallic strips in the probe are eroded by solids in the well stream. This has advantages since the probe (in principle) has no lower limit for sand detection, requires limited on site calibration and is suitable for multi-phase flow conditions.

Sand sampling and detection techniques are covered in more detail in chapter 5 of report EP 92-1150 .

## 4. ANALYTICAL METHODS

### 4.1. GENERAL

This section gives some background to the analytical methods that are recommended for obtaining the required data. Most of the analytical methods employed are covered by industry standards and if not, are detailed in in house standard methods. The standard methods to be applied for each required analysis are summarized in Appendix 1.

A more general discussion of some pertinent aspects of oil and gas analysis is given in the following paragraphs

### 4.2. FLUID PREPARATION

Transfer of a sample into or out of a transport container should always be carried out at pressure and temperature conditions at which it is present in single phase. For gas samples this should involve heating the sample vessels (both the transfer and receiving containers) to 90 °C or at least 10 °C above the sampling temperature for 24 hr prior to sample transfer (ref ISO 6975).

For liquids this will involve setting pressure at the original value during sampling. A check of the bubble point of the sample will ensure that it is in single phase.

There is always a risk that the sample will undergo a phase change during transport which is difficult if not impossible to reverse. Non-hydrocarbons (eg carbon dioxide, or sulphur compounds) or even some condensate may become absorbed onto container walls in a gas sample. Wax or other potential solid components may precipitate irreversibly in a liquid sample.

If wax precipitation is likely, additional precautions will be necessary prior to sample transfer. The sample container should be heated to above the inversion point (see 4.15.10) of the crude to ensure dissolution of all wax for the transfer. Care must be exercised to ensure that sample pressure does not exceed the container design pressure during heating.

### 4.3. GAS CHROMATOGRAPHY (GC) TECHNIQUES FOR COMPOSITIONAL ANALYSIS

#### 4.3.1. General

Gas chromatography has been used to establish the relative volumes of lighter hydrocarbon components in a fluid sample for many years. National and international standards organizations have therefore developed specifications for equipment and methods.

It should be noted that measurements using GC equipment give results in terms of mole percent. The sequencing of components by GC in most cases is in the order of boiling point. Heavier components (greater than C6) are normally grouped by carbon number (For example, all components detected after decane up to and including undecane will be designated C11 components). Correlations of Molar Mass with GC column residence time

are therefore frequently used to determine liquid sample molar mass and then to determine the molar rate of the liquid stream to be used in the recombination. The assumed molar mass for the carbon number grouping will therefore influence the calculated molar ratio for recombination. Different laboratories use different approaches - such as using the molar mass of the corresponding 1-alkane or using generalized petroleum fraction properties. The effect on the recombined well stream fluid composition is relatively minor but the use of these assumed properties for the heavier fractions is unacceptable in the final composition used for process design or reservoir development calculations. Engineers should therefore be confident that the properties reported for these fractions have been physically measured.

For gas and liquid samples taken from the outlets of test separator, the composition of the well fluid is normally obtained by mathematically re-combining the measured gas and liquid compositions in the molar proportions based on measured or derived molar masses, densities and the field measured GOR corrected for differences in meter factors as a result of using measured fluid properties rather than estimates.

Repeatability of GC measurements should be as follows:

fractions > 10% (mole/mole)	± 0.1% (relative)
fractions 1% - 10%	± 1%
fractions 0.1% - 1%	± 10%
fractions 0.01% - 0.1%	± 30%
fractions 0.001% - 0.01%	± 50%

#### 4.3.2. GC Determination of Components C1 - C8

For analysis of natural gases for inert components (including carbon dioxide and nitrogen) and hydrocarbons up to C8 the latest revision of ISO 6974 must be followed. The method can be readily adapted to report a C8+ fraction rather than octanes.

#### 4.3.3. Extended GC analysis (C4 - C16)

For extended analysis, up to C16, ISO 6975 must be followed. ISO 6975 requires the sample container to be heated to  $\pm 75$  C for 24 hr prior to analysis to ensure sample homogeneity (paragraph 7.1.4). The temperature should ideally at least 10 °C above the sampling temperature however the sample pressure should be closely monitored to ensure that the vessel pressure rating is not exceeded during the heating process.

The method can be readily adapted to report a C16+ fraction rather than C16.

Both ISO 6974 and ISO 6975 are currently (1992) under revision.

#### 4.3.4. Commercial Propane and Butane

For analysis of commercial propane and butane ISO 7941 is adequate but this is only intended for analysis up to and including pentanes in concentrations greater than 0.1% (m/m).

#### 4.4. MOLAR MASS (RELATIVE MOLECULAR MASS - MOLECULAR WEIGHT) MEASUREMENTS

##### 4.4.1. Molar Mass of liquids

Molar mass of liquids should be determined according to SMS 1346. The average molar mass of a sample is estimated from the freezing point depression of a benzene solution. The method claims repeatability of 3% (relative) of mean and reproducibility of 6% .

Notes: 1) using SMS 1346 a correction should be made for the benzene content of the sample.

2) Benzene is carcinogenic so all operations must be carried out in a fume hood so that vapours are not inhaled.

The method can only be applied to stable liquids at atmospheric pressure. Unstable liquids must first be flashed to atmospheric pressure. The flashed vapour must be measured then analysed by GC (4.3.2) and then the total molecular weight calculated by mathematical recombination.

For gasoline fractions the total evaporation method should be used (SMS 2294).

Measurement of molar mass of petroleum fractions in well equipped laboratories can now also be made using mass spectrometry in conjunction with gas chromatography (GCMS). However no standardised procedures exist for this.

##### 4.4.2. Molar Mass of Gases

Average molar mass of a gas sample is normally determined from an extended GC analysis (4.3.3). This implies a knowledge of the molar mass of all the heavier fractions which is unlikely to be available. However use of assumed molar masses is unlikely to significantly influence the accuracy of the calculation of the bulk molar mass.

#### 4.5. WATER CONTENT OF GAS

While water dew point is not a direct measurement of water content, it is frequently the most easily applied indicator of water in gas for field operations. ISO 6327 describes the recommended procedure for determining the water dew point of natural gases using a cooled surface condensation hygrometer.

Apparatus for determining water content of gas by measuring the change in resistance of a probe (frequently an aluminium oxide probe - eg from Panametrics) has also proved to be robust and reliable for field operations.

In the laboratory the water content should be determined via a Karl Fischer titration method. Use SMS 1329 for high pressure gas and SMS 1553 for atmospheric pressures.

#### 4.6. MEASUREMENT OF RELATIVE DENSITY OF A GAS SAMPLE

On site determination of gas relative density is made using a Schilling effusiometer according to IP 59 Method C . The method is based around the principle that the times taken for equal volumes of gases to flow through a small orifice under the same conditions

are proportional to the square root of the densities of the gases. This is adequate for preliminary analysis and process monitoring.

In the laboratory the density of a gas sample is calculated from its molar composition according to ISO 6976 although this implies a knowledge of properties of components heavier than C8 which is usually not available. The relative density for these heavier components is therefore assumed to be equal to that of a C8 hydrocarbon. They are rarely present in the gas to the extent that they will cause gross errors in bulk density of the gas.

#### 4.7. MEASUREMENT OF THE HYDROCARBON DEWPOINT OF NATURAL GAS

Determination of the Hydrocarbon dewpoint temperature of a natural gas sample in the field is made using the US Bureau of Mines dewpoint apparatus. This relies on visual observation of condensation on a cooled mirror.

**Note:** Distinguishing between hydrocarbon and water dew points is extremely difficult when these dew points are less than 8 °C apart.

In the laboratory, dew point pressure is determined at constant temperature by visual detection of the onset of liquid formation in a windowed PVT cell. No standardised procedures are known. Normally the pressure is reduced in small steps ( $\pm 300$  kPa) until the first drop of liquid is observed to form. The sample pressure is then raised above dewpoint and reduced again in finer steps ( $\pm 50$  kPa) in order to more precisely determine dewpoint.

**Note:** Some samples will form a finely dispersed mist at a pressure slightly above "dewpoint". This mist does not always form and even on the same sample does not always form at precisely the same pressure.

The ease at which the dewpoint can be detected is very much dependent on the sample. The repeatability of a dewpoint measurement is therefore estimated to be of the order of 100 to 300 kPa. If a depletion experiment is also carried on the sample (see 4.16.4) then the retrograde liquid volume curve may be extrapolated to zero liquid in order to help confirm the observed dewpoint measurement.

ISO 6570 describes a standardised procedure to determine the weight or volume of liquid which will be condensed from a gas sample at a specified pressure and temperature. This could be used iteratively to determine gas dewpoint but in itself already gives valuable information on phase behaviour of the gas being sampled. The method is applicable on-line or from a sample cylinder.

#### 4.8. GAS CALORIFIC VALUE

Calorific value can be measured directly with suitable equipment but the achievable accuracy is only 1-1.5%. Greater accuracy can be obtained by first determining the composition of the gas and then calculating the required property from the known composition and component basic data. This approach is strongly recommended, particularly where the gas sales contracts are written in terms of thermal content of the gas sold.

ISO 6976 must be used for calculating gas calorific value from the gas composition.

This method can however only be applied for compositions up to and including C8 since pure component data for only these components is provided in ISO 6976. Because of the

low concentration of components greater than C8, there will not normally be significant error introduced by assuming heating value of octane for C8+

#### 4.9. WOBBE INDEX OF A GAS SAMPLE

Wobbe index is defined as:

$$\text{Wobbe No.} = \frac{\text{Gross heating value}}{\sqrt{\text{gas relative density}}}$$

The GHV is determined according to (4.8) and relative density determined according to (4.6).

#### 4.10. DETERMINATION OF THE CONCENTRATION OF NON-HYDROCARBON COMPONENTS

##### 4.10.1. Helium

Gas samples may be analyzed for helium by GC according to ISO 6974 using nitrogen or argon as the carrier gas.

##### 4.10.2. Hydrogen

Gas samples may be analyzed for hydrogen by GC according to ISO 6974 using nitrogen or argon as the carrier gas.

##### 4.10.3. Nitrogen

Nitrogen in natural gas must be determined according to ISO 6974.

##### 4.10.4. Carbon Dioxide

In the field, carbon dioxide must be determined using stain tubes (eg. Draeger) according to the manufacturers instructions. Determination in the field is preferred.

In the laboratory carbon dioxide must be determined according to ISO 6974.

**Note:** Sample containers must be constructed from an inert material if carbon dioxide concentration is to be determined in the laboratory.

##### 4.10.5. Traces of Individual Sulphur Compounds in Gas

In the field stain tubes (eg. Draeger, Gastech etc.) can be reliably used to determine hydrogen sulphide and other sulphur compounds in concentrations from about 2% (m/m) down to very low levels. See the manufacturers instructions for the procedures involved and the ranges covered by the tubes available. Measurement in the field is much preferred over the significant additional complications involved in using inert sample containers (see note below) in order to analyse in the laboratory.

For sulphide concentrations above 2% (m/m) ISO 6326 should be used. ISO 6326 describes GC, potentiometric titration and combustion methods to be applied in



appropriate circumstances. The absorption of hydrogen sulphide and mercaptans into an alkaline solution with subsequent potentiometric titration (ISO 6326 Part 3 - similar to SMS 217) offers advantages over the other parts of ISO 6326 because the absorption step may be carried out in the field and the subsequent titration carried out in the laboratory. The method however has limitations on the ratios of hydrogen sulphide and mercaptans in the sample.

Other methods of sulphide determination which are currently in use in the Group include the Tutweiler method (Starch iodine titration method suitable for field laboratory application). However ISO 6326 is likely to be the most robust and universally applicable method available.

**Note:** Sample containers must be constructed from an inert material if hydrogen sulphide concentration in a gas sample is to be determined in the laboratory. Salinized glass containers have been used by some OPCO's but these carry obvious pressure limitations and require extra care.

#### 4.10.6. Mercury

The detection and analysis of mercury is complicated by the number of phases (gas, hydrocarbon liquid, water, glycols and sludges) in which mercury is found and by the different forms (free mercury, organic mercury compounds, inorganic mercury) in which mercury occurs.

