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Chartered Engineers**

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"Pipeline Oil Analysis for Allocation at Ecofisk"

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Pipeline oil analysis for allocation at Ekofisk.

1.0 Introduction

Flow metering is not complete without some sort of quality parameters on the gas or liquid measured.

This paper will give an overview on how we at Ekofisk perform crude oil analysis so that you can see what crude oil analysis for allocation on component basis involves.

I will give you a background for the need of the analysis, the quality parameters that are required, how we find these and share our offshore experience on methods and equipment with you.

2.0 Background

As you know, Ekofisk Centre is an important part of the transport route of both oil and gas in addition to a process plant. The high vapour pressure oil is processed at Ekofisk Centre and Teeside takes out products before the oil is ready for sale. This is the reason for the need of component allocation. The mass of each component must be allocated back to the fields delivering the oil and gas to Ekofisk Centre.

The Ekofisk lab is both an allocation lab and usual process lab. We analyse 13 oil streams for allocation purpose and the samples are based on spot samples, monthly flow proportional samplers and daily composite samplers.

3.0 Parameters required.

This is regulated in the agreements between involved parties and companies.

The appendix B&C to the agreements gives the guidelines for the sampling and analysis. The following analysis is required for owner ship allocation of oil:

- Water content.

- Salt content.

- Composition of oil in wt%,grouped as:
  Nitrogen
  Carbondioxide
  Methane
  Ethane
  Propane
  Iso and normal butane
  Iso and normal pentane
  Hexanes
  Heptanes plus (C_7+)

- Sp.gravity of heptanes plus (C_7+)

- Average molecular weight of heptanes plus (C_7+).

It is also required that the analytical work on samples should be in an identical manner for all like samples.

The sampling required is monthly composite sampling, this is backed up with spot samples.
In addition we have Daily composite samplers for water determination on the major streams.
ISO 3171, Petroleum liquids-Automatic pipeline sampling is our reference for the automatic sampling of oil.

4.0 Analysis.

I will concentrated on the phase after a representative sample has been obtained, but i will stress that without a representative sample the rest of the work is worthless.

The analytical parameters will be described in the following order:
4.1 Water content of oil.
4.2 Salt content.
4.3 Composition.
4.3.1 Specific gravity.
4.3.2 Average molecular weight.

4.1 Water analysis.

Reference:ASTM D4377-86

Introduction:

The ASTM D4377-86 describes the use of potentiometric titration instrument, but we use a coulometric instrument.It has been proved that this technique is capable of producing the same result as the potentiometric titration. Some of the advantages with coulometric instrument is less chemical cost, less man-handling and no calibration required.

In addition we checked if any of the inhibitors in use had any effect on the results prior to implementing the method.

Apparatus:
Aquatest or equivalent coulometric instrument.

Principle:

A subsample is taken out after proper homogenization and titrated with pyridine free Karl Fisher reagent to an electronic end point. The standard used is one unit of electrolytic current, 96 500 coulombs = 1 chemical equivalent of water. (1 coulomb=1 Amperesecond)

Overall reaction:

$$H_2O + I_2 + SO_2 \rightarrow 2HI + SO_3$$
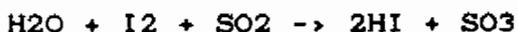
The iodine needed for this reaction is generated by the instrument, and the current consumption used for this is the basis for the measurement.
The result is reported as weight %.

Precision Pyridine-Free Karl Fischer reagents:

Repeatability = 0.037 ($X^{1/2}$)
where X = sample mean from 0.0 to 2%.

4.2 Salt determination (Electrometric method)

Reference :ASTM 3230-83

Summary :

The method is based on the conductivity of a solution of crude oil in a polar solvent when subjected to an alternating electrical stress,
This method will measure conductivity due to salts in the crude oil. A calibration curve is made by using a salt solution with a composition typical for a wide range of crude oils.
($NaCl:CaCl2:MgCl2$, 70:10:20)
The sample is dissolved in a mixed solvent(n-butanol,methanol) and placed in a test cell consisting of a beaker and two parallel stainless steel plates. The resulting current is shown on a milliammeter. The salt content is obtained by reference to the calibration curve. (Current versus salt content of known mixtures.)

