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Determination of the cadmium content of various types of crude oil

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Summary

The Dutch Ministry of Housing, Spatial Planning and the Environment (VROM) commissioned TNO in 1993 to investigate the presence of cadmium in crude oil. This research project should be seen as a follow-up of an earlier study [1] by the Dutch National Institute of Public Health and Environmental Protection (RIVM). On the basis of a literature survey, RIVM in its study had estimated that the Refining Industry was a major source (490 kg/year) of the cadmium emissions resulting from combustion of oil products in The Netherlands (total cadmium emission is 960 kg/year). The data in the literature survey show a wide variation in the cadmium concentrations measured, from which RIVM derived an average cadmium concentration of 150 $\mu g.kg^{-1}$ in crude oil. However, the validity of this average concentration was questioned and also the conclusions in the RIVM report which were based on this figure. The Ministry decided that an extensive sampling and analysis programme should be launched to investigate the presence of cadmium in crude oils representative of the crude oils processed in the Netherlands. This research programme should answer the question whether the Refining Industry is to be comsidered as a major source of cadmium emissions or not.

At the request of VROM, TNO was asked to determine the cadmium concentration of the main crude oils imported in the Netherlands. Therefore, TNO developed a method for:

1) sampling crude oil from ships and from the in-line sample
2) determining cadmium in samples of several types of crude oil, representative for 80% of the crudes processed in Dutch refineries.

To avoid contamination of the samples, a specific sampling protocol was drawn up, using a custom-made sampler.

The applied analytical method (ZETA-AAS) has been validated. The performance data of the method are:

- Linearity : 0 - 60 µg Cd/kg crude oil
- Limit of detection (3Õ) : 0.4 µg Cd/kg crude oil
- Repeatability : 5 %
- Reproducibility : 10 %

The crudes investigated were Arabian Heavy, Arabian Light, Iranian Heavy, Iranian Light, Ural, Stattfjord, Kuwait and Oseberg. For each type of crude oil one cargo was sampled, except for Iranian Heavy and Arabian Light.

For Iranian Heavy and Arabian Light five different cargoes were sampled in order to assess whether the different batches show any variation and to establish possible seasonal variation.

According to this sampling scheme (6 x 1) + (2 x 5) = 16 cargoes were sampled in total.

Whenever permission was given for sampling on board of the vessel, five samples were taken from each cargo, i.e. :

- one sub-sample from the in-line sample. The in-line sample was obtained by an automatic sampler from the discharge pipeline, whose contents were continuously mixed by means of a so-called Power Mixer system. Sub-samples were taken from the in-line sample at the Terminal-lab after careful mixing using a closed-loop static mixer system. In all cases the static mixer system, used for mixing the in-line sample was previously rinsed with the type of oil under investigation.
- two samples taken about one metre below the oil surface of two randomly chosen centre tanks on board the tanker
- two samples from the bottom of the same tanks

The in-line sample is a time proportional sample and represents the total cargo, which consists of oil including some water and sediment. The in-line sample would yield data on cadmium imported in the Netherlands through crude oil cargoes irrespective whether the cadmium is indigeneous to the crude oil or present as (a random) contamination. The top and bottom samples from the ships tanks serve as a back-up and could provide a possible way to assess the nature of the cadmium source, e.g. the oil itself or random contamination.

For all 16 cargoes sub-samples of the in-line sample were analysed. For three cargoes also the top and bottom samples were analysed.

The cadmium contents of the crude oils investigated based on the in-line samples were found to be:

Type of oil*	Average cadmium content in crude oil (n=10)									
	cargo 1		cargo 2		cargo 3		cargo 4		cargo 5	
	µg Cd/kg	date	µg Cd/kg	date	µg Cd/kg	date	µg Cd/kg	date	µg Cd/kg	date
Iranian Heavy	0.5	Dec.'93	1.3	March'94	3.2	May '94	1.0	May '94	0.5	May '94
Arabian Light	0.7	March'94	0.5	April'94	3.7	July'94	5.3	Aug.'94	0.1	Dec.'94
Arabian Heavy	0.5	May '94								
Iranian Light	0.8	June'94								
Ural	0.7	Feb.'94								
Stattfjord	2.4	May '94								
Kuwait	0.2	Dec.'94								
Oseberg	2.1	Feb.'95								

*) The two most frequently processed crudes, i.e. Arabian Light and Iranian Heavy were sampled from five different cargoes and the other ones from a single cargo.

Conclusions

- The crudes investigated contain low amounts of cadmium, roughly 100 times less than estimated by RIVM. It can therefore be concluded that crude oil is not a major source of cadmium emission in the Netherlands. The much lower concentration of cadmium as established in this study compared to some data reported in literature [3,4] is probably due to improper sampling and/or analysis of those former studies. Utmost precautions have been taken in this study to avoid contamination and, in addition, the analytical method has been validated before use.

- For Arabian Light the different crude cargoes show some variation in cadmium concentration, indicating that there could be a seasonal influence.

- Analysis of the top and bottom samples of three selected crudes show that the bottom samples contain the highest cadmium concentration: about 10 µg $Cd.kg^{-1}$ sample, probably due to the elevated sediment concentration in bottom samples. This indicates that cadmium in crude oil cargoes is associated with the sediments present rather than with the hydrocarbon matrix.

The project was conducted under the guidance of a Steering Committee chaired by VROM and comprising representatives of VROM, SHELL, ESSO, BP and DCMR (Regional Environmental Authority of Rotterdam, NL).

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1. Introduction

1.1 Motive and goal

The environmental objectives as listed in the National Environmental Policy Plan define reduction targets for the emissions of heavy metals in the Netherlands. The Dutch Ministry of Housing, Spatial Planning and Environmental Protection (VROM) aims at reducing the emissions of heavy metals by 70% in the year 2000. One of the heavy metals of interest is cadmium.

In the 'Baseline Study on Cadmium' [1], performed by the Dutch National Institute of Public Health and Environmental Protection (RIVM), the Refining Industry was identified as a major source of cadmium emission within the whole set of emission sources in the Netherlands, which is 960 kg/year. The emissions of cadmium from the processing of mineral oils in refineries, according to this study, leads to a total cadmium emission of about 490 kg/year. The estimate of this study was based on a literature survey [1] which indicated an average cadmium content in crude oils of 150 $\mu g.kg^{-1}$.

However, the 'Baseline Study on Cadmium' [1] also mentioned the possibility that this value could be too high, since measurements at Shell [2], performed in 1984, showed an average cadmium concentration of 11 $\mu g.kg^{-1}$ (range 1-1200 $\mu g.kg^{-1}$). So the validity of the data used for the estimation in the 'Baseline Study on Cadmium' [1] was questioned and more accurate data were needed.

Furthermore, a very wide range of cadmium concentrations in crude oils is found in literature [2]. In 1984, Narres et al. [3] reported an average cadmium concentration of 0.10 $\mu g.l^{-1}$, which is very close to the detection limit of 0.06 $\mu g.l^{-1}$, in four crude oil samples from different origins. In 1983, Ali et al. [4] found an average of 900 $\mu g.kg^{-1}$ in fourteen different Arabian crudes. The two averages differ by a factor of approximately 7000.

More recently, in 1990, Al-Swaidan [5] confirmed the magnitude of the values reported by Ali et al. [4] using ICP-MS techniques. In five different Arabian crudes an average cadmium concentration of 500 $\mu g.kg^{-1}$ was found.

The above-mentioned data also emphasize the need for a correct analytical method to determine cadmium concentrations in various crude oils with better accuracy.

1.2 Assignment and organisation

At the request of VROM (see Annex 1), TNO was asked to determine the cadmium concentration of the main crude oils imported in The Netherlands with better accuracy.

Due to wide variations in cadmium concentrations measured (vide supra), the Steering Committee decided in an early stage of this project that the investigation into the presence of cadmium also had to establish whether high concentrations of cadmium, if present, were the result of high natural background levels of cadmium for some crudes or resulted from contamination of the crude by 'other' sources[1] or could be due to sampling and/or analytical problems.

Therefore, it was decided that the research programme should allow for sampling and subsequent analysis of top and bottom samples taken directly from the cargo tanks of the vessel, thereby allowing further investigation, where this would be useful, to establish the possible causes (vide supra) whenever substantial higher cadmium levels were found in the subsamples of the in-line samples[2].

Accordingly, TNO set up and executed a research proposal (see Annex 2), which comprised:

- Preparation of a sampling protocol aimed at establishing a set of procedures to be used during sampling and storage.
- Development of a special sampler for taking top and bottom samples on board of crude carriers.
- A validation study for the determination of cadmium in crude oil by graphite furnace atomic absorption spectrometry (ZETA-AAS).
- Determination of the cadmium content of various types of crude oil regularly processed in Dutch refineries.