TRC are currently (1992) completing a review of available techniques for analysis and are likely to conclude that the use of atomic fluorescence spectroscopy on liquid samples digested into aqueous solutions potentially offers a more reliable method for measuring total mercury concentrations (ie in all three forms) but does not allow any distinction between free mercury, organic mercury and inorganic mercury.

Various other Shell organisations are currently involved in the enhancement of analysis techniques for mercury in its various forms but a general approach is yet to be resolved.

The Production Engineering Association (PEA) is also presently organizing a joint industry project which will look at many aspects of the problem of mercury in the petroleum industry including analytical methods and HSE and corrosion implications.

##### 4.10.6.1. Mercury Content of Gas Streams

To determine mercury in gas, samples are passed through an adsorption tube in the field and then further analysed in the laboratory by desorption followed by cold vapour atomic absorption spectroscopy following ISO 6978 (equivalent to SMS 2555). The adsorption process must be carried out in the field because mercury will otherwise be lost into the walls of the sample vessel during transport.

The precise analysis method used depends upon the expected mercury concentration.

Greater than  $0.5 \mu\text{g}/\text{m}^3$  (ISO 6978 method A):

- Gas from the stream to be sampled is passed through a glass absorber vessel containing an acidified potassium permanganate solution. The volume of gas passed through the absorber is recorded by an accurate gas meter. The excess of the permanganate solution is then destroyed by a hydroxylamine hydrochloride solution and the mercuric ions are reduced by a stannous chloride solution to produce elemental mercury which is evaporated in a nitrogen stream. The nitrogen is passed through an absorption cell in a flameless atomic absorption spectrometer.

Less than  $0.5 \mu\text{g}/\text{m}^3$  (ISO 6978 method B):

- Gas is passed through a quartz absorber tube filled with silver lint which adsorbs the mercury present. For very low concentrations of mercury, the adsorber tube should be mounted in a high-pressure container so that gas at line or separator pressure can be used to reduce sampling time and to minimise the risk of erroneous results to adsorption of mercury into pressure let down valves and Joule Thompson effects.
- Mercury collected by this method is desorbed in the laboratory by a nitrogen stream passed through the heated tube then readsorbed onto gold lint to eliminate interference by hydrocarbons and finally analyzed by flameless atomic absorption spectroscopy.

#### 4.10.6.2. Mercury in Aqueous and Condensate Samples

The determination of mercury in aqueous sample and condensates must be carried out according to AMS-607 by mixing or boiling with potassium permanganate solution to digest the condensate/aqueous sample then analysis for elemental mercury by reduction with stannous chloride, nitrogen stripping and atomic absorption spectroscopy as described in ISO 6978 method A.

Errors due to variations in solution acidity, the presence of emulsifying agents, etc. are eliminated by the application of a standard addition/calibration technique.

Note: If gas and condensate samples are to be analyzed for total mercury, then the production water should also be so analyzed in order to provide the total mercury balance.

#### 4.10.7. Radioactive Elements

Gas samples to be analyzed for radon-222 must be transported in clean dry stainless steel cylinders and analyzed within 4 days of capturing the sample. The sample is analyzed by flushing the gas through the ionization chamber of an analyzer. The radon-222 activity is measured using an electrometer. AMS 743-2 describes the method that must be followed.

Clearly it will be better to analyse for radon-222 on site if at all possible.

The Polonium-210 (and Po-208) activities of condensate samples are determined according to AMS 780. Each sample is digested with a strong acid and the Po-210 thus extracted is plated on to a silver disc. The Po-210 activity is then measured with a photographic plate.

#### 4.11. MEASUREMENT OF GAS VISCOSITIES

No standardised method is available for the measurement of gas viscosities. Viscosities reported are most often calculated although development is on going to produce a viscometer capable of measuring gas (and liquid) viscosities at high pressures (see 4.16.5.)

#### 4.12. MEASUREMENT OF RELATIVE DENSITY OF A LIQUID SAMPLE.

Field measurements for identification purposes must be carried out according to ASTM D 1298. This is the standard test method for density, relative density (specific gravity), or API

gravity of crude petroleum and liquid petroleum products (RVP less than 179kPa) by the hydrometer method. This method is also suitable for the laboratory measurement of relative density of bulk crudes.

ASTM D 1298 allows measurement of relative density at convenient temperatures and then refers to standard petroleum measurement tables in ASTM D 1250 (equivalent to API D 2450 or IP 200/52 (81)) for conversion to standard temperature.

Repeatability of measurements carried out according to ASTM D 1298 is of the order of 0.0005 to 0.0006 (0.1 to 0.2 API) for transparent and opaque samples respectively. Reproducibility is of the order of 0.0012 to 0.0015 (0.3 to 0.5 API).

Measurement of density of petroleum fractions (where insufficient sample is available for measurement according to ASTM D 1298 ) should be carried out according to ASTM D 5002 by measuring the resonance frequency of an oscillating sample tube containing the fraction (a Mettler/Paar Model DMA45 or DMA46 digital density meter or equivalent). A volume of only 0.7 cm<sup>3</sup> is required. Repeatability and reproducibility with this method are 0.0001 and 0.0005 respectively for samples with relative density in the range of 0.68 - 0.97.

A cheaper alternative for determining density of small samples is to use a pycnometer. The Reischauer pycnometer and method described by SMS 1347 should be used in preference to industry standard pycnometer procedures.

Note that measurements of the molar mass and relative density of a total sample allow the corresponding molar mass and relative density of the residual fraction (eg. C7+) to be calculated once the molar mass and density of the lighter components has been subtracted (in proportion to their fractions as determined by a GC analysis). Accuracy of these calculated properties for Cn+ fractions is further reduced for high vapour pressure liquids (eg. separator liquids) since the liquid must be first flashed to atmospheric conditions and the properties of the stable fluid measured. It is only possible to directly measure molar mass or relative density of the Cn+ fraction of a sample if this fraction has been produced from a distillation procedure (eg TBP).

Measurement of the relative density of light hydrocarbons including LPG's should be carried out according to ASTM D 1657 which utilises a pressure hydrometer. The method is valid up to a pressure of 1,400 kPa.

Field measurement of unstable hydrocarbon liquids (NGLs) at high pressure can be made using a sample bomb (with known weight and calibrated volume) in a sample loop. The NGL is flushed through the sample container for several hours (while ensuring minimum pressure drop across the sample bomb and sample loop). The bomb is then removed from the loop and weighed and the temperature recorded. Relative density can then be calculated by reference to ASTM D 1250.

#### 4.13. DISTILLATION ANALYSES

For crude evaluation purposes the standard distillation method is the potstill distillation described in SMS 2767.

For process design a TBP analysis of a liquid sample will be required. This should be carried out according to ASTM D 2892 which utilizes a 15 theoretical plate column and so obtains significantly finer fraction cuts than the D 86 or D 1160.

ASTM D 2892 may only be used for stable samples. Samples with RVP greater than 83 kPa (eg. well test separator liquid samples) should first be flashed to ambient conditions

and the vapour released quantified and analysed by GC to ensure that these light ends are not lost when the recombined stream composition is calculated.

ASTM D 2887 describes a GC alternative to ASTM D 2892 which is quicker and easier to perform. However the GC technique will not allow measurement of relative density and molar mass of fractions so is unsuitable as a source of data for process simulation.

#### 4.14. DEHYDRATION AND DE-OILING ANALYSES

The reader is referred to report EP 89-0150 for details of the numerous test which are carried on oil/water samples in order to design and monitor crude oil dehydration and de-oiling facilities.

It should be noted that many of these tests must be carried out onsite (eg. emulsion settling tests for testing screening of demulsifiers/de-oilers) while others can be carried out off site. However, in general crude oil and/or emulsion samples should be processed as soon as possible (within 24 hours) of sampling.

#### 4.15. OTHER CRUDE OIL PROPERTIES

##### 4.15.1. Water Content

For field (preliminary) evaluation of BS&W ASTM D 96 (centrifuge method) is to be used.

Laboratory crude evaluation must be carried out according to ASTM D 4006. The crude petroleum is distilled under total reflux with a solvent which is immiscible with water. The water is collected in a graduated side arm of the distillation apparatus (Dean Stark) and the solvent returned to the crude. Repeatability increases to 0.08%(v/v) up to 0.085% (v/v) of water collected then remains at this value. Reproducibility increases to 0.105% (v/v) up to 0.085% (v/v) water collected and then remains at this value.

##### 4.15.2. Kinematic Viscosity

To be carried out according to ASTM D 445 (equivalent to IP 71/84). The method measures the time for the liquid to flow through a calibrated glass capillary viscometer and is only intended for Newtonian fluids (shear stress proportional to shear rate). For clean transparent oils repeatability can be expected in of the order of 0.3% of the mean and reproducibility 0.7% of the mean. For crude oils, viscosity data are less precise. Precision depends on the type of viscometer used (ie suspended level or reverse flow type). The former is used for transparent Newtonian liquids whereas dark opaque samples are recommended to be measured in the reverse flow type.

##### 4.15.3. Dynamic Viscosity

Dynamic viscosity is defined as the ratio of kinematic viscosity to the density of the sample and is therefore a calculated property.

However for non-Newtonian waxy crudes, *apparent* dynamic viscosity must be determined using a Bingham viscometer for a range of temperatures and shear rates chosen to be representative of future (pipeline) transport conditions.

Determination of viscosities of fluids under pressure (reservoir fluids) is made using a rolling ball viscometer. Accuracy is expected to be within 2%.

#### 4.15.4. Sulphur Content

Total sulphur can be determined according to ASTM D 129 which is applicable to almost any petroleum product but is very time consuming. Repeatability is given as  $0.016x + 0.06$  and reproducibility as  $0.037x + 0.013$  where  $x$  is the mean of duplicate measurements. However the preferred method for total sulphur content of crude oils is given in SMS 1807. This involves oxygen flash combustion (Schöniger combustion) of a sample. Repeatability is  $0.01 + 0.01x$  for less than 1% (m/m) sulphur and  $0.02 + 0.01x$  for greater than 1% (m/m) where  $x$  is the mean of duplicate measurements. Reproducibility is 0.1% (m/m).

ASTM D 2622 is used for total sulphur in liquid petroleum *products*. The latest version of this method is also claimed to be applicable to crude oils, however matrix effects due to differences in H/C ratio (and the presence of other interfering compounds) between the test sample and the calibration sample will effect the accuracy of the data. For refined products repeatability of ASTM D 2622 is given as  $0.017(x + 0.8)$  and reproducibility as  $0.055(x + 0.8)$  where  $x$  is the mean of duplicate measurements.

Mercaptan sulphur at levels between 0.0003 and 0.01% (m/m) in *distillate* fuels are determined according to ASTM D 3227. The method has a repeatability of  $0.00007 + 0.027x$  and reproducibility of  $0.00031 + 0.42x$  where  $x$  is the wt% mercaptan sulphur in the sample. SMS 177 is a method similar to ASTM D 3227 but has better precision and allows measurement of mercaptans in the presence of hydrogen sulphide.

SMS 177 should only be used for mercaptan content of crude oils with caution.

#### 4.15.5. Hydrogen Sulphide

Existent hydrogen sulphide in crude oils is determined according to SMS 2268. This involves a lengthy (16 hr) stripping process with an inert gas (nitrogen) to drive out the hydrogen sulphide and absorb it into caustic solution with subsequent potentiometric titration of the aqueous solution.

A similar procedure is possible for use in field applications but using stain tubes to measure the amount of hydrogen sulphide driven off in the nitrogen instead of potentiometric titration.

Potential hydrogen sulphide is determined according to SMS 2269.

#### 4.15.6. Total Nitrogen

Total nitrogen in refined products is measured by a microcoulometric method after hydrogenation according to SMS 1730. SMS 1730 is a variation on the method used in ASTM D 3431 and allows a slightly lower limit and wider application.