Apparatus: GCA salt in crude analyzer or equivalent.

Precision:

The ASTM 3230-83 does not give any repeatability data but we use the IP265 as a guideline, this gives the repeatability as 0.3 times the square root of the salt reading.

4.3 Composition

References:
The method is based on the following ASTM methods:
ASTM-D2892-84 Distillation of crude petroleum.
ASTM-D2163-87 Analysis of liquid petroleum gases by gas
                        chromatography.
ASTM-D1945-81 Analysis of natural gas by gas chromatography.

Summary:

The method is a combination of fractional distillation and gas chromatography. The high vapour pressure sample is split into 3 fractions that can be handled separately and then recombined to find the composition.

The method requires the following equipment:

Distillation unit (3650 Semical distillation unit or similar)

Vacuum pump

Calibrated vapour receivers (2 ea 19 1, 1 ea 32 1)

Cooling system

Pressure control system

Pressure indicators

Gas chromatographs (HP 5890 or similar)

Integrators (HP3392 A or similar)

Computer system.
We use an HP A600 computer to control the gas chromatographs and
to collect the data. The software for this is delivered by HP.
The calculation, reporting and transmission to the main computer
onshore are handled by a program developed by PPCON.

Summary of the procedure:
A sample is collected into a sample cylinder (sliding piston
type.)

This sample is in our case a high vapour pressure liquid sample
that is difficult to handle directly into gas chromatographs.
Due to this we need to split this sample into fractions that are
more easy to handle.
The distillation unit is used for this purpose.

The distillation unit and the vapour receivers are evacuated
until constant pressure is obtained. (1-4 mmHg)

The sample cylinder is connected to the 1 l distillation flask at
the bottom of the distillation unit.

The valve on the sample cylinder is opened carefully and the
evaporated gas from the sample is taken over to the vapour
receivers at a controlled rate.

The sample cylinder is disconnected when the whole sample is
charged to the distillation flask.

We continue to take off gas until the distillation temp is 28
degree celsius. This phase is called vapour phase or C_1-C_4
fraction.

The next phase is collected into a liquid receiver with a coolant
jacket. The collection of this phase is stopped at 93 degree
celsius.This phase is called C_5-C_6 fraction.

The remaining phase in the kettle is called kettle bottoms or C_7+ fraction.

The next step is to use the gas chromatograph.

A few words about the principle of a gas chromatograph:The main component of a gas chromatograph is a coiled tubing, called column. This column can be filled with a support (example:finely crushed firebricks 0.15-0.25 mm or 60 -100 mesh ASTM) and covered with a stationary phase(example:Silicon oil.)
This column is placed in a temperature controlled oven, and the gas sample is transported through the column using an inert gas (helium). The components in the gas will be delayed more or less and reach the detector at different times. The component is then detected on the detector and recorded as a peak on the integrator. This peak is integrated and used to quantify the component.

The original high pressure crude oil sample is now split into 3 fractions that can be handled for further component analysis.

The 3 fractions are:
C_1-C_4 vapour fraction
C_5-C_6 liquid fraction.
C_7+, kettle bottoms, liquid fraction.

They are analyzed in the following way:

C_1-C_6

The sample in the vapour receivers are mixed and a subsample is transferred to a sliding piston type sample cylinder.

This sample is analyzed on a gas chromatograph and we find the mol% of each component including C_7+.

The composition, temperature, volume and pressure is used to calculate the amount of vapour and the weight of each component in the vapour.

C_5-C_6

This sample is also analyzed on the GC but here we get the weight % directly. Also the total weight of this fraction is known and this together with the composition gives us the weight of each component.

C_7+

This fraction is analyzed for specific gravity and molecular weight.

4.3.1 Specific gravity measurement.

Reference:
The method used is based on ASTM D 4052-86

Summary:
Approximately 1 ml liquid sample is introduced into a oscillating sample tube. The mass change of the tube cause a change of the oscillating frequency.
Calibration factors is found by using air and deionized water as reference.