Sampling on board of the vessels was conducted by Saybolt Nederland BV under supervision of and in close cooperation with TNO.

To avoid misleading results caused by sampling or the analytical method, special measures were taken as described in this report.

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1 With respect to 'other' sources, crude oil may be contaminated with cadnium originating from remnants of an earlier cargo (non-crude oil, e.g. ore), ballast water, sand, dust, mud, seawater, paint, etc..

2 The in-line sample is a time-proportinal sample and represents the total cargo, which consists of oil including some water and sediment.

The project was conducted under the guidance of a Steering Committee chaired by VROM and comprising representatives of VROM, SHELL, ESSO, BP and DCMR (Regional Environmental Authority of Rotterdam, NL).
All Steering Committee meetings were recorded.

2. Sampling

2.1 Sampling strategy

It was decided that a set of 10 different crude oils, regularly processed in the refineries in the Netherlands, would provide a sufficient matrix for the investigation whether cadmium present in crude oil was a major source of total cadmium emissions in The Netherlands or not. The original set of crude oils selected for the investigation and their share in the total crude quantity processed in The Netherlands is listed below. Note should be taken that it became clear during the final stage of the sampling programme that within the timespan of 1_ year taken for the whole sampling programme, no cargoes of the two selected Nigerian crudes (Bonny Medium and Forcados) had arrived or would arrive within a reasonable timespan at the Rotterdam terminals participating in the project. Therefore, the sampling and also the analysis of these two crudes had to be abandoned, and thereupon it was decided to limit the programme to eight crudes instead of the ten crudes listed below. Nevertheless, on the basis of their relative weight the eight crudes that where sampled in the programme represent about 72% of the total quantity of crudes processed in the refineries in the Netherlands in the period 1992-1994.

Relative Share of Crudes Processed in Dutch refineries 1992-1994

Crude type/origin	Relative share (%)
Arabian Light	18
Iranian Heavy	9
Arabian Heavy	8
Iranian Light	8
Arabian Medium	2
Kuwait	16
Stattford	6
Oseberg	5
Nigerian crudes	6
Other crudes	22
Total	100

As data reported in literature had shown wide variations in the cadmium levels measured, the sampling scheme was set up in such a way as to allow an analytical investigation into the possible causes of significant higher cadmium levels that might turn up during the analytical part of the programme. Subsequent analysis of top and bottom samples taken on-board of the vessel of "suspected" cargoes would then provide additional information on the basis whereof conclusions might be drawn on the likely causes of the higher cadmium concentrations.

In addition, the two most frequently processed crudes were sampled from five different cargoes in order to assess whether the different cargoes show any variation and to allow a judgement as to whether there is any seasonal variation in the cadmium content.

Consequently (6 x 1) + (2 x 5) = 16 cargoes have been sampled.

A sub-sample of each cargo was taken from the 'in-line' sample, which is a time proportional sample, after mixing it in a so called 'Power Mixer'. From the same cargo samples were taken on board from the top (approximately one meter below the surface) and the bottom layers of two randomly chosen tanks. The first and last tanks which were loaded were excluded from sampling (see section 2.2).

2.2 Sampler and sampling procedure

In order to assure uncontaminated sampling from the ships tanks a special sampler was constructed. It consists of a glass bottle mounted in a teflon-coated stainless steel holder (see Annex 3). Because of its size it could only be lowered through butterworth holes on deck.

The following tanks on board of the vessel were omitted from the selection in advance:
- the first tank that was loaded (in view of any possible line fills).
- the last tank that was loaded (in view of possible stripping).
- wing tanks (owing to possibly irregular bottom surfaces, which would obstruct the proper sample taking).

From the remaining centre tanks two were selected at random for sampling.

A sampling protocol was drawn up to ensure proper sampling. The protocol gives detailed measures to ensure that the samples were representative and uncontaminated (see Annex 2).

2.3 Terminal location

Most of the cargoes were discharged into shore tanks at the Texaco-Esso Maatschap Europoort Terminal (TEM[1]), with some of the oil being transported to Maasvlakte Oil Terminal (MOT), resulting in two in-line samples of one cargo (two Power Mixer samples).

One cargo was directly discharged at MOT and one cargo was discharged at the Shell Terminal (Europoort Terminal, Shell Nederland Raffinaderij B.V., Rijndwarsweg 21, 3198 LC Europoort).

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1 The name TEM was changed during the project into TEAM.

The sub-samples of the in-line samples were taken from the 'Power Mixer' at Nerefco Laboratory (all samples from TEM/TEAM) and for the cargo discharged at the MOT at the local MOT-laboratory, and for the cargo discharged at the Shell Terminal at the local Shell-laboratory.

3. Samples

3.1 Types of crude oil and samples

Whenever permission was given for sampling on board of the vessel, five samples were taken from the cargo, i.e.:

- one sub-sample from the in-line sample. The in-line sample is obtained by an automatic sampler from the discharge pipeline, whose contents are continuously mixed by means of a so-called Power Mixer system
- two samples taken about one metre below the oil surface of two randomly chosen centre tanks on board the tanker
- two samples from the bottom of the same tanks

Appropriate cargo data were taken from the logbooks of the crude carriers involved (Annex 5). The actual depth of the tanks was measured after sampling.

Table 1 lists the types of crude oil that were sampled. As permission for on-board sampling was sometimes refused, it was not always possible to take five samples of each cargo. If on board sampling was refused, only the sub-sample of the in-line sample (PM-sample) was retained.

The samples taken are listed in Annex 6, together with their TNO sample codes.

The sub-sample of the in-line sample represents the total cargo, which consist of oil including some water and sediment. The sub-sample is taken from the in-line sample at the lab after careful mixing by means of a closed-loop static mixer system. In all cases the static mixer system, used for mixing the in-line sample was previously rinsed with the type of oil under investigation.

Since water and sediment tend to settle to the bottom of the tanks during the voyage, the top sample will contain rather little water and sediment, whereas the bottom sample may contain a substantial quantity of water and sediment.

3.2 Sample bottles and labelling

2-Litre bottles made of colourless borosilicate glass were used for sub-samples taken from the in-line samples (PM-samples).

The samples taken one metre below the surface of the crude oil, and those taken as near as possible to the bottom of the tanks were collected in 1-litre bottles made of colourless borosilicate glass.

All sample bottles were cleaned inside and outside with nitric acid (Merck, Suprapur), followed by rinsing with demineralised Milli-Q water. Before use each sample bottle was packed in a closed plastic bag.

After taking samples the sample bottles were closed by a plastic screwcap with teflon inlay.

Immediately after being taken the samples were labelled. Labels were filled in fully with the following information:

- Sample taken from (Power Mixer/vessel)
- before/during/after loading/discharge/transfer
- Product
- Installation
- Sample description
- Date/hour of sampling
- Where applicable: vessel's cargo tank designation (PS1, C3, SB7 etc.)
- Name of inspector

An example of the label is shown in Annex 7.

3.3 Storage

The samples were transported by TNO to the TNO laboratory and stored in the dark at 4°C. All samples will be kept for three years after completion of the Study.

Table 1 Tankers which were sampled and some relevant particulars

Name of ship/type of oil/date	Type of sample taken*)	Remarks
Mega Hawk; Iranian Heavy; 27 December 1993	PM	Sampling on board the ship was not allowed due to the excessive H_2S content of the oil.
ESSO Langedoc; Iranian Heavy and Arabian Light; 7 January 1994	no samples taken	as above
Stena Conductor; Iranian Heavy; 8 January 1994	no samples taken	as above
Sereno; Ural Crude; 14 February 1994	PM; T1, T2, B1, B2	Relatively large amounts of sludge were found on the bottom of the centre tanks
Astro Alpha; Arabian Light; 21 March 1994	2xPM; T1, T2, B1, B2	Oil pumped to TEM and MOT
ESSO Demetia; Iranian Heavy; 24 March 1994	2xPM; T1, T2, B1, B2	High H_2S content; Oil pumped to TEM and MOT
ESSO Normandie; Arabian Light; 25 April 1994	PM; T1, T2, B1, B2	
Kristhild; Iranian Heavy; 2 May 1994	2xPM; T1, T2, B1, B2	Oil pumped to TEM and MOT
ESSO Demetia; Arabian Heavy; 9 May 1994	PM	Sampling on board the ship was not allowed due to the excessive H_2S content of the oil.
ESSO Demetia; Iranian Heavy; 9 May 1994	PM	
Bergina; Stattfjord; 21 May 1994	2xPM; T1, T2, B1, B2	Oil pumped to TEM and MOT
TV Irian; Iranian Heavy; 22 May 1994	2xPM	Oil pumped to TEM and MOT.
		Sampling on board the ship was not allowed due to the excessive H_2S content of the oil.
Edin.Satsuma; Iranian Light; 22 June 1994	2xPM; T1, T2, B1, B2	Oil pumped to TEM and MOT
Vanadis, Stockholm; Arabian Light; 20 July 1994	2xPM; T1, B1	Oil pumped to TEM and MOT. No time enough to sample the second centre tank
Esso Hawaii; Arabian Light; 25 August 1994	PM; T1, T2, B1, B2	
Pollux; Arabian Light; 7 December 1994	PM; T1, T2, B1, B2	
Kristen; Kuwait crude; 10 December 1994	PM; T1, T2, B1, B2	Sampled at MOT; PM-sample from power mixer MOT
Sunetta; Oseberg crude; 9 February 1995	PM; T1, T2, B1, B2	Sampled at Shell-terminal; PM-sample from power mixer Shell-terminal

*) PM = Power Mixer sample (= sub-sample of the in-line sample), T1 = Sample from top of first centre tank, T2 = Sample from top of second centre tank, B1 = Sample from bottom of first centre tank, B2 = Sample from bottom of second centre tank

4. Quality Assurance

The analytical method for the determination of cadmium concentrations in crude oils was validated as described in Section 6. The validation protocol that was used can be found in Annex 8.