Neither of these methods is however suitable for products containing more than  $\pm 0.05\%$  (m/m) sulphur such as crude oils. Total nitrogen in crude oil in the range 0.015% (m/m) to 2% (m/m) should be determined using the Kjeldahl method following ASTM D 3228.

#### 4.15.7. Salt as NaCl

Use ASTM D 3230 which is based on conductivity of a solution of crude oil in a polar solvent when subjected to an alternating electrical stress. The extraction and titration method of IP 77/79 is equally applicable.

#### 4.15.8. RVP

RVP is determined according to ASTM D 323. Precision is as follows:

Gauge range	Repeatability	Reproducibility
0 - 100 kPa	1.7	3.8
0 - 200 or 300 kPa	3.4	5.5

#### 4.15.9. TVP

TVP is normally calculated as the sum of the vapour pressures of the individual components if the composition is known or approximated by correlation from an RVP measurement (ref GPSA Engineering Data Book). Such RVP/TVP correlations assume typical crude or condensate compositions so can only be used as indications of likely TVP.

There is no standardised procedure for measuring TVP although several simple procedures have been used to measure the vapour pressure of a sample at controlled temperature.

#### 4.15.10. Pour Point

To be carried out according to ASTM D 97 which gives both maximum and minimum pour points. The pre-heated (to 45 °C for maximum pour point and to 105 °C for minimum pour point) sample is cooled under controlled conditions and examined for its flow characteristics at 3 °C temperature intervals. The actual pour point without heat is always between the maximum and minimum. For refined products repeatability is 3 °C and reproducibility is 6 °C. These precision data should be regarded as optimistic for crude oils. The inversion point (the minimum temperature to which the sample should be re-heated so that it will return to its minimum pour point) is determined by repeating the pour point test for repeated starting temperatures.

#### 4.15.11. Cloud Point

The cloud point of an oil is the temperature at wax precipitation begins. Cloud point is determined according to ASTM D 2500 for semi transparent crudes with cloud point less than 49 °C. The method has a repeatability of 6 °C and reproducibility of 6 °C for oils other than distillates.

For less transparent, crude oils AMS 259-1 (microscopic cloud point) must be used.

#### 4.15.12. Wax Content

Wax content of petroleum products is determined according to SMS 1769. Precision is

reported as follows:

% (m/m)	Reproducibility % (m/m)
1.8 - 4.0	0.7
4.1 - 6.0	0.8
6.1 - 10.0	0.9
> 10	10% of mean

#### 4.15.13. Wax Congealing Point

The congealing point of a wax is determined according to ASTM D 938. Repeatability is of the order of 1 °C and reproducibility is 2.5 °C for residual waxes.

#### 4.15.14. TAN (Total Acid Number)

TAN values of petroleum products are determined by potentiometric titration according to ASTM D 664. Repeatability and reproducibility are of the order of 10% and 40% respectively for crude oils.

For internal Shell purposes TAN may also be determined according to SMS 2384 but the ASTM method will be more universally accepted outside the company.

Note: Samples taken by acidified brine displacement may give erroneously high acid numbers

#### 4.15.15. Asphaltenes

Asphaltene content of crude oil and petroleum products is measured by precipitation with heptane or pentane according to IP 143.

#### 4.15.16. Heavy Metal Content

Concentration of heavy metals in a crude sample should be determined via atomic absorption spectroscopy, following the guidelines provided in SMS 1803.

#### 4.16. PVT EXPERIMENTS ON WELL STREAM SAMPLES

Following compositional analyses (by GC) and accurate determination of liquid densities, the meter factors used for determining separator gas and liquid flow rates in the field are checked using the laboratory determined fluid properties (densities) and the field GOR adjusted if necessary. The gas and liquid samples are then physically re-combined in a ratio corresponding with the corrected test separator GOR. This re-combined well fluid sample is then used for various experiments designed to determine the relationships between pressure, volume and temperature (PVT) for the reservoir fluid in question. The standard experiments performed are described below. In addition there are many less common tests that may sometimes be required but are not described here (ref report EP 91-0703).

The standard tests will normally require a PVT cell rated to 70,000 kPa at 150 °C but these

are now frequently available up to 100,000 kPa and 200 °C. All pressure and temperature measurements must be accurate to within 0.5% and 0.5 °C respectively. All volumetric data must be accurate to within 0.001 cm<sup>3</sup>.

#### 4.16.1. Constant Composition Expansion Test

The (re-combined) oil sample is conditioned to reservoir temperature and a pressure  $\pm 2,500$  kPa above reservoir pressure. The pressure of the cell is then reduced in a number of even steps (10 - 20) while maintaining a constant temperature and sample agitation. Pressure and volume are reported at each step and a plot of the pressure volume relationship will indicate bubble point of the sample. Bubble point pressure should also be determined at a temperature midway between ambient and reservoir temperature.

From the mass charge of the cell and the volume, the density variation with pressure (compressibility) of the liquid above bubble point must be determined and reported.

The pressure volume relationship for a gas or gas condensate sample is determined in the same way with the exception that a calibrated windowed cell should be used so that the onset of liquid formation can be visually detected with an optical device and the liquid volume with pressure can be determined. Dew point pressure should be determined at reservoir temperature, a temperature mid way between reservoir temperature and ambient, and at ambient temperature.

#### 4.16.2. Separation Tests

A measured sample of (re-combined) reservoir fluid is pumped (with a calibrated positive displacement pump) into a visual cell. The pressure and temperature of the cell are maintained at the equivalent to the likely first stage separator pressure and temperature in future process operations (to be provided by the process engineer). The gas separated is measured into evacuated spheres for subsequent GC analysis for hydrocarbons to C8 and inerts according to (4.3.2) above. The remaining liquid is then brought to the proposed second stage separator conditions and the process repeated. This is repeated for as many stages of separation as envisaged in future operations until the fluid is at stock tank conditions. Finally the amount, density and composition of the stock tank liquid is determined.

For the gas and the liquid at each separator stage (including the tank) the following should be reported:

- Composition to C8+ including individual aromatics and inerts (ISO 6974 )
- Total molar mass
- Gas density
- Tank oil density
- Tank oil viscosity
- GOR (v/v and molar ratio)
- Separator volume factor
- Formation volume factor from bubble point to stock tank and from reservoir pressure to stock tank.
- Buckley plot (5.4.1)

Note: Compositional analysis to C8+ is a minimum requirement. In many instances an analysis to C16+ would be beneficial.



#### 4.16.3. Differential Liberation

This test is to be carried out for oil samples and simulates the depletion of an oil reservoir with the gas being continuously removed. A sample of (recombined) reservoir fluid is charged to reservoir pressure and temperature. While maintaining a constant temperature, the pressure is reduced in a series of 10 equal steps until the sample is at stock tank pressure and is brought to stock tank temperature. At each pressure reduction step liberated gas is displaced from the cell and its volume and composition determined. The following must be reported:

- oil formation volume factor
- solution gas-oil ratio
- compressibility factor
- gas formation volume factor
- gas gravity
- composition of liberated gases (ISO 6974)
- reservoir fluid density
- residual oil gravity

After the final pressure reduction step and bringing the sample to stock tank temperature the composition and properties of the stock tank liquid are determined.

Note: Compositional analysis to C8+ is a minimum requirement. In many instances an analysis to C16+ would be beneficial.

#### 4.16.4. Constant Volume Depletion

This test is to be used for primarily for gas gas/condensate systems and simulates the production of gas from a condensate reservoir while leaving behind the liquids (once the reservoir is depleted below its dew point). Although it is not strictly applicable to reservoirs containing volatile oils, the constant volume depletion test may also prove useful for these as well.

A volume of reservoir fluid is charged to a pressure  $\pm 2,500$  kPa above saturation pressure. The pressure is then reduced in about 10 even steps at constant temperature. After stabilizing at each pressure reduction step the volume of the cell is returned to its original value at constant pressure by displacing some of the gas phase from the cell. The volume of gas displaced from the cell is measured accurately along with the liquid remaining. The following should be reported at each step:

- composition of produced gas (C1 - C8, aromatics and inerts - ISO 6974)
- molar mass of C7+ in produced gas
- volume of gas produced
- residual liquid composition and density
- gas compressibility factor
- two phase compressibility factor

The gas sample displaced may also be flashed through a two stage separation to stock tank conditions to simulate condensate yield at each pressure depletion stage.

The final pressure reduction step will take the sample to stock tank conditions where upon the composition of the remaining liquid must be determined.

All volumetric data reported are to be referenced to the volume of the sample at the dew point pressure.

Note: Compositional analysis to C8+ is a minimum requirement. In many instances an analysis to C16+ would be beneficial.

#### 4.16.5. Viscosity of Reservoir Fluid (Oil) at Reservoir pressure

This is currently measured using a rolling ball viscometer which is usually accurate to within 2%. Measurements are made up to a pressure limit of about 55,000 kPa and down to a lower viscosity limit of  $0.08 \times 10^{-3}$  Pa.S. Viscosities reported for pressures above 55,000 kPa are usually an extrapolation from lower pressures and are not actually measured.

Viscometers for measuring gas and liquid viscosities up to 135,000 kPa are currently under development.

## 5. DATA VALIDATION

### 5.1. GENERAL

This section describes the techniques used to check that samples and their analysis results are valid.

There are a number of relatively straightforward numerical checks that should be performed to help establish the validity of the reported data. These may be used to supplement validation checks carried out by the contract laboratory as part of their normal procedures.

It should be noted that the overall validity of results obtained from PVT laboratory measurements will depend to a large degree on whether or not the samples were representative of the reservoir fluid. It is imperative therefore that every effort is made to obtain representative samples through proper well conditioning and sampling, as described in the previous sections. The validation checks described below are aimed at establishing the consistency of the measured data and are unlikely to detect non representative sampling.

### 5.2. ON SITE SAMPLE VALIDATION FOR SUB -SURFACE PVT SAMPLE

Several samples are taken until at least two samples sample from separate runs with the tool have the same bubble point (measured according to Appendix 5. ). All subsequent samples taken for analysis should have the same bubble point to within 2%. This bubble point should be compared with that expected for the reservoir being sampled bearing in mind that the bubble point determination has been made at ambient temperature not at reservoir temperature. Usually the bubble point will be near the original reservoir pressure.

The first sample taken may be opened to determine it's contents and rejected if it contains free water. If this is the case the sampling depth will need to be reviewed. Alternatively, the compressibility of the sample may indicate the presence of water which has lower compressibility than most hydrocarbon liquids.

### 5.3. SAMPLE VALIDATION CARRIED OUT BY THE CONTRACT PVT LABORATORY

Upon receipt in the PVT laboratory, gas and liquid samples, taken from a test separator should be subjected to the following checks:

#### 5.3.1. Gas samples:

The sample cylinder is brought to a temperature as close as possible to the on site sampling temperature and the opening pressure of the cylinder is measured. This pressure must be reported in the PVT (analysis) report. Any significant deviation from the original sampling pressure indicates leakage during transit and the sample should be rejected.

During analysis, the concentration of air present in the sample is determined. It is not uncommon for small amounts of air to be present due to failure to thoroughly purge the

sample bottle prior to sampling and ingress during sample transfer procedures. This may not be a problem since it is common practice to adjust the measured nitrogen concentration in the sample for the nitrogen present due to air contamination (air being ca. 78% nitrogen by volume) and report the composition on an air free basis. The presence of air is however indicative of poor sampling techniques.

#### 5.3.2. Liquid samples:

Upon receipt in the laboratory the sample saturation pressure (i.e. bubble point pressure) must be determined at sampling temperature. The measured saturation pressure should correspond with the sampling pressure when collecting the sample from the liquid outlet of a gas liquid separator. A significantly lower saturation pressure would indicate sample leakage with loss of light ends and the sample should be rejected.

All sample containers should be checked for contaminants (eg. water or mud).