Apparatus:
Anton Paar DMA 46 or equivalent.

Formula:
Density = $(T^2 - B) / A$
T=Period of the oscillation
A, B=calibration factors.

Precision:
Range	Repeatability	Reproducibility
0.68 - 0.97	0.0001	0.0005

4.3.2 Average molecular weight.

Reference:
This method is developed by PPCo R&D .

Summary:
The method is based on freezing point depression of benzene.
A known amount of C_7+ is added to benzene. The difference of freezing point between the pure solvent and the mixture is used to estimate the molecular weight of the C_7+ fraction.
The freezing point is reached by supercooling and seeding to create a sudden freezing. The instrument is calibrated with a benzil standard (Molwt 210.23) before each analysis.

Apparatus:
Roebling Kryometer or equivalent.

Precision:
Repeatability:Maximum allowable deviation between two parallels is 4.

The measured specific gravity and molecular weight of C_7+ is corrected for C_7+ present in the other fractions.

When the specific gravity , the molecular weight and the weight of the C_7+ are found we are ready for the recombination calculation.
The weight of each component in the 3 fractions are recombined and the composition of the original sample is found.

The final report is transmitted to the main computer and after a
final check by the production control unit it is ready for use in
the allocation report.

Precision.
No precision data available from ASTM on this composition method.
But the following guidelines was given in the initial method:

Component	Liquid, Wt.% % of amount present.
Nitrogen	–
Methane	5.0
Ethane	3.0
CO_2	3.0
Propane	2.0
Isobutane	2.0
n-Butane	2.0
Isopentane	2.0
n-Pentane	2.0
Hexanes	2.0
C_7+	1.0

Molecular Weight of C_7+ 2% of value.
Specific Gravity of C_7+ Value +/- 0.001

The repeatability checks performed are usually well within these
limits, typical value for C_7+ is 0.3 - 0.4% of amount present.

4.4 Experience on analytical methods and equipment.

Personnel
Allocation analysis must be performed by skilled people, the
importance of these data requires that. This work can not be
left to an operator as a part time job, this includes the
important sampling step.

Quality control.
The personnel, instruments, methods and calculations must be
followed up on a regular scheduled basis to ensure quality
allocation data. All reports are checked thoroughly before
transmission to the main computer.

Equipment:

Water determination.
The coulometric Karl Fischer instrument has been used for general
water determination since around 1980. The instrument is easy to
use and require minimum service. Two new instruments were
installed during 1988. Due to the environmental aspects we use
Pyridine free Karl Fischer solutions.

Salt in crude.
This method and instrument is used fieldwide by both us and the operators(on well test samples). The method has been used since start up of Ekofisk. The construction is rugged with few moving parts, but those that can be moved need regular replacement (Potentiometers etc).

Density measurements.
The instrument used is reliable and during approx 10 years service only normal maintenance work has been required.
It is also easy to use and calibrate.

Average molecular weight C_7+.
The present instrument was bought in 1984, and only normal maintenance has been required. The instrument require zeroing and recalibration before each analysis.

Distillation unit.
The original equipment has been modified several times since it was installed around 1975.
The modifications include change out of mercury switch and use of non mercury pressure indicators. This was done to avoid mercury spill sources and to simplify the operation of the equipment. The column handles our distillation needs very well.

We are now looking into more automated equipment to replace the old unit. A new unit can save manhours and give us more space.

Gas chromatographs, integrators and computers.

We increased our analytical capacity in 1985 when we bought new gas chromatographs (GC), integrators and computers. We have also replaced an old GC with a new GC this year.
The investment in 1985 was also a change in instrument layout, we changed from integrated all in one modules to a modular system which i easier to maintain on stream and a less vulnerable system. In my view this is the best approach for an offshore installation, it may be difficult to get a service man offshore and in many cases the module failing can be sent onshore for repair.