One of the Test Samples, i.e. Arabian Heavy, was taken as a 'reference material'. From earlier experiments (see Annex 6) the 'reference' concentration of cadmium in this sample was found to be 0.52 ± 0.13 µg/kg crude oil (n = 30).

In the course of the project the cadmium content of the 'reference material' was repeatedly determined. The results are listed in Table 2.

Table 2 'Reference' concentrations of cadmium, measured in the course of the project

Date of analysis	Result (µg Cd/kg crude oil)
8 April 1994	0.62
13 July 1994	0.52
14 July 1994	0.62
15 July 1994	0.65
16 July 1994	0.65
19 July 1994	0.64
14 February 1995	0.47
14 February 1995	0.53
15 February 1995	0.48
26 April 1995	0.57

It can be concluded that in the course of the project all samples of crude oil were analysed under the same analytical conditions.

5. Analytical method

Several methods are described in literature ranging from direct methods (dilution of the sample as the only pre-treatment) to indirect methods (measuring the diluted digest of the sample). However, digestion of the oil matrix is sensitive to contamination and gives a rather high detection limit. For these reasons direct methods are preferred.

5.1 Scope

The method applied is based on a procedure described by Narres et al. [3], which is a direct analytical method, using graphite furnace atomic absorption spectrometry with Zeeman background correction (ZETA-AAS) involving a single dilution as the only pre-preparation of the sample.

The method has been tested by TNO for ruggedness of the graphite furnace temperature programme, repeatability, reproducibility, linearity, limit of detection, sensitivity, and accuracy.

The accuracy has been determined by comparing the method with an alternative method which differs both in sample pre-processing and the measuring method. The alternative method, i.e. wet ashing of the crude oil sample followed by dissolution of the ashing residue in nitric acid [6] was applied. The cadmium content of the resulting solution was measured by ZETA-AAS and, as an alternative, ICP/MS. This alternative method (indirect analytical method) has not been validated exhaustively. A rough agreement with the results of Narres's method was taken to be satisfactory.

The performance data of the direct (ZETA-AAS) method are:

- Linearity : 0 - 60 µg Cd/kg crude oil
- Limit of detection (3Õ) : 0.4 µg Cd/kg crude oil
- Repeatability : 5 %
- Reproducibility : 10 %

A summary of the direct method is given in this section, full details are given in Annex 9.

5.2 Principle

The cadmium content in crude oil is determined after dilution with carbon tetrachloride. The diluted sample is injected into a graphite furnace with L'VoV-platform and oxygen addition during the charring step. The spectrometer is equipped with Zeeman background compensation and an auto sampler.

5.3 Reagents

- Oxygen 99.9999%
- Argon 99.999%
- Carbon tetrachloride (Baker, reagent grade)
- Cyclohexanol (Baker, reagent grade)
- Nitric acid (65%) (Merck, Suprapur)
- Solution of cadmium benzenesulphonate, 5000 mg Cd/kg in a base oil (CONOSTAN®)
- Cadmium standard solution I, 10 mg Cd/kg
  0.2 g of the cadmium solution (5000 mg Cd/kg) was weighed out into a conical flask and made up to 100 g with cyclohexanol.
  (Note: the solution is stable for at least a month)
- Cadmium standard solution II, 100 µg Cd/kg
  1.0 g of the cadmium solution (10 mg Cd/kg) was weighed out into a conical flask and made up to 100 g with cyclohexanol.
  (Note: the solution is stable for at least a month)

5.4 Equipment

- Perkin Elmer 5100 PC Atomic Absorption Spectrometer adjusted to a wavelength of 228.8 nm, connected to a graphite furnace and provided with a facility for simultaneous correction of the background signal with the aid of a Zeeman correction system (ZETA-AAS) and an auto sampler
- A Perkin Elmer electrodeless discharge tube for cadmium.
- Diluter-dispenser, adjustable pipettes.
- Standard laboratory glassware.
  Immediately before use, all glassware was cleaned with warm, dilute nitric acid (Merck, Suprapur) and rinsed with Milli-Q water until free of acid. The glassware was then rinsed with acetone and dried.
- Ultra Turrax Mixer with a titanium shaft, type T25 IKA; 8000 - 24000 r.p.m..

5.5 Pre-preparation of the sample

After the sample bottle was unscrewed, the oil was homogenised for ten seconds using the Ultra Turrax Mixer and at once subsampled for analysis by weighing 2 grammes of the homogenised oil in a conical flask, followed by addition of 6 grammes of carbon tetrachloride was added. The resulting mixture was homogenised by hand.

5.6 Measurement procedure

The atomic absorption spectrometer was adjusted for the measurement of cadmium in accordance with the user's manual. A calibration curve was prepared for a cadmium content of 0 tot 10 µg Cd/kg crude oil, using a sample of crude oil with a low concentration of cadmium.

The following temperature programme[1] was applied:

Temperature Programme

step	Temp. (°C)	Ramp time (s)	Hold time (s)	Int. gas flow (ml/min)
1	150	10	0	300 O_2
2	250	60	0	300 O_2
3	450	100	0	50 O_2
4	650	100	100	50 O_2
5	650	1	39	300 Ar
6	650	1	5	0 Ar
7	1900	1	5	0 Ar
8	2400	1	3	300 Ar
9	20	1	9	300 Ar

The injection volume was 10 µl. The atomic absorption was determined at a wavelength of 228.8 nm, measured as a peak surface area. All injections were carried out in duplicate, unless otherwise stated. The calibration curve was corrected for the natural cadmium content of the oil matrix, using the instrument's incorporated software "Method of addition calibration".

1 This programme is based on the test results obtained in the validation study (see Annex 9).

5.7 Calculation

The cadmium content of the oil sample was calculated as follows:

$C = c \times d$, where

C = Cd concentration in undiluted sample (µg/kg)
c = measured Cd concentration in diluted sample (µg/kg)
d = dilution factor (w/w)

6. Validation of the analytical method

The results of the validation study are given in full detail in Annex 9. A summary is given in this section.

6.1 Influence of sample storage on the cadmium content of crude oil

Samples were collected in glass bottles (colourless borosilicate) and stored in the dark at 2- 8°C prior to analysis.

In a period of 4 weeks no evidence was found that (prolonged) storage of samples causes any loss of cadmium.

6.2 Distribution of cadmium in a sample crude oil after homogenisation

A Test Sample (in-line sample Arabian Heavy, taken by TNO on 23 March 1993 at Nerefco Laboratory) was homogenised for ten seconds with the Ultra Turrax Mixer and at once subsampled for analysis from ten positions within the sample for analysis. These positions were evenly distributed over the height of the sample bottle. The subsamples were measured for cadmium. The cadmium concentrations are listed in Table 3.

Table 3 Cadmium content of sub-samples crude oil taken from a Test Sample after homogenisation

Sample no.	Cadmium content (µg Cd/kg crude oil)	Sample no.	Cadmium content (µg Cd/kg crude oil)
1	0.95	6	1.04
2	1.02	7	1.44
3	0.99	8	0.89
4	1.02	9	1.15
5	1.43	10	1.91

The average concentration amounts: 1.18 ± 0.32 µg Cd/kg crude oil

The results show that the applied method of homogenisation is satisfactory.

6.3 Ruggedness of the graphite furnace temperature programme

The ashing and atomisation temperature of the graphite furnace was optimised in steps of 25°C using a Test Sample crude oil. When the final temperature programme for the graphite furnace had been decided upon, it was tested for suitability on different days with fresh graphite tubes.