#### 5.4. CHECKS FOR PVT RESULT VALIDITY

Before any experimental PVT data are used for design or study purposes, it is necessary to ensure that there are no errors or major inconsistencies that would render any subsequent work useless. Two such means of data validation are the Campbell Diagram (Buckley plot) and the Mass Balance Diagram. These techniques are described below:

##### 5.4.1. Buckley Plot (or Campbell Diagram)

For hydrocarbon gas and liquid phase in equilibrium, there is a linear relationship between the log of the individual component K-values (mole fraction of a component in the gas phase divided by the mole fraction of the same component in the liquid phase) and their respective critical temperatures squared (see Figure 3 ). This technique is described by Campbell. Note that as components become less paraffinic in nature, the greater will be the deviation from linearity. Thus, it is common for the components heavier than C5 to show such deviations.

For the light components, any significant deviations from the linear relationship indicate possible non equilibrium separation, suspect analyses or numerical errors in the data reporting. Because it is a log scale any variation of log K of more than 0.1 is significant.

##### 5.4.2. Mass Balance Diagram:

The mass balance diagram is based on the following general flash equation describing the individual component material balances around a flash separation stage:

$$F.Z_i = L.X_i + V.Y_i$$

where F, L and V are the molar flow rates of Feed, flashed Liquid and flashed Vapour respectively and  $Z_i$ ,  $X_i$  and  $Y_i$  are the mole fractions of component i in the feed, flashed liquid and flashed vapour respectively.

For one mole of feed the above equation can be rearranged to:

$$Y_i/Z_i = -L \cdot X_i/V \cdot Z_i + 1/V$$

This is a linear equation and thus a plot of  $Y_i/Z_i$  versus  $X_i/Z_i$  should result in a straight line of gradient  $-L/V$  (see Figure 4):

**Note :** The well fluid composition reported in PVT reports are normally obtained from a mathematical recombination of the test separator gas and liquid compositions in a mole ratio corresponding with the measured separator GOR, i.e. the well fluid composition is calculated by a component mass balance. In such cases, deviations on a mass balance diagram normally indicate arithmetic errors in the data recombination.

Fluid composition of the recombined fluid is also usually measured. This functions as an additional check on the mathematical recombination.

## 6. REFERENCES

Wherever possible, industry accepted standard procedures have been referenced. For improved understanding, summaries of the industry standards have sometimes been included in the text. However the original document should always be consulted for a working description of the procedure referred to. A list of all the documents referred to is given below.

**Note:** Unless specifically designated by date, the latest edition of each publication must be used, together with any amendments/supplements/revisions thereto.

### 6.1. SHELL DOCUMENTS

#### 6.1.1. Shell Standards

AMS 259-1; Paraffin Wax Cloud Point of Dark Fuel Oils: Microscopic Method  
 AMS 607-2; Mercury in Aqueous Solutions, Water Soluble Materials, Urine, Clay and Drilling Materials: Flameless AAS Method  
 AMS 743-2; Radon 222 Activity in Natural Gas: Ionization Chamber Counting Method  
 AMS 780-2; Po-210 Radioactivity Concentration in Hydrocarbon Condensates: Gas Proportional Method

DEP 31.38.01.11-Gen; April 1992; Piping - General requirements

DEP 31.22.05.11-Gen "Gas/Liquid Separators - Type Selection and Design Rules"; February 1991.

DEP 32.31.50.10-Gen; "On-line Process Stream Analysis; Part 1; Sample Take off and Transportation"

DEP 32.31.50.11-Gen; "On-line Process Stream Analysis; Part 2; Sample Conditioning"

DEP 32.31.50.12-Gen; "On-line Process Stream Analysis; Part 3; Analysers"; In preparation

DEP 32.31.50.13-Gen; "On-line Process Stream Analysis; Part 4; Analyser Houses"

DEP 20.04.10.10-Gen; "Manual: Glycol Type Gas Dehydration and Hydrate Inhibition Systems"; In preparation 1992

EP 55000-32; SIPM EPO/53/63; "Hydrogen Sulphide in Production Operations"

SMS 177; Hydrogen Sulphide, Elemental Sulphur and Mercaptans in Organic Liquids Potentiometric Titration Method

SMS 217; Hydrogen Sulphide, Mercaptans and Carbonyl Sulphide in Gases, Potentiometric Titration Method

SMS 1329; Water in High Pressure Gases, Fischer Reagent Method

SMS 1346; Average Molar Mass, Freezing point Depression Method

SMS 1347; Density of Liquids, Reischauer Pycnometer Method

SMS 1553; Water in Gases, Fischer Reagent Method

SMS 1730; Nitrogen in Organic Materials, Hydrogenation-Microcoulometric Method

SMS 1769; Wax Content of Petroleum Products, Crystallization Method

SMS 1803; Atomic Absorption Spectroscopy, Supporting Method

SMS 1807; Sulphur in Organic Materials, Oxygen Flask Combustion Method

SMS 2268; Existent Hydrogen Sulphide in Crude Oils, Absorption Method

SMS 2269; Potential Hydrogen Sulphide in Crude Oils, Steam Distillation Method

SMS 2294; Average Molar Mass of Gasoline, Total Evaporation Method

SMS 2336; Individual Sulphur Compounds, GC Method with Microcoulometric Detection

SMS 2384; Acid Value of Dark-Coloured Petroleum Products - Potentiometric Titration Method

SMS 2767; Distillation of Heavy Petroleum Residues, Vacuum Potstill Method

#### 6.1.2. Shell Reports

- EP 05-0758; Hearn, R.S. and Dixon, L. "Recommendations on the surface sampling and analysis of natural gas"; June 1979
- EP 87-1006; SIPM EPO/53; "Well Services Guidance Manual"
- EP 88-2515; Sutton, J.N., Langenberg, A. and Marshal, J.D.; "A guide for the heavy-end characterization of hydrocarbon streams using the C7PLUS program"
- EP 89.0150; SIPM EPD/24; "Dehydration and De-oiling Manual"; January 1989.
- EP 91-0951; Boer, J.J.den; "Measuring the Wetness of Wet Gas in Producing Flow Lines: Field Trial of a Prototype Tracer Method and a Commercially Available Sampling Method"
- EP 91-0703; W. Scherpenisse; "PVT Sampling, Analysis and Quality Control Manual"; March 1991.
- EP 92-1150; EPD/41; "Sand Control Manual"; Revised July 1992
- MF 81-0340; "Shell Crude Oil Evaluation Schemes (Laboratory Manual)"
- TNER.88.006; Dixon, A.G., Ebbrell, H.K., Rimmer, C.P., Wilde, R.G.; "Hydrocarbon Fluid Evaluation By Split-Phase Methods: Field Equipment and Procedures"

#### 6.2. INTERNATIONAL AND NATIONAL STANDARDS

##### AMERICAN STANDARDS

##### API RP 44; Recommended Practice for Sampling Petroleum Reservoir Fluids

Issued by  
American Petroleum Institute,  
Publications and Distributions Section,  
2101 L Street Northwest,  
Washington, DC 20037,  
USA

##### ASME section VIII; ASME Boiler and Pressure Vessel Code, Section VIII

Issued by  
American Society of Mechanical Engineers,  
345 East 47th Street,  
New York, N.Y. 10017,  
USA

##### ASTM D 96 ; Standard Test Method for Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure)

Issued by  
American Society for Testing and Materials  
1916 Race Street,  
Philadelphia, PA 19103-1187  
USA

- ASTM D 97; Standard Test Method for Pour Point of Petroleum Oils
- ASTM D 129; Standard Test Method for Sulphur in Petroleum Product (General Bomb Method)
- ASTM D 323; Standard Test Method for Vapor Pressure in Petroleum Products (Reid Method)
- ASTM D 445; Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the calculation of Dynamic Viscosity)
- ASTM D 664; Standard Test Method for Acid Number of Petroleum Products by

	Potentiometric Titration
ASTM D 938;	Standard Test Method for Congealing Point of Petroleum Waxes, Including Petrolatum
ASTM D 1250;	Standard Petroleum Measurement Tables
ASTM D 1298;	Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
ASTM D 1657;	Standard Test Method for Density or relative Density of Light Hydrocarbons by Pressure Hydrometer.
ASTM D 1835 ;	Standard Specification for Liquefied Petroleum (LP) Gases
ASTM D 2500;	Standard Test Method for Cloud Point of Petroleum Oils
ASTM D 2622;	Standard Test Method for Sulphur in Petroleum Products by X-Ray Spectrometry
ASTM D 2887;	Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography
ASTM D 2892;	Standard Test Method for Distillation of crude Petroleum (15-Theoretical Plate Column)
ASTM D 3227;	Standard Test Method for Mercaptan Sulphur in Gasoline, Kerosine, Aviation Turbine and Distillate fuels (Potentiometric Method)
ASTM D 3228;	Standard Test Method for Total Nitrogen in Lubricating Oils and Fuels by Modified Kjeldahl Method
ASTM D 3230;	Standard Test Method for Salts in Crude Oil (Electrometric Method)
ASTM D 3246;	Standard Test Method for Sulphur in Petroleum Gas by Oxidative Microcoulometry
ASTM D 3431;	Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons (Microcoulometric Method)
ASTM D 4006;	Standard Test Method for Water in Crude Oil by Distillation
ASTM D 5002;	Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer
GPA standard 2166;	Obtaining Natural Gas Samples for Analysis by Gas Chromatography

#### BRITISH STANDARDS

IP 59 Method C , Density or Relative Density of Gases - The Effusion Method

Issued by

The Institute of Petroleum  
61 New Cavendish Street,  
London W1M 8AR  
England

IP 77/79; Salt Content Crude, and Petroleum Products

IP 143; Asphaltenes Precipitation with Normal Heptane

#### INTERNATIONAL STANDARDS

IATA Dangerous Goods Regulations

available from:

IATA  
2000 Peel Street  
Montreal  
Quebec  
Canada H3A2R4

or:

Payload Asia  
35 Duxton Road  
Singapore 0208

or:

Freight Merchandising Services  
Green Lane  
Hounslow  
Middlesex TW4 6DD  
England

IMDG (International Maritime Dangerous Goods) regulations

available from:

International maritime Organisation  
4 Albert Embankment  
London SE1 7SR  
England



**ISO 3170;      Manual Sampling of Liquid Hydrocarbons**

Issued by  
International Organization for Standardization  
1, Rue de Varembe,  
1211 Geneva 20,  
Switzerland

ISO 3171	Automatic Pipeline Sampling of Liquid Hydrocarbons
ISO 4257;	Liquefied Petroleum Gases- Method of Sampling
ISO 5167;	Measurement of Fluid Flow by Means of Orifice Plates, Nozzles and Venturi Tubes inserted in Circular Cross-section Conduits Running Full.
ISO 6326	Natural Gas - Determination of Sulfur Compounds (parts 1 - 5)
ISO 6327;	Natural Gas- Determination of Water Dew Point of Natural Gas- Cooled Surface Condensation Hygrometers
ISO 6570	Natural Gas - Determination of Potential Hydrocarbon Liquid Content
ISO 6974;	Natural Gas- Determination of hydrogen, Inert gases and Hydrocarbons up to C8- Gas Chromatographic Method
ISO 6975;	Natural Gas- Determination of Hydrocarbons from Butane (C4) to Hexadecane (C16)- Gas Chromatographic Method.
ISO 6976;	Natural Gas- Calculation of Calorific Value, Density, and Relative Density
ISO 6978;	Natural Gas- Determination of Mercury at High and Low Pressure
ISO 7941;	Commercial Propane and Butane- Analysis by Gas Chromatography