Since our deadlines can be tight we need to be able to provide results all the time, even if something breaks down. Our system is relative flexible in that aspect, a major break down of several modules is needed to stop our work.

Software

LAS

A program called LAS (Lab Automation System) is a part of the set up. This programs controls the gas chromatographs and collect data from the integrators. This ensure exact control of the instrument set up and reliable data. Also each run get a unique data file which cannot be altered, this give good data security and confidence in the system.

Calculation and transmission.

The calculation and transmission program was written by Information Services group in PPCoN in close cooperation with us. Involving the users at an early stage as possible is important and this program was up and running from the first day of installation, and the users were satisfied with the program. The Information Services group is responsible for maintaining this program and some additional options have been added after the installation.
The transmission program is used to transfer the data to a holding file after we have checked the report. The data is then transferred to the final destination after a check by Production Coordination Unit (PCU).

The transmission program replaced manual entry of our data to the main computer, this saved manhours and we got rid of a possible error source.

Methods.

The average molweight determination is not covered by an international standard, and we have not yet found an equivalent standard method. The molecular weight measured is in the range 100 - 300.

The other parts of the composition analysis are covered by standards, but the total composition method does not have a separate standard. This has caused different approach to parts of the method, especially the handling of the vapor.
The following variations are known:

- Displacement of Helium + wet meter + sampling bag.

- Vacuum + Receivers + Pressure measurements.

- Vacuum + Water displacement + Volume water displaced.

A standardization would be beneficial and it would also make it possible to establish reproducibility limits.

5.0 Conclusions.

Analysis of crude oil for allocation require skilled people and reliable instruments and methods.

It is important to include quality control as a part of the normal laboratory routines.

6.0 Future work.

-Contribute to a standardization of the composition method.

-Establish reproducibility limits for composition analysis of high pressure crude oil.

-Follow up the development within gas chromatography.
 Injection of high vapour pressure crude directly on a
 gas chromatograph can be a standard method in the future.

ATTACHMENTS

1. Distillation Equipment.

2. Flow chart oil analysis.

3. Recombination example.
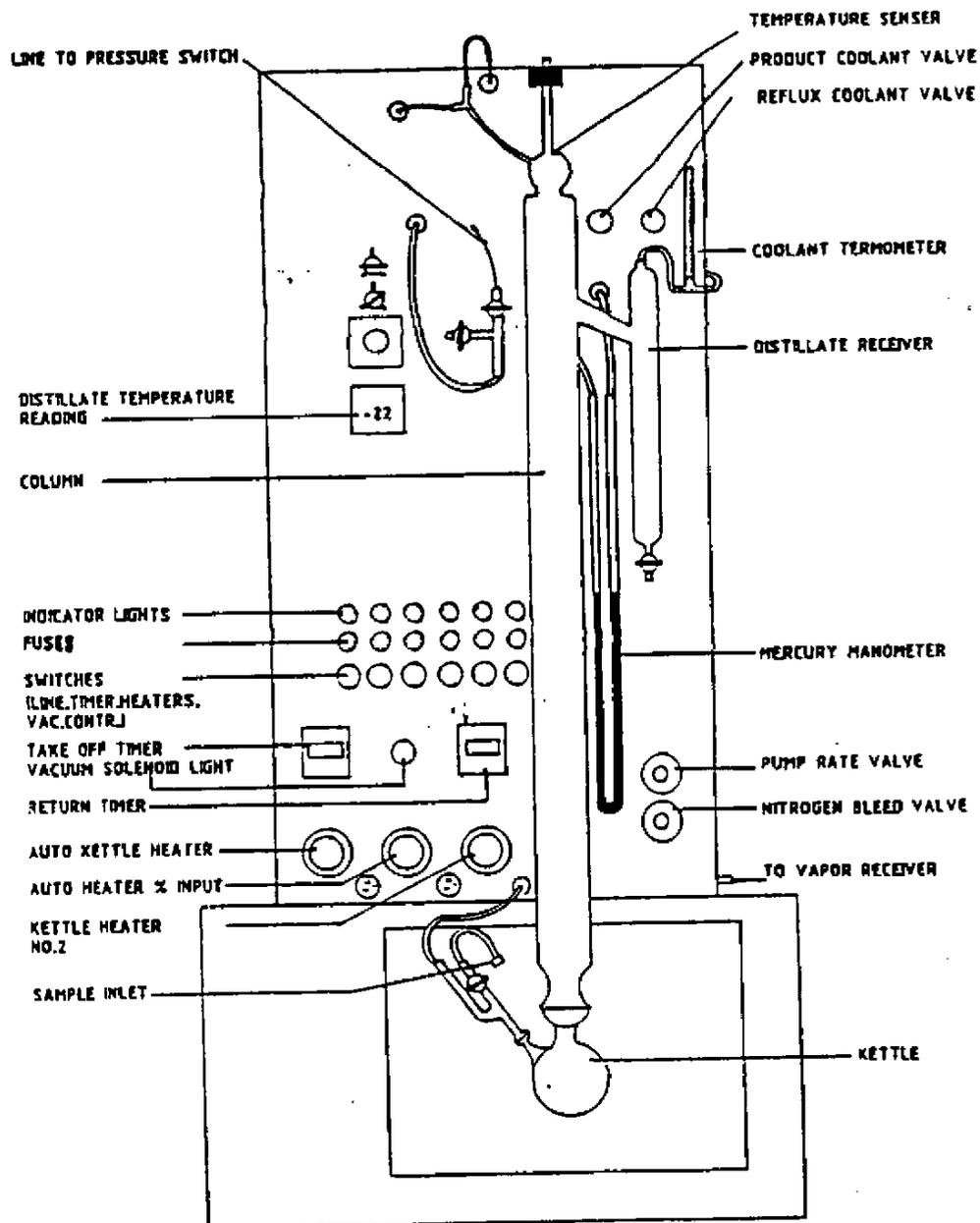
Figure 4.2.1. Arrangement of Semi-Cal Distillation
Apparatus, Series 3650