6.4 Repeatability and reproducibility

The **repeatability** was assessed in order to gain an insight into the experimental error under 'constant' conditions. This means that the variance of the method was determined within the course of a day for the same equipment, the same operator and the same type of sample. The repeatability was determined for two different cadmium concentrations.

The **reproducibility** was assessed in order to gain an insight into the experimental error under non-constant conditions. The variable was taken to be the day on which the analysis was carried out.

The repeatability, according to ISO 5725-2,1994 was found to be: 6% (RSD^r at 5 µg/kg level).

The reproducibility, according to ISO 5725-2,1994 was found to be: 9.6% (RSD^r at 5 µg/kg level).

6.5 Linearity, limit of detection, limit of quantisation

The limit of detection is defined as three times the standard deviation of the cadmium content of a test sample with low amount of cadmium.

Consequently, the limit of quantisation is defined as 10 times the standard deviation of the cadmium content of the Test Sample.

The results for linearity, lower limit of detection and limit of quantisation are as follows:

- Linearity : 0 - 60 µg Cd/kg oil (undiluted sample)
- limit of detection : 0.4 µg Cd/kg oil (undiluted sample)
- limit of quantisation : 1 µg Cd/kg oil (undiluted sample)

6.6 Accuracy

The accuracy of a method is normally determined by the analysis of certified reference materials. However, for cadmium in crude oil, no such materials are available. Therefore the accuracy has been determined by comparing the method with another method differing from it both in sample pre-processing and measuring method, i.e. wet ashing of the sample followed by dissolution of the ashing residue in nitric acid.
The cadmium content of the resulting solution was measured with the aid of ZETA-AAS and, as an alternative, ICP/MS.
This method has not been exhaustively validated. A rough agreement with the results of the direct method was taken to be satisfactory.

Specimen of the Test Sample (Arabian Heavy crude oil) were pre-ashed with concentrated sulphuric acid and the residues were then ashed in a muffle furnace at 550°C. The ashing residues were then dissolved in diluted nitric acid, upon which the cadmium concentration of the solutions were determined with ZETA-AAS and ICP/MS.

The method was validated to a limited extent by analysis of a specimen of the Test Sample oil spiked with a known amount of cadmium[1]. The experiment was repeated several times, with inclusion of a blank.

The results of the wet ashing method are listed in Table 4.

Table 4 *Cadmium content of (spiked) crude oil, determined by wet ashing in combination by ICP-MS and ZETA-AAS. Also the results of the direct method by ZETA-AAS are given.*

Sample	Cd content in µg/kg crude oil		
	Method: wet ashing + ICP-MS	Method: wet ashing + ZETA-AAS	Method: direct by ZETA-AAS
Test Sample	1	1.3	0.58 ± 0.07 (n=10)[1]
Test Sample, duplicate[2]	12	10	
detection limit[3]	1.0	0.5	
Test Sample + 1000 ppb Cd[4]	1130	1230	
Test Sample + 1000 ppb Cd[4], duplicate	1190	1310	

1) Measured on different days (see Annex 6)
2) Duplicate Test Sample probably contaminated
3) The detection limit is defined as three times the standard deviation of the Cd signal of a blank solution (digest).
4) CONOSTAN[r] metallo-organic standard (organic sulphonate in a base oil)

Conclusion

The results of the wet ashing method corroborate the direct method.

Note: The dilution preceding wet ashing causes the cadmium content to approach the lower detection limit.

1 CONOSTAN® metallo-organic standard (organic sulphonate in a base oil).

7. Cadmium content of various types of crude oil

7.1 In-line samples

The cadmium content of sub-samples of the in-line samples (PM-samples), analysed in tenfold, are summarised in Table 5, together with some other relevant details.

Table 5 Cadmium content of various types of crude oil regularly processed in Dutch refineries

Type of oil/date	In-line sample (PM-sample)/Terminal	Average Cd content + s.d. (µg/kg) of in-line sample (n=10)	Other samples available
Iranian Heavy; December 1993	PM-TEM	0.46 ± 0.26	
Iranian Heavy; March 1994	PM-TEM	0.82 ± 0.21*	T1, B2
	PM-MOT	1.76 ± 0.38	T2, B2
Iranian Heavy; May 1994	PM-MOT	0.55 ± 0.07	T1, B1
	PM-TEM	5.86 ± 0.89	T2, B2
Iranian Heavy; May 1994	PM-TEM	1.03 ± 1.02	
Iranian Heavy; May 1994	PM-MOT	0.57 ± 0.12	
	PM-TEM	0.44 ± 0.35	
Arabian Light; March 1994	PM-TEM	0.48 ± 0.09	T1, B2
	PM-MOT	0.92 ± 0.39	T2, B2
Arabian Light; April 1994	PM-TEM	0.50 ± 0.15	T1, B1
			T2, B2
Arabian Light; July 1994	PM-TEM	2.08 ± 0.30	T1, B1
	PM-MOT	5.32 ± 1.70	
Arabian Light; August 1994	PM-TEM	5.25 ± 1.09	T1, B2
			T2, B2
Arabian Light; December 1994	PM-TEM	0.10 ± 0.10	T1, B2
			T2, B2
Arabian Heavy; May 1994	PM-TEM	0.54 ± 0.18	
Iranian Light; June 1994	PM-MOT	0.68 ± 0.11	T1, B1
	PM-TEM	0.84 ± 0.36	T2, B2
Ural Crude; February 1994	PM-TEM	0.69 ± 0.18	T1, B1
			T2, B2
Stattfjord; May 1994	PM-MOT	1.98 ± 0.35	T1, B1
	PM-TEM	2.77 ± 1.71	T2, B2
Kuwait; December 1994	PM-MOT	0.20 ± 0.10	T1, B1
			T2, B2
Oseberg; February 1995	PM-Shell	2.12 ± 1.00	T1, B1
			T2, B2

*) n = 9

PM = Sub-sample from the in-line sample. The in-line sample is obtained by an automatic sampler from the discharge pipeline, whose contents are continuously mixed by means of a so-called Power Mixer system. The sub-sample was taken from the in-line sample sample at the Terminal-lab after careful mixing by means of closed loop static mixer system
T1 = Sample from top of first centre tank
T2 = Sample from top of second centre tank
B1 = Sample from bottom of first centre tank
B2 = Sample from bottom of second centre tank.

Where the results of two PM-samples from the same crude are listed, the cargo was unloaded at two terminals.

7.2 Top and bottom samples from three selected crudes

The in-line sample is a time proportional sample and represents the total cargo, which consist of oil with some water and sediment. At first sub-samples of these samples are analysed. From three cargoes of different crude oil types, the ones with the highest concentration of cadmium in the in-line sample were selected for analysis of also the retained top and bottom samples. These samples were analysed in the same manner as the in-line samples to allow a judgement as to whether the cadmium is related to the oil or sediment. The results are listed in Table 6.

Table 6 Cadmium content of top and bottom samples of three crude oil cargoes, including those of the in-line samples involved

Type of oil	Cd content (µg/kg)		
	Top-sample (n=2)	Bottom-sample (n=2)	In-line sample (n=10)*
Iranian Heavy (Kristhild)	< 0.4	7.1 - 9.9	0.6 - 5.9
Stattfjord (Bergina)	< 0.4	12.7 - 7.8	2.0 - 2.8
Arabian Light (Esso Hawaii)	0.67 -2.7	12.0 - 8.1	5.3

* See also Table 5.

Note:
The research proposal prescribes that the bottom samples should be separated into oil, water and sediment and that each should be analysed separately. However, the water content of the bottom samples was so small (about 1400 mg/kg or less) that such a separation was not justified (see Table 7).
As the analysis of the top and bottom samples showed cadmium concentrations well within the range of expected values and could be explained by contaminations not related to the hydrocarbon matrix, it was decided not to investigate these contaminations into further detail.

Table 7 Water content of three top and bottom samples

Type of oil	Water content (mg/kg)	
	Top sample	Bottom sample
Iranian Heavy (Kristhild)	575	516
Stattfjord (Bergina)	260	1290
Arabian Light (Esso Hawaii)	390	1390

Method: Karl Fisher, ASTM D 4377
Performed by: Saybolt Nederland BV in presence of TNO

8. Conclusions

- The crudes investigated contain low amounts of cadmium, roughly 100 times less then was estimated from literature. This means that crude oil is **not** a major source of cadmium emission in the Netherlands. The much lower concentration of cadmium as established in this study compared to literature (ref. 3,4) is probably due to improper sampling and/or analysis of those former studies. Utmost precautions have been taken in this study to avoid contamination and, in addition, the analytical method has been validated before use.

- For Arabian Light the different batches show some variation in cadmium concentration, indicating that there could be a seasonal influence.