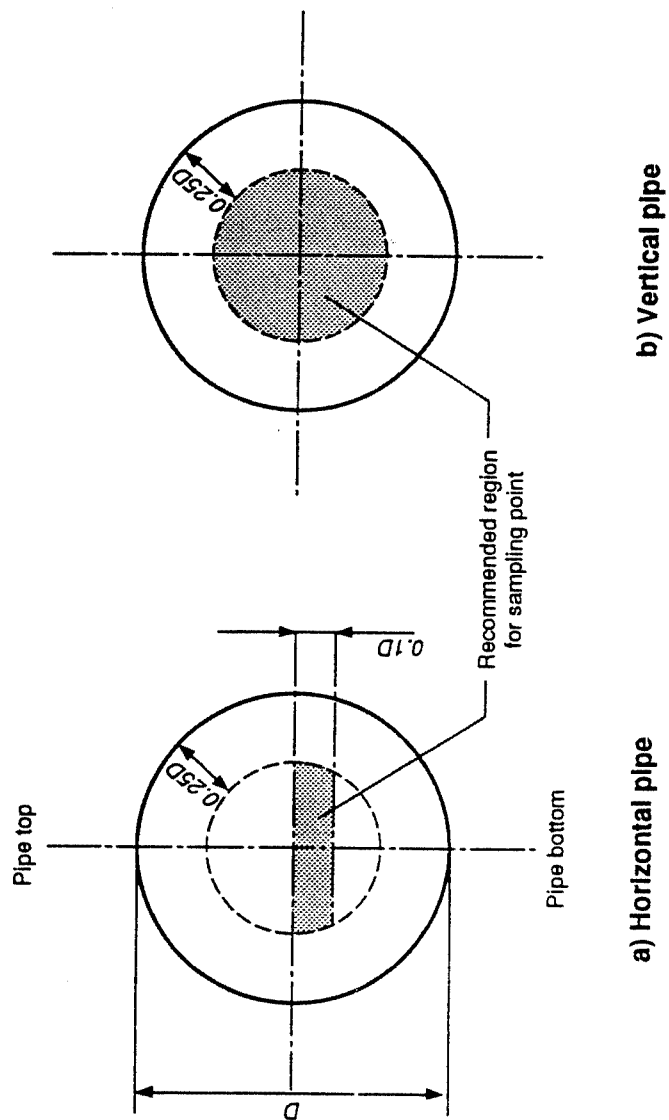
**6.3.      OTHER DOCUMENTS REFERENCED**

Campbell, J.M.; "Gas conditioning and processing"; 6th Edition, 1988; Campbell Petroleum Series, 1215 Cross Roads Blvd., Norman Oklahoma 73072, USA

GPSA;            Engineering Data Book;

## **7. FIGURES**

- Figure 1. Location Of Sampling Point
- Figure 2. Diagrammatic Representation of the Effect Sampling Rate on Measured LGR
- Figure 3. Example Buckley Diagram
- Figure 4. Example Mass Balance Plot
- Appendix 2, Figure 1 Liquid Sampling Arrangement
- Appendix 4, Figure 1. Sampling Manifold and Mixing Device for Sampling from Two Phase Flow Lines
- Appendix 5, Figure 1. Sample Transfer and Bubble Point Determination Apparatus for Subsurface PVT Samples



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DRAW. No.: H73622/2 D232.1

LOCATION OF SAMPLING POINT

FIGURE No.

1

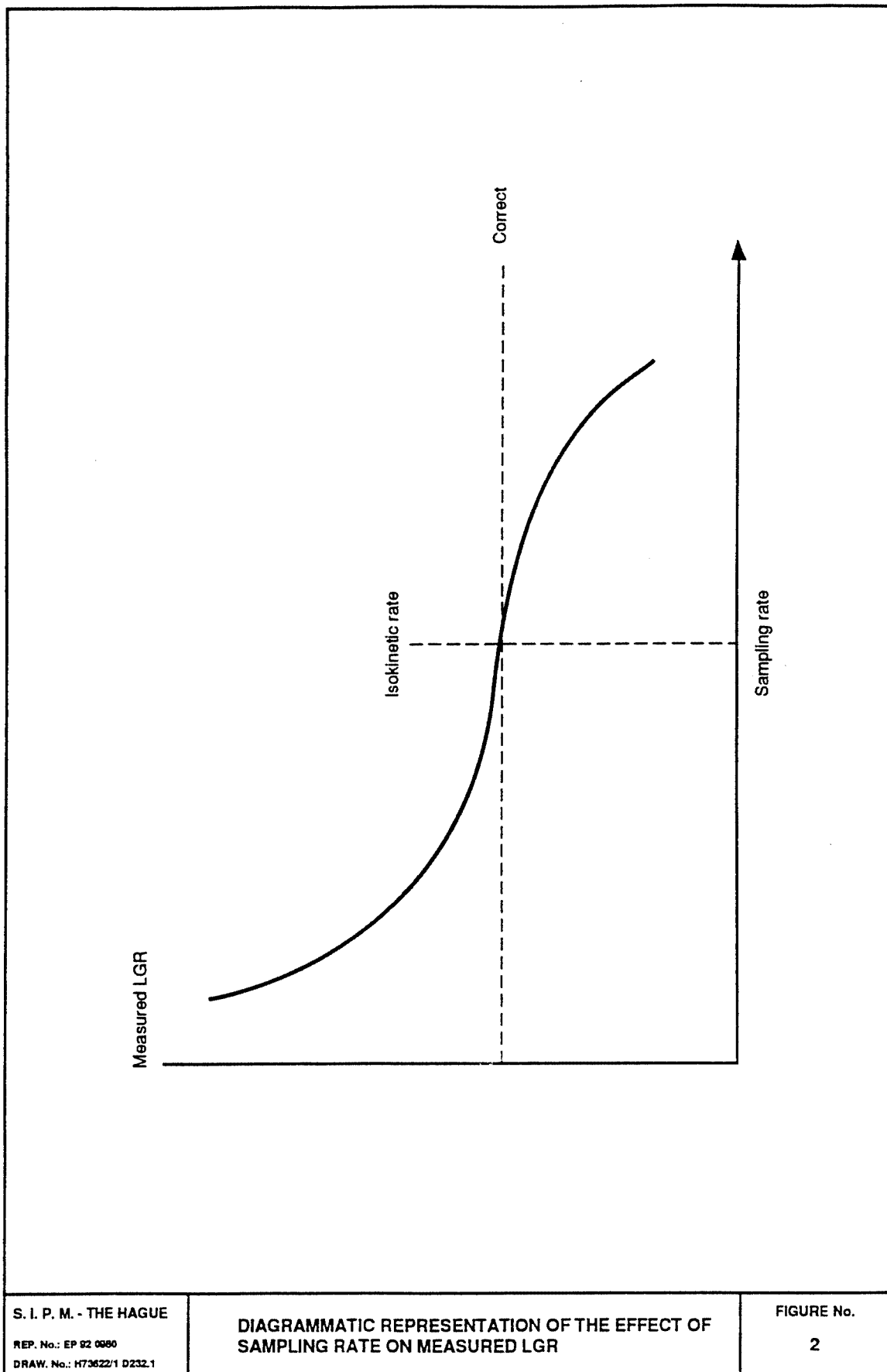


Figure 3.

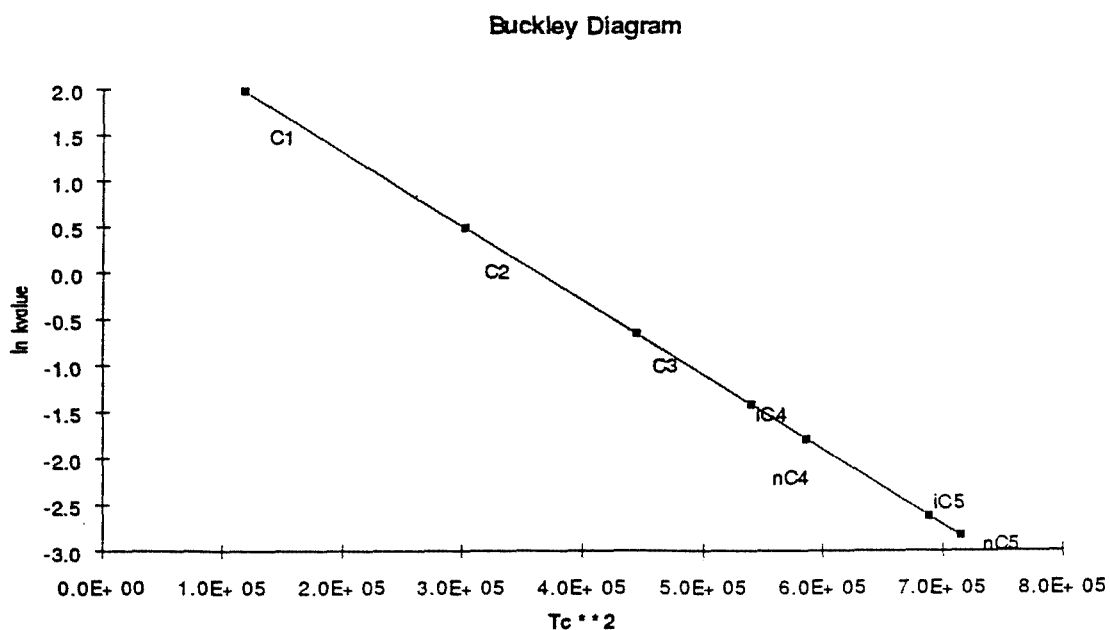
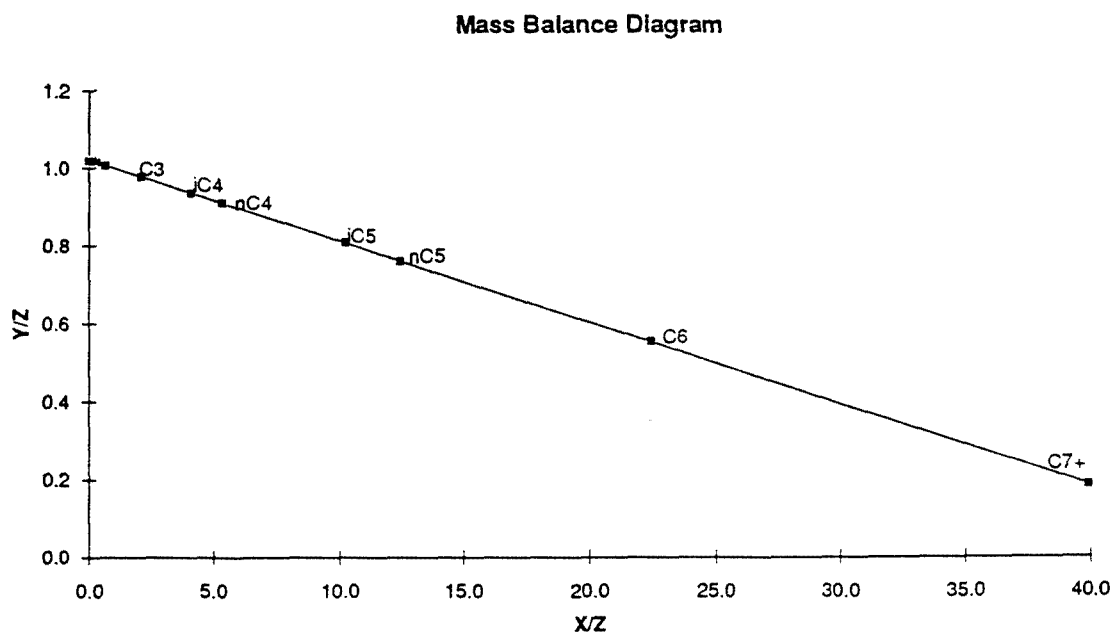


Figure 4.