Attachment 2   Flow chart oil composition analysis.

```
                    ┌─────────────────────────────┐
                    │    Pressurized oil sample    │
                    └─────────────────────────────┘
                                   │
                         ┌───────────────────┐
                         │   Distillation     │
                         └───────────────────┘
                                   │
        ┌──────────────────────────┼──────────────────────────┐
        │                          │                          │
┌───────────────────┐    ┌───────────────────┐    ┌───────────────────┐
│   C1-C4 fraction   │    │   C5-C6 fraction   │    │    C7+ fraction    │
└───────────────────┘    └───────────────────┘    └───────────────────┘
┌───────────────────┐    ┌───────────────────┐    ┌───────────────────┐
│ Composition.       │    │ Composition.       │    │ Total weight.      │
│ Total weight.      │    │ Total weight.      │    │ Average mol        │
│ Weight of each     │    │ Weight of each     │    │ weight.            │
│ component.         │    │ component.         │    │ Specific           │
│                    │    │                    │    │ gravity.           │
└───────────────────┘    └───────────────────┘    └───────────────────┘
        │                          │                          │
        └──────────────────────────┼──────────────────────────┘
                          ┌───────────────────┐
                          │   Recombination    │
                          └───────────────────┘
                                   │
                          ┌───────────────────┐
                          │      Report        │
                          └───────────────────┘
```
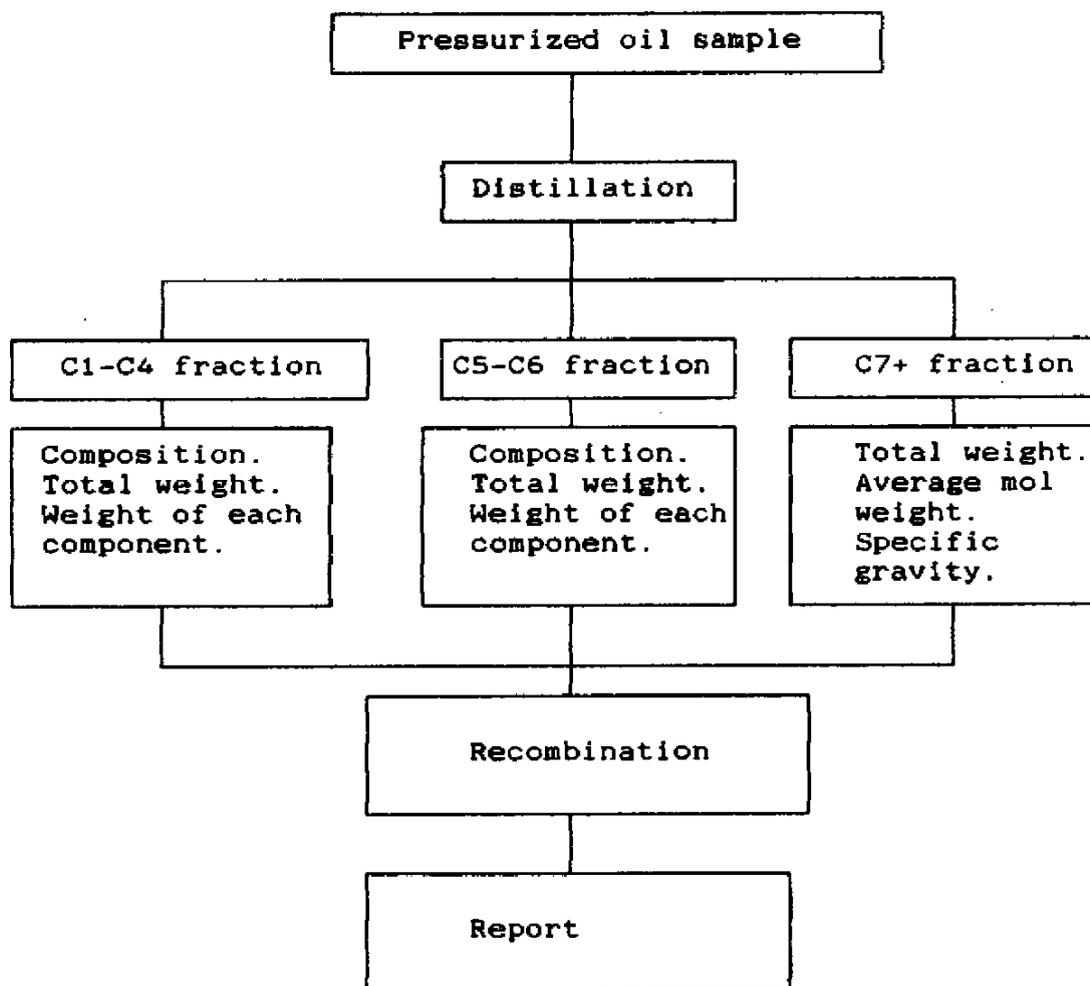
The final composition is determined by adding the weight of each component in the 3 fractions.

Compo-nent	Vapor (C_1-C_4)		Distillate (C_5-C_6)		Kettle residue (C_7^+) wt.	Combined	
	wt%	Wt. of each component	wt%	Wt. of each component		gram	wt%
N_2	0.06	0.02	0.00	0.00		0.02	0.01
CO_2	0.66	0.21	0.00	0.00		0.21	0.09
C_1	1.48	0.48	0.00	0.00		0.48	0.20
C_2	17.98	5.83	0.01	0.00		5.83	2.47
C_3	33.27	10.79	0.11	0.04		10.83	4.58
IC_4	10.10	3.27	0.63	0.24		3.51	1.48
NC_4	24.69	8.00	5.32	1.99		9.99	4.22
IC_5	4.62	1.50	10.43	3.91		5.41	2.29
NC_5	4.22	1.37	16.56	6.21		7.58	3.21
C_6	2.08	0.68	44.21	16.57		17.25	7.29
C_7^+	0.84	0.27	22.73	8.52	166.57	175.36	74.16
Total	100.00	32.42	100.00	37.48		236.47	100.00

References

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

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