- Analysis of the top and bottom samples of three selected crudes show that the latter contains the highest cadmium concentration: about 10 $\mu g\ Cd.kg^{-1}$ sample, probably due to the elevated sediment concentration in bottom samples. This indicates that cadmium in crude oil is associated with the sediment and **not** with the hydrocarbon matrix.

9. References

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10. Authentication

Name and address of the commissioner

Dutch Ministry of Housing, Physical Planning and the Environment (VROM),
Directorate-General for Environmental Protection, Air & Energy/640
Industry Branch
P.O. Box 30945
2500 GX The Hague
The Netherlands

Names and functions of the cooperators

S.J. Spijk	Research coordinator
Ing. E.M. Stofberg	Researcher
Drs R. Bosman	Project supervisor
Dr P.M. van Berkel	Research coordinator

Period in which the research took place

from December 1993 until August 1995

Signatures

Dr P.M. van Berkel
Research coordinator

Drs R. Bosman
Head of Department Analytical Chemistry & Sensor Development, TNO

Annex 1: Letter of Assignment

Ministerie van Volkshuisvesting,
Ruimtelijke Ordening en Milieubeheer

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en Emissiebeleid
Directie Lucht en Energie
Afdeling Bedrijven

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T.a.v. de heer dr. ir. E.W.B. de Leer
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Uw kenmerk	Uw brief van	Kenmerk	Datum
EWBdL/SJS/ms	16 april 1993	DGM/LE/Bd/CD041 MBL 16493015	VERZONDEN 2 5 MEI 1993

Onderwerp

Projecttitel : Onderzoek naar Cadmium in Ruwe Olie
Projectnr. : 611.103.01 / 611.103.99–reservering fase II
opdrachtnr. : 93.14.0913 / 93.14.0914

Geachte heer de Leer,

Onder verwijzing naar uw brief van 16 april 1993 inhoudende een voorstel voor een onderzoek naar Cadmium in Ruwe Olie en de briefwisseling tussen DGM en TNO over dit onderzoek alsmede de gesprekken die sedert januari 1993 hierover met u hebben plaatsgevonden, deel ik u hierbij mede dat het Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer u de opdracht tot het uitvoeren van de eerste fase van een onderzoek naar de aanwezigheid van cadmium in ruwe olie, e.e.a conform uw projectvoorstel dat als bijlage is gevoegd bij uw brief van 16 april 1993.

Conform uw projectvoorstel dient u deze eerste fase van het onderzoek er toe te leiden dat een protocol wordt opgesteld over het nemen van monsters van ruwe olie uit de zgn. Power Mixer van de T.E.M. olieterminal, alsmede twee top– en twee bodemmonsters aan boord van het schip waarmee de ruwe olie is aangevoerd, daarop volgend het prepareren van de monsters voor opslag over een periode van 3 jaar en vervolgens het feitelijk opslaan en bewaren van die monsters gedurende deze periode.
In deze eerste fase van het onderzoek dient voorts een tweede protocol te worden opgesteld waarbij als analytische methode de GFAAS met Zeeman correctie wordt gevalideerd voor het meten van Cadmium op ppb niveau, en gedetailleerd de werkwijze wordt beschreven hoe de feitelijke analyse in de tweede fase van het onderzoek zal dienen te geschieden, zodra in deze Fase II van het onderzoek de monsters van 10 soorten ruwe olie conform zijn verkregen.

Bijlagen

Verzoeke bij beantwoording onderwerp, datum en kenmerk van deze brief te vermelden.
Bereikbaar met de bussnummers 18(HTM) en 90(NZH) vanaf stations CS en HS

Kenmerk	Datum	Bladnummer
DGM/LE/Bd/CD041		2.

Conform het projectvoorstel van TNO stel ik voor deze eerste fase van het onderzoek een bedrag ter beschikking van *f* 88.540,– excl. BTW, verdeeld in *f* 32.620,– ter dekking van de kosten van Fase I–A, t.w. de oriëntatie t.b.v. het onderzoek, het opstellen van het Sampling Protocol en het uittesten van de monstername, en *f* 50.200,– voor Fase I–B ter dekking van de kosten voor het testen van de analytische methoden, de validatie van de GFAAS methode en de voorbereiding van een Protocol voor de analyse van de monsters, en tenslotte een bedrag van *f* 5.720,– ter dekking van de kosten voor overleg met het Steering Committee in deze Fase I van het onderzoek. Inclusief 17,5% BTW wordt voor deze Fase I van het project derhalve een bedrag van ten hoogste *f* 104.034,50 ter beschikking gesteld.

Het is het voornemen van dit Ministerie dat op basis van een gedetailleerd projectvoorstel van TNO tot de uitvoering van de tweede fase van het onderzoek zal worden besloten. De opdracht daartoe zal evenwel eerst worden verstrekt nadat beide protocollen zijn opgeleverd, en geaccordeerd door de Steering Committee die het onderzoek zal begeleiden. Conform uw projectvoorstel wordt voor deze Fase II van het onderzoek vooralsnog een bedrag van *f* 112.995,– excl. BTW gereserveerd. De opdracht tot het uitvoeren van deze tweede fase van het onderzoek zal geschieden op basis van een aanvullende opdracht, nadat hiertoe door TNO een aanvullend projectvoorstel zal zijn ingediend. Indien bij de uitvoering van Fase II van het onderzoek zou blijken dat van de 10 crudes die bij het onderzoek geanalyseerd zullen worden aanvullende monsternamen van een of meerdere soorten ruwe olieën gewenst is, dan zal zulks eerst kunnen geschieden op basis van een tweede aanvullend voorstel van de zijde van TNO, en een daartoe aan TNO verstrekte opdracht in aanvulling op de opdracht tot uitvoering van Fase II.

TNO zal zo spoedig mogelijk na ontvangst van deze brief met de uitvoering van deze eerste fase van het onderzoek beginnen, teneinde tenminste één week voor de vergadering van het Steering Committee van 9 juni 1993 het concept Sampling Protocol en het concept Protocol for Analysis ter beschikking te hebben voor verzending naar de leden van het Steering Committee zodat in deze vergadering beide protocollen kunnen worden besproken en geaccordeerd. In elk geval zal het protocol voor de monstername zover gereed dienen te zijn, dat eventueel na verwerking van de aanvullingen van het Steering Committee op basis van het sampling protocol een gedetailleerde kostenbegroting voor de tweede fase kan worden opgesteld en besloten kan worden tot uitvoering ervan.

Conform de eerdere aan u verzonden brief met kenmerk MBL 23293010 zullen op de opdracht tot dit onderzoek de Algemene onderzoeksvoorwaarden VROM 1993 van toepassing zijn, zulks met uitsluiting van de door u doorgaans gehanteerde en/of bijzondere voorwaarden.

DGM/LE/Bd/CD041 3.

In aanvulling op dan wel in afwijking van de AOV 1993, alsmede in aanvulling op de bestaande afspraken tussen VROM en TNO, zullen voorts onderstaande uitgangspunten en aanvullende voorwaarden worden gehanteerd:

1. Projectcoördinator namens het Ministerie van VROM is Drs. C.P.A. Dekkers.

2. De studie zal beleidsmatig worden begeleid door een Steering Committee, dat zal bestaan uit de volgende personen:
   C.P.A. Dekkers, VROM/DGM/LE/Bedrijven (voorzitter)
   F.O. Dorgelo, VROM/DGM/SVS
   G. Stobbelaar, VROM/DGM/DWL/WE
   P. Spapens, VROM/DGM/LE/Kv (secretaris)
   Mw. J. van Daalen, Dienst Centraal Milieubeheer Rijnmond
   M.L. Daane, Shell Research Amsterdam
   A.R. Goddard, BP Research Analytical Division, Sunbury-on-Thames
   P. van Driesten, Esso laboratorium, Esso raffinaderij Botlek.

3. TNO zal het Sampling Protocol en het Protocol for the Analysis of Crude Oil Samples alsmede de tussenrapportages en het eindrapport over het gehele project opstellen in de Engelse taal. Inhoud en lay-out van de beide protocollen en van het eindrapport alsmede de engelse tekst van deze rapportages zullen van zodanig hoge kwaliteit zijn dat deze rapportages zich lenen voor verspreiding in internationale, wetenschappelijke kaders. TNO zal tijdig de nodige voorbereidingen treffen met betrekking tot de wijze waarop deze rapportages zullen worden opgezet, en daartoe in een vroeg stadium met voorstellen richting Steering Committee komen, zodat voor de bespreking van het rapport in het Steering Committee de daartoe geplande vergaderingen voldoende zullen zijn.