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**SAMPLE ANALYSIS VALIDATION  
BUCKLEY AND MASS BALANCE DIAGRAMS**

FIGURES

3 and 4

## 8. APPENDICES

### 8.1. APPENDIX 1: SUMMARY OF DATA REQUIREMENTS, SAMPLING METHODS AND ANALYSIS METHODS

Reason for Sample	Data Required	Analytical Method	Sampling Method
Preliminary Analysis	density liquid BS&W crude	ASTM D 1298 ASTM D 96	Liquids: ISO 3170
	H <sub>2</sub> S, CO <sub>2</sub> (in gas)	Eg. Draeger (Man. Proc)	Gases: GPA 2166
	Density gas <i>Comp. C1 - C6 (gas)</i>	IP 59 Method C <i>ISO 6974</i>	
Operational control & process monitoring	Density liquid BS&W (crude)	ASTM D 1298 ASTM D 96	Liquids: ISO 3170
	Salt	ASTM D 3230	
	RVP	ASTM D 323	
	H <sub>2</sub> S (in crude)	SMS 2268	
	TAN	ASTM D 664	
	Sand		see (3.9)
	density gas	IP 59 Method C	Gases: GPA 2166
	Water in gas	ISO 6327	
	Calorific Value	ISO 6976	
	Wobbe index	(4.9)	
	Comp C1 - C8+	ISO 6974	
	H <sub>2</sub> S, CO <sub>2</sub> (in gas)	Eg. Draeger (Man. Proc)	
Custody Transfer	Density liquid	ASTM D 1298	Stable Liquids: ISO 3170
	Water content	ASTM D 4006	
	Salt	ASTM D 3230	
	RVP	ASTM D 323	Wild crude: Appendix 2
	H <sub>2</sub> S (in crude)	SMS 2268	
	TAN	ASTM D 664	
	Total sulphur in crude	ASTM D 2622	LPGs: ISO 4257 (not for comp. anal.)
	<i>TBP Distillation</i>	<i>ASTM D 2892</i>	
	density gas	IP 59 Method C / ISO 6976	Dry Gases: GPA 2166
	Water in gas	ISO 6327/Panametrics	
	Calorific Value	ISO 6976	
	Wobbe index	(4.9)	
	Comp C1 - C8+	ISO 6974	
	H <sub>2</sub> S, CO <sub>2</sub> (in gas)	Eg. Draeger (Man. Proc)	
	Nitrogen	ISO 6974	
	<i>Sulphur Compounds in gas</i>	<i>SMS 2336</i>	
	<i>Comp. C1 - C16+</i>	<i>ISO 6975</i>	

*Items in Italics may be required in some cases*

**Appendix 1: Summary of Data Requirements, Sampling methods and Analysis Methods**  
(continued)

**Analytical data Required for Crude Evaluation**  
(Sampling Method: ISO 3170)

BULK CRUDE PROPERTY		ANALYSIS REQUIRED?										KEY						
water (%v/v)		A										A = ANALYSIS						
salt as NaCl (mg/kg)		A										A <sub>o</sub> = NOT FOR SIMPLE						
sediment (% (m/m))		A <sub>o</sub>										S = ONLY FOR SIMPLE						
RVP (kPa)		A										(1) = GC ON 4- FRACTION						
Existent H2S content (mg/kg)		A <sub>o</sub>										(2) = >20 °C ABOVE POUR POINT						
Potential H2S content(mg/kg)		A <sub>o</sub>										(3) = REL. DENS. 25/25 IF NOT 70/4						
Potential HCl content(mg/kg)		A <sub>o</sub>										POTSTILL DISTILLATION ONLY TO BE PERFORMED ON CRUDES OF SIGNIFICANT COMMERCIAL INTEREST						
DISTILLATION FRACTIONS °C	Crude	ASTM D 2892										0.5m Vigreux		Potstill Distillation				
		CS - 65	65 - 100	100 - 150	150 - 200	200 - 250	250 - 300	300 - 350	350 - 370	370 +	370 - 475	475 +	370 - 475	475 - 525	525 - 565	565 +		
YIELD ON CRUDE OIL (%M/M)	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A		
DENSITY AT 15 °C	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A		
DENSITY AT 70 °C	A	A	A	A	A	A	A	A	A	A	A	A	A(3)	A	A	A(3)		
TBP/GLC	A(1)										A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A	A	A		
GLC/GC UP TO & INCL C5		A	A	A <sub>o</sub>														
GLC/GC UP TO & INCL C9																		
KIN. VISC. AT 10 °C MM2/S	A(2)																	
KIN. VISC. AT 20 °C MM2/S					A <sub>o</sub>	S												
KIN. VISC. AT 20 °C MM2/S					S	A <sub>o</sub>												
KIN. VISC. AT 40 °C MM2/S	A						A <sub>o</sub>		A <sub>o</sub>									
KIN. VISC. AT 40 °C MM2/S							S		S									
KIN. VISC. AT 60 °C MM2/S																		
KIN. VISC. AT 60 °C MM2/S											A	A	A	A	A	A		
KIN. VISC. AT 100 °C MM2/S											A	A	A	A	A	A		
KIN. VISC. AT 130 °C MM2/S																A		
SULPHUR CONTENT MG/KG	A	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>														
SULPHUR CONTENT % (m/m)					A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A	A	A	A	A	A		
SULPHUR CONTENT % (m/m)	A <sub>o</sub>				S	S	S	S	S	S								
TOTAL NITROGEN MG/KG						A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A	A <sub>o</sub>	A <sub>o</sub>	A	A	A		
BASIC NITROGEN MG/KG																		
TAN	A				A	A	A	A	A	A		A	A	A	A	A		
RESEARCH ON - CLEAR		A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>														
RESEARCH ON+ .15 G PB/L (TEL)		A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>														
MOTOR ON - CLEAR PB/L (TEL)		A <sub>o</sub>	A <sub>o</sub>		A													
TOTAL PARAFFINS % (m/m)		A <sub>o</sub>	A <sub>o</sub>	A	A													
TOTAL NAPHTHENES % (m/m)		A <sub>o</sub>	A <sub>o</sub>	A	A													
TOTAL AROMATICS % (m/m)		A <sub>o</sub>	A <sub>o</sub>	A	A													
I/N PARAFFIN RATIO		A <sub>o</sub>	A <sub>o</sub>	A	A						A <sub>o</sub>	A <sub>o</sub>		A	A	A		
UV AROMATICS % V/V																		
FIA AROMATICS % V/V					A <sub>o</sub>	S	A											
FIA AROMATICS % (m/m)					S	S												
NAPHTHALENES % V/V					A <sub>o</sub>	A <sub>o</sub>	A											
NAPHTHALENES % V/V					S	S												
SMOKE POINT MM					A <sub>o</sub>	A <sub>o</sub>	A											
SMOKE POINT MM					S	S												
FREEZING POINT °C					A <sub>o</sub>	A <sub>o</sub>	A											
FREEZING POINT °C					A	A												
CLOUD POINT °C						A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>									
CLOUD POINT °C	A					A	A	A	A	A	A	A	A	A	A	A		
POUR POINT (ASTM-MAX) °C						A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>									
POUR POINT (ASTM-MAX) °C																		
POUR POINT (ASTM-MIN) °C	A																	
POUR POINT (ASTM-MIN) °C	A																	
WAX CONTENT (SHELL) % (m/m)	A																	
CONGEALING POINT WAX °C	A																	
REFRACTIVE INDEX ND20C					A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>	A <sub>o</sub>		A		A	A	A			
REFRACTIVE INDEX ND70C																		
C7 ASPHALTENES CONTENT % (m/m)											A		A <sub>o</sub>			A		
CONRADSON CARBON RES. % (m/m)											A	A <sub>o</sub>	A <sub>o</sub>	A	A	A		
VANADIUM MG/KG											A <sub>o</sub>							
NICKEL MG/KG											A							
IRON MG/KG											A							
PEPTIZING POWER											A							
FLOCCULATION RATIO											A <sub>o</sub>		A <sub>o</sub>			A		

**Appendix 1: Summary of Data Requirements, Sampling methods and Analysis Methods**  
(continued)

Reason for Sample	Data Required	Analytical Method	Sampling Method
Process & pipeline Design	density liquid water content Salt Comp. C1 - C16+ H <sub>2</sub> S (in crude) TBP distillation PVT experiments Kinematic viscosity dynamic viscosity pour points <i>Total sulphur of liquid</i> <i>Emulsion properties</i> <i>Heavy metals</i> <i>TAN</i>	ASTM D 1298 ASTM D 4006 ASTM D 3230 ISO 6975 SMS 2268 ASTM D2892 (4.16) ASTM D 445 (4.15.3) ASTM D 97 <i>ASTM D 2622</i>  <i>Report EP 89-0150</i> <i>Atomic Adsorption Spec.</i> <i>ASTM D 664</i>	Liquids: Appendix 2.
	density gas Water in gas H <sub>2</sub> S, CO <sub>2</sub> (in gas) Nitrogen Comp. C1 - C16+ TBP Distillation PVT experiments dynamic viscosity <i>Helium</i> <i>Hydrogen</i> <i>Mercury</i> <i>Radon</i> <i>Polonium 210</i> <i>Polyaromatics</i> <i>Sulphur compounds in gas</i>	ISO 6976 ISO 6327 Eg. Draeger (Man. Proc) ISO 6974 ISO 6975 ASTM D 2892 (4.16) section 4.11.3 <i>ISO 6974</i> <i>ISO 6974</i> <i>ISO 6978</i> <i>AMS 732-2</i> <i>AMS 780</i>  <i>(4.10.5)</i>	Dry Gases: GPA 2166  Rich Gases: split-phase sampling (3.7.2)

*Items in Italics may be required in some cases*



**Appendix 1: Summary of Data Requirements, Sampling methods and Analysis Methods  
(continued)**

Reason for Sample	Data Required	Analytical Method	Sampling Method
Reservoir Studies	density gas Comp C1 - at least C8+ H <sub>2</sub> S, CO <sub>2</sub> (in gas)	ISO 6976 ISO 6974 Eg. Draeger (Man. Proc)	Liquids: Appendix 2
GOR < 150M <sup>3</sup> /M <sup>3</sup>	constant composition expansion test differential liberation exp. separator expts. oil viscosity with press. at reservoir temp.	(4.16.1) (4.16.3) (4.16.2)	
GOR 150-350M <sup>3</sup> /M <sup>3</sup> (light oils)	constant composition expansion test  constant volume depletion separator expts. oil viscosity with press. at reservoir temp. <i>specialised expts.</i>	(4.16.1)  (4.16.4) (4.16.2)  <i>EP 91-0703</i>	Dry Gases:  GPA 2166
GOR > 350M <sup>3</sup> /M <sup>3</sup> (gas/condensates)	constant composition expansion test  constant volume depletion separator expts. oil viscosity with press. at reservoir temp. <i>specialised expts.</i> <i>Miscibility expts.</i>	(4.16.1)  (4.16.4) (4.16.2)  <i>EP 91-0703</i>	Rich gases/condensates  Split phase sampling

*Items in Italics may be required in some cases*

## 8.2. APPENDIX 2: SAMPLING METHOD FOR HYDROCARBON LIQUIDS FOR COMPOSITIONAL ANALYSIS

The sampling arrangement for use with a floating piston sampler is shown in Figure 1. of this Appendix , where C is the sample valve on the process line to be sampled. The instructions for taking samples are as follows:

1. Sample containers should be transported to the work site with the secondary side full of displacement fluid. The displacement fluid should preferably be hydraulic oil because of the corrosion risks associated with the use of aqueous fluids.
2. Thoroughly clean the connecting line (C to B) and the outlet of valve C with analytical reagent grade toluene. (use gloves and do not inhale the vapours. Be aware of the health hazards of toluene)
3. Make up the connection line to connect valve B of the sampling vessel to the separator line valve C.
4. Remove any remaining contamination in the connection CB by flushing about 5 litres of the fluid to sampled through valves C, B and A. The valves must be opened in the order C-B-A. The purged liquid must be vented to a flare, closed hydrocarbon drain or collected in an earthed (to prevent static electricity sparks) metal waste bucket in a safe, well ventilated area. Fluid collected in the waste bucket must be disposed of in an environmentally sound manner.  
  

Note: Some samplers have flushing ports to enable the purging of lines all the way to the sample container. In that case the valve A is an integral part of the sampler.

If the sampler has no purging arrangement then the connection at E should be made up loosely and the sample line B to E purged through the loose connection .
5. If the hydrogen sulphide concentration of the liquid being sampled is such that vapour in equilibrium with this liquid at atmospheric pressure may be greater than 50mg/m<sup>3</sup> then breathing apparatus must be worn and an observer acting as a safety standby must be in place a safe distance from the sampling operation. (see EP 55000-32)
6. Close valve A.
7. Open valve E on the sampling vessel.
8. Very carefully release valve D, allowing 85% of the displaced fluid to drain from the secondary side of the sampler into the measuring cylinder. The sampling rate should be slow enough in order that the pressure drop into the sample container will be negligible so as to prevent gas from breaking out (monitor pressure gauges during sampling). As a guide-line the sample should be collected over a 20 minute period.
9. Close valve D then record the sampling pressure from the sample gauge. Close valves E then B. For shipment, the pressure in the sample cylinder must be released by allowing a maximum of a further 10% of the displaced fluid to drain into the measuring cylinder by opening valve D, keeping valve E closed.
10. Release pressure in the sampler connections by opening bleed valve A.
11. Close valve C, bleed off pressures in CB (through A) and disconnect line CB from valve

B.