4. In verband met de complexiteit van het project en de verwachting dat in een latere fase tot vervolgopdrachten zal worden besloten is een goed inzicht in de benodigde menskracht en kosten gewenst. Daartoe zal tijdens de projectuitvoering ten alle tijde een urenregistratie beschikbaar zijn aan de hand waarvan kan worden beoordeeld welk tijdsbeslag is gemoeid met de uitvoering van de verschillende onderdelen van het project. Dit geldt met name ten aanzien van de tijdsbesteding voor de monstername.

5. Declaraties zullen zijn gebaseerd op vergoeding van werkelijk gemaakte kosten (conform art. 7.1 AOV vergoeding op basis van standaardvoorschotten), waarbij in afwijking van uw projectvoorstel, voor Fase I van het onderzoek 40% betaalbaar wordt gesteld gelijktijdig met de opdrachtverstrekking, 40 % bij oplevering van beide protocollen die in deze eerste Fase van het onderzoek dienen te worden opgesteld, en de resterende 20% bij akkoordverklaring van de twee beide protocollen;

Kenmerk

DGM/LE/Bd/CD041

Bladnummer

4.

6. Gespecificeerde declaraties dienen te worden gericht aan het Directoraat–Generaal Milieubeheer, Directie Financieel–Economische Aangelegenheden, afd. Divisie Filiaaladministratie/ Interne postcode 615, Postbus 30945, 2500 GX Den Haag, onder vermelding van project– en verplichtingennummer, alsmede datum en nummer van deze brief. Betaling van de declaraties zal plaatsvinden op de bankrekening van TNO 51.65.06.315 bij de ABN–AMRO te Delft.

7. Definitieve vaststelling van de bijdrage zal plaatsvinden na acceptatie van een door u in te dienen overzicht van de werkelijk gemaakte kosten.

Indien u zich niet kunt verenigen met de in deze brief opgenomen voorwaarden, dient u mij dit schriftelijk te berichten binnen twee weken na ontvangst van deze brief.

De minister van Volkshuisvesting,
Ruimtelijke Ordening, en Milieubeheer,
voor deze,
het hoofd van de afdeling Bedrijven,

ing. L. de Jonge

Ministerie van Volkshuisvesting,
Ruimtelijke Ordening en Milieubeheer

Adreswijziging vanaf 20 november 1992:
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Postbus 30945, 2500 GX DEN HAAG

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Directie Lucht & Energie
Afdeling Bedrijven

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Uw kenmerk	Uw brief	Kenmerk	Datum
IMW 93/2742 WH/ms	24 september 1993	DGM/LE/Bd/CD075 MBL 05o93002	

Onderwerp

VERZONDEN 25 OKT. 1993

Projecttitel : Investigation of Cadmium in Crude Oils
Project N° : 611.103.99
Zaak N° : 93.14.0914

Geachte heer Harder,

Onder verwijzing naar uw brief van 24 september 1993, inhoudende een verzoek tot toestemming voor de uitvoering van Fase II van het project 'The determination of the cadmium content in crude oil', en de brief d.d. 25 mei 1993 (MBL 16493015) waarmee u opdracht werd gegeven tot uitvoering van Fase I van het onderzoek, deel ik u mede dat het Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer u hierbij opdracht verstrekt tot het doen uitvoeren van Fase II van het Cadmium onderzoek. Voor de uitvoering van Fase II verwijs ik naar hetgeen telefonisch op 29 september en 1 oktober is besproken en overeengekomen tussen de heer de Leer van TNO en de heer Dekkers, opdracht-coördinator voor dit project. Bij de uitvoering van Fase II zal onderscheid gemaakt worden tussen Fase IIA, t.w. werkzaamheden direct verband houdend met het nemen van monsters van 10 soorten ruwe olie alsmede de opslag en het bewaren van die monsters e.e.a. conform het daartoe in Fase I opgestelde Sampling Protocol, en Fase IIB, t.w. de werkzaamheden direct verband houdend met het analyseren van de verkregen monsters op de aanwezigheid van Cadmium en de rapportage daarover, e.e.a. conform het daartoe opgestelde Analytical Protocol.

In lijn met de elementen genoemd in uw voorstel van 24 september j.l. en de annex bij die brief (Enclosure to quotation number 93/3344 dated 23 September 1993) stel ik voor de werkzaamheden van Fase IIA een bedrag ter beschikking van maximaal *f* 96.605,00 excl. BTW (*f* 113.510,90 incl. BTW). De budget-onderdelen voor deze werkzaamheden zijn gespecificeerd in Bijlage A behorend bij deze brief.

Bijlagen

Verzoeke bij beantwoording onderwerp, datum en kenmerk van deze brief te vermelden
In verband met het regeringsbeleid om het aantal auto-kilometers terug te dringen wordt het zeer op prijs gesteld

Kenmerk	Datum	Bladnummer
DGM/LE/Bd/CD075		2.

Eveneens in lijn met uw brief van 24 september stel ik voor de werkzaamheden van Fase IIB een bedrag ter beschikking van *f* 41.355,00 excl. BTW (*f* 48.592,10 incl. BTW). De budget-onderdelen voor de werkzaamheden van Fase IIB zijn gespecificeerd in Bijlage B behorend bij deze brief. Voor Fase IIA en Fase IIB tezamen wordt derhalve een bedrag van max. *f* 137.960,00 (excl. BTW) en *f* 162.103,00 incl. BTW toegekend. Hiermee is de in mijn brief van 25 mei 1993 genoemde reservering voor fase II, groot *f* 112.995,- excl. BTW komen te vervallen.

Zoals tussen de heren de Leer en Dekkers besproken, is het onderscheid in Fase IIA en Fase IIB van belang voor een juist financieel en projectmatig beheer van het gehele onderzoek. Met name is het onderscheid in Fase IIA en Fase IIB gewenst met het oog op het voornemen van het ministerie om het Cadmium onderzoek zo spoedig mogelijk uit te breiden met een onderzoek naar een zestal andere metalen. De in Fase IIA te verkrijgen monsters zullen immers ook worden gebruikt voor de analyses naar die andere metalen. Zodra met de olie-industrie over de uitbreiding overeenstemming is bereikt, zal in de Steering Committee worden besproken onder welke technisch-wetenschappelijke condities deze aanvullende analyses plaats dienen te vinden, en op welke wijze deze condities dienen te worden vastgelegd in een aanvulling op het analyseprotocol voor Cadmium, dan wel in een nieuw analyseprotocol. Het ligt in de rede beide analyses, t.w. het nu lopende Cadmium onderzoek en straks die naar de andere metalen, te koppelen waar zulks beheersmatig en financieel-administratief nuttig is en wetenschappelijk verantwoord kan worden. Tegen die achtergrond dient u bij het projectbeheer van Fase IIA en Fase IIB, althans voorzover dat binnen de financiële randvoorwaarden van Fase II mogelijk is, rekening te houden met een toekomstige uitbreiding van het onderzoek.

TNO dient zo spoedig mogelijk na ontvangst van deze brief met de uitvoering van Fase II van het onderzoek te beginnen. In Bijlage C behorend bij deze brief treft u de lijst van ruwe oliesoorten aan alsmede de frequentie waarmee die oliesoorten bemonsterd dienen te worden op een wijze die conform is aan het gestelde in het Sampling Protocol. Vervolgens zal TNO deze monsters prepareren voor opslag voor een periode van 3 jaar en deze monsters feitelijk opslaan en bewaren onder de condities zoals in het Sampling Protocol vastgelegd. Zo spoedig mogelijk na ontvangst van deze opdrachtbrief zal TNO met de Steering Committee in een zgn. kick-off meeting die details van Fase IIA en Fase IIB bespreken die een goede start van beide projectonderdelen waarborgen.

Evenals voor Fase I van het onderzoek zijn ook op Fase IIA en Fase IIB en mogelijke vervolgfases van het onderzoek de Algemene onderzoeksvoorwaarden VROM 1993 van toepassing, alsmede de bestaande afspraken tussen VROM en TNO, en voorts de aanvullende voorwaarden 1 t/m 7 die zijn genoemd in mijn brief d.d. 25 mei 1993 (MBL 16493015) waarnaar ik hierbij kortheidshalve verwijs. De volgende aanvullingen en wijzigingen zijn van belang:

Kenmerk	Datum	Bladnummer
DGM/LE/BD/CD075		3.

1. De heer ing. H. Holtring zal voor dit project als plaatsvervangend projectcoördinator optreden bij afwezigheid van de heer Dekkers;
2. Door haar vertrek bij DCMR is Mw J. van Daalen als lid van de Steering Committee vervangen door de heer ir. J.W.Th. Voerman;
3. In aanvulling op punt 4 van de brief van 25 mei 1993 en conform het eerder gestelde in deze brief, dient u voor een goed projectmatig en financieel beheer van het project in uw administratie onderscheid te maken in de werkzaamheden en kosten gemaakt voor Fase IIA en die voor Fase IIB;
4. Voorts dient bij punt 5. van mijn brief van 25 mei 1993 voor Fase I uiteraard Fase IIA resp. Fase IIB gelezen te worden. Tevens geldt dat voor kasbetaling voor 1993 40% van Fase IIA en Fase IIB betaalbaar wordt gesteld en de resterende 60% in 1994 bij akkoordverklaring van de eindrapportage over de monstername (Fase IIA), dan wel de eindrapportage over de analyse (Fase IIB);
5. In uw offerte heeft u de personeelstarieven voor 1994 opgenomen. Deze wijken af van de tarieven voor 1993. Overeenkomstig de afspraken tussen TNO en VROM/DGM kan aanpassing van de tarieven pas plaatsvinden na definitieve acceptatie door DGM van de tarieven voor 1994.

Indien u zich niet kunt verenigen met de in deze brief opgenomen voorwaarden, dient u mij dit schriftelijk te berichten binnen twee weken na ontvangst van deze brief.

De minister van Volkshuisvesting,
Ruimtelijke Ordening, en Milieubeheer,
voor deze,
het hoofd van de afdeling Bedrijven,

Ing. L de Jonge

Bijlage A. behorend bij brief DGM/LE/BD/CD075
MBL 05o93002

Fase IIA Cadmium Onderzoek:

Kostenbegroting van de werkzaamheden in het kader van de monstername van tien soorten ruwe olie, gespecificeerd in Bijlage C.

#	Monstername van 18 crude cargoes (TNO representative)	*f* 32.480
	Reiskosten	*f* 1.800
#	Monstername van 18 crude cargoes (surveyor)	*f* 29.600
	Reiskosten	*f* 1.800
#	Registratie van monstername gegevens	*f* 9.000
#	Opslag van de monsters gedurende een periode van 3 jaar	*f* 4.000
	Vernietiging van monsters	*f* 1.000
#	Supervisie (6 x *f* 275 + 6 x *f* 290)	*f* 3.390
#	25 x 2 ltr flessen, incl. doppen +	
	130 x 1 ltr flessen, inclusief doppen	*f* 5.595
#	Fabrikage van 1 monstername-apparaat	*f* 5.000
#	Vergaderingen van de Steering Committee	
	2 x 4 uur Spijk (1993 en 1994)	*f* 1.800
	1 x 4 uur De Leer (1993 en 1994)	*f* 1.140

Totaal *f* 96.605,00 excl. BTW

***f* 113.510,90 incl. BTW**

Bijlage B. behorend bij brief DGM/LE/BD/CD075
MBL 05o93002

Fase IIB Cadmium Onderzoek:

Kostenbegroting van de werkzaamheden voor het analyseren van 10 soorten ruwe olie op de aanwezigheid en concentraties van Cadmium

# Vaststellen van het Protocol voor het Analyse Protocol 12 uur de Leer	*f* 3.300
# Tienvoudige analyse van 18 monsters uit de Power Mixer (18 x *f* 100,00)	*f* 18.000
# Analyse van Top en Bodem Monster van 5 soorten ruwe olie	
– top monsters: tweevoudige analyse van 10 monsters (2 x 10 x *f* 150,00)	*f* 3.000
– bodem monsters: tweevoudige analyse van 10 monsters naar olie, water en sediment: (2 x 10 x 3 x *f* 150,00)	*f* 9.000
# Inspectie bij interne QAU (5 x *f* 275,00 + 5 x *f* 175,00)	*f* 1.725
# Supervisie (6 x *f* 275,00 + 6 x *f* 290,00)	*f* 3.390
# Vergaderingen van de Steering Committee	
2 x 4 uur Spijk (1993 en 1994)	*f* 1.800
1 x 4 uur De Leer (1993 en 1994)	*f* 1.140

Totaal *f* 41.355,00 excl. BTW

***f* 48.592,10 incl. BTW**

Bijlage C. behorend bij brief DGM/LE/BD/CD075
MBL 05o93002

Fase IIA Cadmium Onderzoek:
De soorten ruwe olie die in het kader van het Onderzoek bemonsterd dienen te worden, alsmede de frequentie van de monstername.

Benaming/Soort Ruwe Olie	Aantal Cargo's
Soorten Ruwe Olie uit het Midden Oosten	
@ Arabian Light	5x
@ Iranian Heavy	5x
@ Arabian Heavy	1x
@ Iranian Light	1x
@ Kuwait	1x
Soorten Ruwe Olie uit Nigeria	
@ Forcados	1x
@ Bonny Light	1x
Russische Ruwe Olie	
@ Ural	1x
Soorten Ruwe Olie uit de Noordzee	
@ Wyth Farm (UK)	1x
@ Stattford (Norway)	1x

Het is mogelijk dat door wijzigingen in de eigendom van de T.E.M. Terminal er operationele aanpassingen in de feitelijke monstername plaats moeten vinden. Deze zullen in de kick-off meeting met de leden van de Steering Committee worden besproken.

Annex 2: TNO Research Proposal: 'Determination of the cadmium content in crude oil' IMW-RV93/011b

IMW - RV 93/011b **Determination of the cadmium content in crude oil**

Research proposal

Author : E.W.B. de Leer and S.J. Spijk

Date : 16 April 1993

Order no. : 06206-CAD

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SUMMARY

The project proposal describes the TNO approach for:

1. The preliminary testing of a sampling method and the development of a sampling protocol for crude oil cargoes
2. The development and validation of an analytical method for the determination of cadmium in crude oil, followed by the description of the method in an analysis protocol
3. The actual sampling of crude oils and the determination of the cadmium content.

Phase 1: Preparation of the Protocols

A. Sampling

TNO familiarises itself with the problems associated with the project and contacts surveyors and the oil companies through the Steering Committee. The methods for sampling, sample treatment, storage and analysis will be discussed.

To obtain a detailed insight in the problems of crude oil sampling in the tanks of a (super)tanker and the Power Mixer, alternative sampling methods will be evaluated in a test exercise.

Based on the information gained in the familiarisation phase, TNO will prepare a draft protocol for sampling, sample treatment and sample storage. The protocol will be in agreement with the current ASTM/ISO/IP guideline when appropriate, and describes the responsibilities of TNO and subcontracting parties or surveyors. TNO witnesses and supervises all actions of the surveyors in relation to the sampling activities.

The protocol will be prepared according to the OECD principles of Good Laboratory Practice (GLP). Phase 1.A will be completed after the Steering Committee has accepted and approved the sampling protocol.

B. Analysis

TNO prepares a proposal for a validation study for the determination of cadmium in crude oil according to the graphite furnace atomic absorption spectroscopy method as described by Narres et al. (1984). The required method performance criteria and the actual work to be carried out, will be described. The validation study starts after approval of the proposal by the Steering Committee.
When the validation study is completed, the application of the method in the further studies will be decided upon in consultation with the Steering Committee.

Phase 1.B will end after the Steering Committee has accepted and approved the validation study.

Phase 2: Sampling and Analysis of Crude Oils

The analytical method will be described in an analytical protocol, according to the GLP guidelines.

Eighteen crude oil cargoes will be sampled. Samples will be taken from the Power Mixer and from the top and bottom of two different tanks, resulting into five samples per cargo. At first, only the samples from the Power Mixer will be analysed. When all or a large number of samples have been taken, the samples of the power mixer will be analysed with a minimum detection level of 1 $\mu g.kg^{-1}$ and an intra laboratory repeatability of 10% at 10 $\mu g.kg^{-1}$. The results of the analyses will be reported to the Steering Committee. Upon discussion the Steering Committee will decide upon further analysis of the top and bottom samples and whether eventually additional crude cargoes have to be sampled.

Sampling and analysis will be performed according to the approved protocols and the results will be reported to the Steering Committee.

1. INTRODUCTION

The Dutch Ministry of Housing, Physical Planning and Environment (VROM), Air Directorate, Industry Branch has requested TNO (Institute of Environmental Sciences) to work out proposals for sampling and analysis of a selected number of crude oil cargoes, with the purpose of investigating the presence of cadmium. After approval of the protocols for sampling and analysis by the Steering Committee, the actual sampling and analysis will be performed by or under supervision of TNO.

The project is part of the policy of VROM to reduce cadmium emissions, in this case the possible emission of cadmium originating from processing mineral oil products.
In the 'Basisdocument Cadmium', the Refining Industry and the burning of heavy residues have been identified potentially as a major source of cadmium in the Netherlands, leading to a total cadmium emission of 0.96 tons/year. The 'Basisdocument Cadmium', however, is based on data that have partially been questioned and more accurate data are needed.