12. Check the sample cylinder for leaks and label clearly with:

Well/Field/Country:

Sample point location

Sampling interval (ie perforated interval open - for a well test sample)

Pressure of shipping container

Temperature at which the container was closed

Date and time of sampling

Identification number of sample

Sample bottle number

Name of the individual who has taken the sample

Name of the individual who has requested the sample.

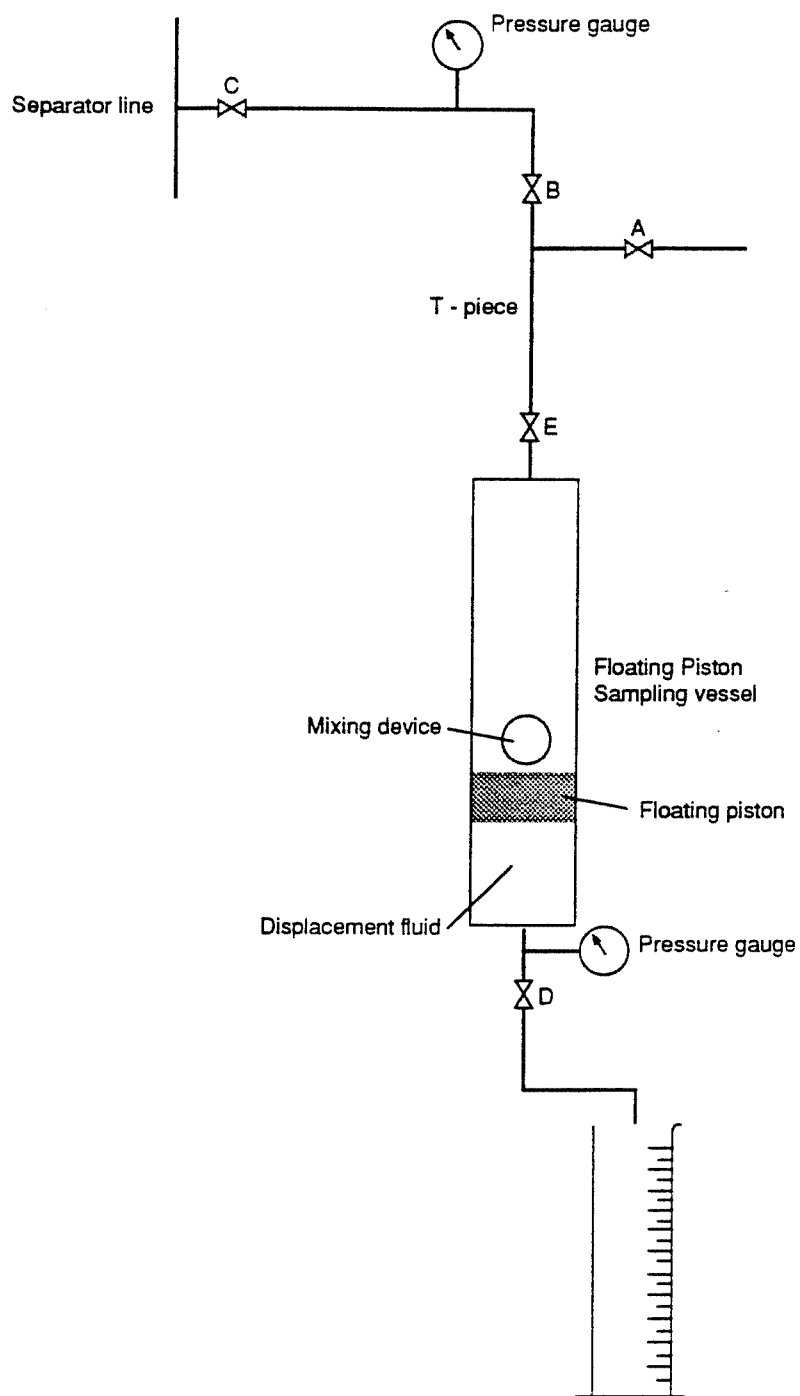
Additional Points to Note:

- Sample containers should be constructed to ASME section VIII division 2 or local regulations (whichever the more stringent) and manufactured in either AISI 316 or AISI 304 stainless steel. Containers should be appropriately pressure rated for the planned sampling conditions. Containers must also have been tested to 1.5 times rated pressure or according to local regulations whichever the most stringent.

Sample containers should include an efficient mixing device to help ensure homogeneity of sample when transferring at the laboratory (eg. a large ball in the primary side of the sampler).

- Sample containers should be cleaned in advance according to the procedure described in Appendix 3
- When sampling cold fluids the sample vessel must be cooled to 5 C below the fluid temperature to prevent gas break out during sampling.

Appendix 2



S. I. P. M. - THE HAGUE

REP. No.: EP 92 0980

DRAW. No.: H73622/4 D232.1

LIQUID SAMPLING ARRANGEMENT

APPENDIX

2

FIGURE No.

1

### 8.3. APPENDIX 3; CLEANING AND PREPARATION OF SAMPLE BOMBS

The following procedure describes a general method for cleaning and preparing of high pressure sample containers (bombs) where the sample will be used in a detailed analysis (eg. for a reservoir study or process design input). Sample cans to be used for collecting low pressure liquid samples for an identification analysis should always be new but should be visually inspected and flushed with a suitable solvent if necessary.

1. Vent the unwanted contents of the cylinder carefully into a metal waste can in a fume hood. The cylinder and the can must be earthed. The fume hood must vent outside the laboratory building. Wear a full face mask and gloves. Do not open the valve fully but ensure that expulsion of the contents occurs at a controlled rate.
2. Remove all old sample labels and clean the exterior surface of the cylinder.
3. Open both cylinder valves and pour in about 200 cm<sup>3</sup> of acetone. Floating piston cylinders should be displaced so that the sample chamber is at it's maximum volume. Close both cylinder valves and thoroughly shake the cylinder for 10 minutes. Discard the acetone into the waste can in the fume hood. Then repeat this wash with acetone until the solvent becomes colourless.
4. Repeat step 3 using 200cm<sup>3</sup> washes of pentane instead of acetone.
5. Ensure all visible traces of pentane are removed.
6. Wash the cylinder with 200 cm<sup>3</sup> of analytical grade toluene. Note that pentane and toluene are highly flammable and that all three solvents are health hazards. Use gloves when handling and do not inhale the vapours. Hydrocarbon solvents should be used in preference to halogenated solvents (dichloromethane, trichloroethane etc) because the environmental damage potential from the latter which is considered to out weigh the inflammability of the former.
7. Completely fill the cylinder with analytical grade toluene and leave it to soak over night.
8. Drain the vessel and check the refractive index of the solvent against that of the pure AR grade solvent. If the refractive indices are not in agreement then repeat steps 6 and 7.
9. If the refractive indices are acceptable the remnant solvent should be evaporated completely by flushing the container with oxygen free nitrogen (in the fume hood) for at least 5 minutes.
10. Glass sample vessels, to be used for collecting samples likely to react with a steel container (eg. hydrogen sulphide), should be given a final wash with dilute hydrochloric acid before drying.
11. Flush and fill the cylinder with oxygen free nitrogen in the manner described for sampling a gas stream in 3.7.1 above.

Appendix 3

12. Evacuate the cylinder with a vacuum pump and fit transit plugs to the valves. The sample cylinder is now ready to be moved to the field.
13. Each sample bomb should be clearly marked with its identification number, capacity, working pressure and test pressure.

#### 8.4. APPENDIX 4 - THE THORNTON DEVELOPED SPLIT PHASE SAMPLING METHOD

In order to be able to carry out a more detailed analysis of heavy ends in rich gas streams, Thornton Research Centre developed a split phase sampling method in the late 1970s. Using the split-phase method (ref. report TNER.88.006), a side stream of the process stream being sampled is continuously separated into discrete gas and liquid streams at a pre-selected combination of pressure and temperature. To accomplish these separations, the sampling equipment for the split-phase method incorporates a separation unit whose pressure and temperature conditions can be tightly controlled. By setting the separation temperature significantly below that of the process stream, a volume of liquid can be obtained adequate for subsequent detailed analysis for the properties required.

The use of separation stages in series makes it possible to carry out split-phase separations in sequence (up to the equipment limit of three stages) at selected conditions on a sample withdrawn from a flowing gas or gas/condensate stream, and then measure and analyze the separate gas/liquid streams from each separation stage. Recombination of the various analyzed phases in their appropriate molar proportions enables reconstruction of the original sample stream.

Thus it is possible not only to obtain an accurate analysis of the stream, but also to gain data on the phase behaviour of the stream (yields and compositions) at different conditions. By judicious choice of separator pressures and temperatures it is also possible to match the expected operating conditions and, thus, simulate the expected process as is often done in standard PVT analysis in a laboratory.

Because the sampling rate represents only a small proportion of the mainstream, separations obtained with the type of equipment used for split-phase sampling are virtually equilibrium separations under dynamic conditions and as such, usually significantly more "efficient" than most of those obtained in normal operations.

A typical example of the use of this on site simulation is the appraisal and production test of an offshore gas/condensate well. The test conditions can be chosen to simulate in series, the offshore production or low temperature separator, the pipeline/slug catcher, the onshore dew point control treatment and/or the sales gas pipeline dew point specification. Repeating the tests at different separator conditions will provide useful data in support of simulation studies for such phenomenon as condensation in the submarine line or the requisite onshore treatment. In most circumstances the combination of measured data and physical evidence carries more weight than theoretical calculations in a computer simulation alone.

It is recognized that only a few stages of simple separations can be physically simulated and that actual processes may be considerably more complex. Nevertheless it is strongly recommended that these experimental process simulations should be used as physical checks on, and to provide supporting data for fluid characterization, for more detailed and complex computer process calculations.

The Thornton split-phase technique was originally developed for sampling gas streams and especially rich gases. The technique has been used primarily for sampling gas/condensate well streams during production testing operations. To help ensure homogeneity of the well (or process) stream being sampled, Thornton developed a special sampling manifold containing a mixing device upstream of the sampling point. The manifold (see figure 1 of this Appendix.), sited upstream of process facilities close to the well head, is skid-mounted in the vertical position with one leg as a normal flow line through which the stream could be directed during clean-up operations until the well is judged to be stable (in the case of a

Appendix 4

well test). The other leg has a restricted diameter section to increase the linear velocity of the stream. Situated in this section is a mixing block containing radial drillings along its axis designed to force the two phases together in a region of turbulence (see Figure 1. of this Appendix). The homogenised sample stream is withdrawn from the turbulent region. Probe orifices are varied to ensure a close to iso-kinetic sampling rate.

The equipment for carrying out this sampling and on site process simulation is incorporated into a transportable sampling and measuring unit which became known as the "Thornton mini laboratory". A Shell subsidiary (Nautilus Ventures BV) was formed in the early 1980s to provide (in part) sampling and analysis services using this technology. The company was however dissolved in 1988 and the equipment and technology eventually transferred to PETROTECH A.S. of Norway. For a full description of the equipment and technology as transferred to PETROTECH see report TNER.88.006 . PETROTECH have since improved the manifold to the configuration shown in Figure 1 of this Appendix after experiencing problems with solids produced during clean-up partially plugging the mixing device. They have also built a 100,000 kPa rated version of the manifold for high pressure well tests and developed an injectable sampling probe so that probe size may be changed under pressure. They are currently developing an injectable mixing device so that it may be readily removed and cleaned during testing operations.

The original testing of the prototype Thornton manifold by TRC was carried out on a gas stream with well known gas/liquid properties (CGR of  $112.5 \text{ m}^3 / 10^6 \text{ std m}^3$ ) at Roden in the Netherlands. The sampling system was demonstrated to produce accurate results at manifold velocities down to about 25m/s ( $500,000 \text{ std m}^3/\text{d}$  at 7,500 kPa). The equipment has subsequently been used throughout the Group in numerous sampling operations in well testing and around surface facilities with success within a wide range of flow rates and gas/liquid ratios.

However Thornton recognized that a weakness of the sampling manifold lay in the mixing device which is unlikely to establish homogeneous gas liquid flow at high CGR's or at low velocities through the manifold. This concern was supported in a recent test where KSEPL employed the Thornton developed manifold (operated by PETROTECH) to measure free water content of a natural gas stream (a known amount of water was injected in to a gas stream which was then sampled; ref report EP 91-0951 ). The fluid velocity through the sampling manifold in the KSEPL test was about 10 m/s with a LGR's up to  $120 \text{ m}^3 / 10^6 \text{ std m}^3$  and the sampling system was shown to produce unreliable results. The design of the mixing block was based on the need to mix small volumes of liquid travelling along the walls of the pipe with gas travelling in the centre. At low velocities (and possibly higher liquid ratios) the current mixing block design may focus liquids to the centre of the sample leg near the sample probe thus resulting in an unrepresentative sample.

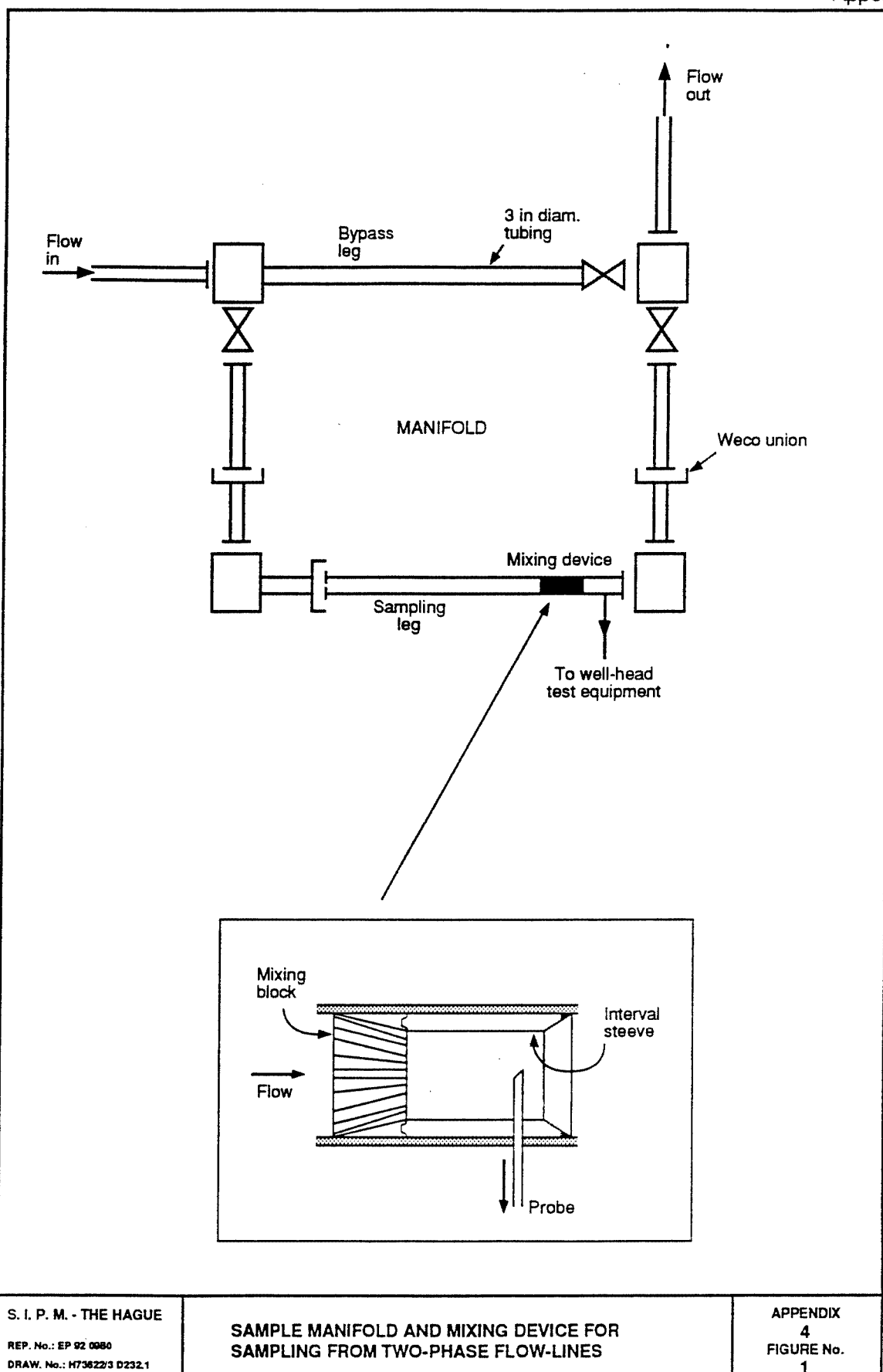
PETROTECH are currently (1992) managing a joint industry sponsored research project which has established the reliable lower limit of the sampling manifold with the current mixing block design at some  $500,000 \text{ m}^3(\text{std})/\text{d}$ . The next phase of the research project will investigate the use of improved mixing devices in the sampling manifold. However until the mixing block design is improved, it is not recommended to be used with flow rates below  $500,000 \text{ m}^3(\text{std})/\text{d}$  (ie. manifold velocities below 25m/s).

Note: Numerous tests have shown the manifold and current mixing device to function correctly below the limit of  $500,000 \text{ m}^3(\text{std})/\text{d}$  but since some tests have demonstrated errors under this rate, it should be used as the guide-line minimum.



Appendix 4

While the weakness of the mixing device in the TRC manifold is recognized, we believe that the TRC developed method remains the best available method for sampling gas gas/condensate well or process streams. The technique is therefore recommended when the analyses from samples taken from such streams are to be used as the basis for reservoir studies and/or process design.



## 8.5. APPENDIX 5: BUBBLE POINT DETERMINATION IN THE FIELD

The following is a general procedure to be used as a guide-line for bubble point determination of subsurface well bore samples in the field. Precise instructions will depend on the manufacturer of the apparatus used.

1. Allow the sample to come to ambient temperature of 22 - 24 °C. This should be carried out in an air conditioned or heated room in environments where ambient temperatures in the open are extreme.
2. Purge the displacement fluid pump with the displacement fluid (diethylene glycol with older single cavity bomb type samplers or hydraulic oil if using the preferred floating piston type sampler - use of mercury is to be avoided and acidified brine can lead to chloride stress cracking in sample containers)
3. Hook up the pump to the shipping container (see figure 1 of this appendix) leaving the final connection loose then purge lines with displacement fluid through this loose connection.

4. With a floating piston type sampling tool the top of the sample chamber is then connected to the top of the shipping container filled with displacement fluid .

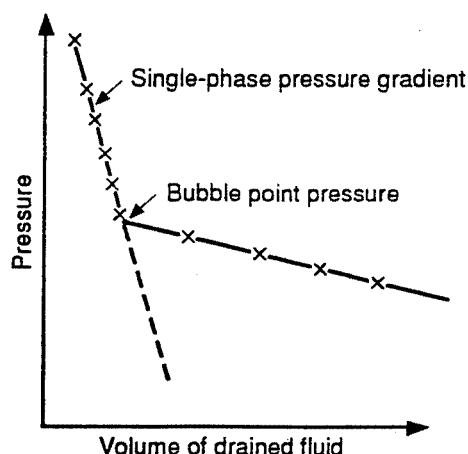
With a simple double valve sampling chamber, the bottom of the sample chamber is connected to the top of the shipping container.

5. Ensure that all parts of the transfer circuit are purged and pressured to sample pressure prior to the transfer.
6. The sample must be in single phase during the transfer operation. For liquids (and subsurface sampling should only be used for liquids!) this can usually be ensured by pressuring the sample chamber and the shipping container to about 1,000 kPa above sampling pressure (or reservoir pressure or hydrostatic if the sampling pressure is unknown). Ensure that the tool and shipping container pressure rating are not exceeded.
7. Open all valves between the sample and shipping containers.
8. Pressure the system using the floating piston (usually with hydraulic fluid and so two pumps will be necessary) until the system pressure returns to  $\pm 1,000$  kPa above the expected bubble point pressure (usually  $\pm 1,000$  kPa above the reservoir pressure).

With the simpler sampling tool (non floating piston type ) the system is pressured by opening all valves between shipping and sample containers then pumping displacement fluid through the shipping container into the sample container.

9. Shake the sample chamber vigorously for 10 minutes. After this time note the system pressure. If it is not still 1,000 kPa above expected bubble point pressure then re-pressurise and shake again.
10. Accurately bleed off 2 cm<sup>3</sup> displacement fluid into a 10 cm<sup>3</sup> measuring cylinder. Shake the sample chamber for at least 2 minutes until the pressure is steady. Note the pressure.

11. Plot a graph of pressure vs volume drained as below.



12. Repeat in  $2 \text{ cm}^3$  steps until the gradient changes. Shake the sample chamber for at least 2 minutes until the pressure is steady at each step. If the oil is light with a high GOR then a sharp change in gradient will be observed. If the oil is heavy or has only a very small amount of dissolved gas then a more gradual change in gradient will occur.

In any event continue draining in  $2 \text{ cm}^3$  steps until a new lower straight line gradient is established. Extrapolate the final gradient and the initial one to their intersection which should be reported as the bubble point.

As a guide-line the following table indicates expected single phase pressure gradients for typical fluids and standard sample volumes:

Fluid Type	Pressure Gradient (approx.) (kPa/ml)
Water	1720 - 2070
Oil	1030 - 1380
Gas	14 - 35

13. If the bubble point is satisfactory (ie matches previous samples or is as expected) then use the floating piston to re-pressure the system to 1,000 kPa above bubble point. Then continue to displace the sample from the tool into the shipping container until the sampling tool is emptied or a maximum of 85% by volume of the displacement fluid has been displaced from the shipping container. Maintain the system pressure 1,000 kPa above bubble point pressure during the transfer by operation of the bottom valve of the shipping container.

With the non floating piston sample chamber, the system must be re-pressured by pumping displacement fluid back into the bottom of the shipping container and then displacing the sample back in to the sampling tool. Transfer of the sample from the tool into the shipping container is then done by connecting the displacement pump to the bottom of the tool and connecting a purged line from the top of the tool to the top of the shipping container. Transfer of the sample is carried by pumping displacement fluid into the tool and operating the valve on the bottom of the shipping container until a maximum of 85% by volume of the displacement fluid has been displaced from the shipping container. Maintain the system pressure 1,000 kPa above bubble point pressure during the transfer by operation of the bottom valve of

## Appendix 5

the shipping container.

14. Close the top and bottom valves of the shipping container and disconnect the shipping container from the sampling chamber. Then drain a further 10% by volume of the displacement fluid in order to provide space for thermal expansion during transport. This should leave approximately 5% by volume of the displacement fluid in the container. Never allow any reservoir fluid to be drained. Always calculate a safe maximum amount of displacement fluid to be drained. The sample cylinder must be kept upright during this process.
15. Make sure that the sample container is not leaking by testing with soap solution and install valve protection where appropriate.
16. Label the shipping container clearly with:
  - Well/Field/Country:
  - Sampling interval (ie perforated interval open)
  - Sampling depth (TV and AH)
  - Pressure of shipping container
  - Field measured bubble point.
  - Temperature at which the container was closed
  - Displacement fluid used (hydraulic oil or DEG)
  - Date of sampling
  - Identification number of sample
  - Sample bottle number
  - Name of the individual who has taken the sample
  - Name of the individual who has requested the sample.