One source reports that the cadmium content in crude oil is extremely low (approximately 0.1 ppb). However much higher concentrations have been reported, and it needs to be established whether these high concentrations are the result of high natural background levels for some crudes, contamination of the crude by 'other' sources or are due to analytical problems. The aim of this proposal is to develop a reliable sampling and analytical method and to distinguish between the possible sources.

The project will be guided by a Steering Committee. Members of the Steering Committee are representatives of the Ministry of VROM, of the Regional Environmental Authority (DCMR), and the Oil Industry.

2. POSSIBLE SOURCES OF CADMIUM

Crude oil may contain cadmium from natural sources, or may be contaminated with cadmium due to 'additives', such as remnants of an earlier cargo, ballast water, sand, dust, mud, sea water, paint etc.

The "Basisdocument Cadmium" estimates a cadmium emission of 0.96 tons per year in The Netherlands, as the result of the combustion of residual oil in the refineries. This estimate is based on a cadmium content of 150 $\mu g.kg^{-1}$ in crude oil. However, the "Basisdocument Cadmium" mentions that the possibility exists that this value is too high.

A large uncertainty exists in the recent literature about the presence of cadmium in crude oil. Narres et al. (1984) reported an average of 0.10 $\mu g.l^{-1}$ (very close to the detection limit of 0.06 $\mu g.l^{-1}$) in four crude oil samples from different origins, while Ali et al. (1983) and Al-Swaidan (1990) found averages of respectively, 900 $\mu g.kg^{-1}$ and 500 $\mu g.kg^{-1}$ in Arabian crudes.

5. SAMPLING

5.1 General

All relevant aspects that may influence the quality of the samples will be considered. Sampling will be performed by a surveyor appointed by TNO. TNO will be responsible for all sampling activities.

5.2 Sampling protocol

TNO will prepare a draft protocol for sampling, sample treatment and storage, in agreement with the current ASTM/ISO/IP guideline when appropriate. The protocol will also state where the responsibilities for the various aspects of the project lie. TNO will witness and supervise all actions of the surveyor in relation to the sampling actions.

The protocol will be prepared according to the OECD principles of Good Laboratory Practice (GLP) and will be discussed in detail with the Steering Committee. This phase will be completed when the Steering Committee has accepted and approved the sampling protocol.

5.3 Sampling Equipment

The sampling equipment and storage units will be chosen in such way that cross-contamination with cadmium or adsorption of cadmium onto glass surfaces will be excluded as much as possible. Since the exact form of cadmium in crude oil is unknown (free cadmium ion, cadmium complexes with for example porphyrin structures or other complexing agents), the effect of the storage conditions on the samples must be investigated.
TNO will focus on sampling equipment made of borosilicate glass and/or titanium.

2-Litre glass bottles (uncoloured glass and acid washed) will be used for samples taken from the "Power Mixer."
The samples taken one metre below the surface of the crude oil, and "as close as possible to the bottom" of the tanks will be collected in 1 litre glass bottles. For samples taken "as close as possible to the bottom", a new type of sampler that can be turned to a horizontal position when it has arrived at the sampling position needs to be developed. The samplers used and the draft protocol will be evaluated in a test sampling exercise.

The choice of the construction material of the sampler holder will be carefully considered, since standard (thief)samplers are made of stainless steel 316 L (manganese 2%, chromium 18%, nickel 12%, molybdenum 2%). The use of titanium or

aluminium, both free of cadmium, or possibly glass coated stainless steel will be considered.

5.4 Samples from the "Power Mixer"

The sub- sampling from the "Power Mixer" sample will be carried out by the in house surveyor, conforming to the standard procedure (ISO 3170). A representative of TNO will witness and supervise the sub sampling.

5.5 Sample bottles and storage

Sample bottles will be made of uncoloured and acid washed glass. Blank experiments will be performed to establish the absence of cadmium.
A TNO representative will take the samples to the TNO laboratory, where the samples will be stored at 4°C. All samples will be kept for three years after completion of the study.

5.6 Splitting of samples prior to analysis

Prior to analysis the samples will be homogenised (Ultra Turrax mixer, titanium shaft and generator) and divided in two equal sub samples. One sub sample is used for the analysis and the other will be stored again at 4°C, to allow for a second opinion at some stage in the future.

6. ANALYSIS

6.1 General

The analyses will be performed according to the rules laid down in the quality manual of the Department of Analytical Chemistry. The quality system of the department is accredited by Sterlab (accreditation number 26, January 1991).

The analysis of the crude oil samples will start, when all or a large number of the samples have been collected. Initially, only the 'Power Mixer' samples will be analysed and the results will be reported to the Steering Committee.
Upon discussion, the Steering Committee will decide upon further analysis of the samples taken from the top and bottom of the tanks of the cargoes. The Steering Committee may also decide that additional sampling of some crudes is necessary in order to establish whether the analytical results are incidental, seasonal or characteristic.

6.2 Analytical methods

The analysis of trace metals in crude oil normally requires atomic emission or adsorption techniques to obtain a sensitive and selective quantification. Zeeman atomic absorption techniques (Zeeman AAS) and inductively coupled plasma (ICP) have been used as rapid and sensitive detection methods. Recently, the combination of ICP with mass spectrometry (MS) has been developed, resulting in a sensitive and selective simultaneous multi element detection method.

Sample preparation for trace metal analysis using wet ashing procedures has been standardised (ASTM, IP). Also other sample preparation methods have been described in the recent literature, including variations to the wet ashing procedures, extraction with acids and cold O_2 plasma ashing. Digestion methods are time consuming and for samples with extremely low concentrations they become susceptible to contamination. In the literature the direct determination without extensive sample preparation has been investigated.

Narres, Mohl and Stoeppler (1984) investigated the direct determination of cadmium in crude oils with graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman compensation. Samples were diluted in tetrachloromethane (1:3) and directly introduced (10 µL) on a L'vov platform. When O_2 was added to the argon during the charring step, a detection limit of 0.06 µg Cd/L was achieved. The procedure gives the lowest reported detection limit for cadmium in crude oil.
However, Narres et al. report that the method is sensitive to aberrations in the experimental conditions (O_2 variations) and TNO expects that the introduction of 10

µl samples may produce repeatability problems when the crude oil is not homogeneous.

Lord III (1991) described the direct introduction in ICP-MS of a microemulsion of crude oil diluted with tetralin in water. The method is rapid and gave a high accuracy (± 2.1% for certified metals in NBS 1634b) and precision (± 2.2%, 6 replicates, 50 ppm). Unfortunately, the method was not applied for the determination of cadmium.

After discussion with the Steering Committee, TNO proposes to focus on the GFAAS-method of Narres et al.

6.3 Validation study of the GFAAS-method

TNO will prepare a document that describes all planned experiments for the validation of the Zeeman GFAAS method for the determination of cadmium in crude oil according to Narres et al. The method will be fully validated for analysis of samples having low (< 10 $\mu g.kg^{-1}$) and high (≥ 10 $\mu g.kg^{-1}$) cadmium concentrations. The heterogeneity of the samples will be assessed with respect to this method.

The validation study will include the determination of intralaboratory repeatability and reproducibility, linearity, detection limit, determination limit, recovery, method blanc value and limited robustness testing. TNO proposes that the final method should have a detection limit of Cd < 1 $\mu g.kg^{-1}$ and a repeatability of < 10% at 10 $\mu g.kg^{-1}$ of Cd. For statistical purposes, 10 determinations per sample are required.

When the nature of the oils being analysed do not require dilution before injection into the GFAAS, the samples will be homogenised using IP356 or similar procedure to ensure that representative 10 x 10 µl aliquots are taken. In other cases, crude oil samples will be homogenised using IP356 or similar procedure and diluted according to the method of Narres et al. In order to validate the GFAAS method, the analysis will also be compared with ICP-MS.
The validation procedure will include analysis of larger samples after pretreatment. The pretreatment methods are:

- Wet ashing (ASTM/IP procedure) using ultra pure acids.
- Cold O_2 plasma ashing.

The Narrres method will be evaluated on crude oil samples collected during the sampling tests or alternatively, crude oil samples may be obtained from oil companies. If necessary, all 'open' manipulations of samples will be performed at the ultra-trace analytical facility at the TNO laboratory.

4. REGISTRATION OF CRUDE CARGOES

The following information has to be listed for each crude:

- type of crude
- loading terminal
- date of loading
- the transport carrier and its "history"
- earlier cargo and its relevant specifics
- copy of the bill of lading, which contains:
  - water content of the crude on loading
  - estimate of ROB (Remain On Board)
  - OBQ (On Board Quantity)
- loading plan (The first tank is probably partly filled with so called "Line-fill" which does not need to be the same type of crude)
- sampling procedure used
- observations made during the actual sampling
- Characteristics of the crude cargo (°API Gravity, wt % water) must be obtained from the surveyor.

TNO will develop a special registration form that is to be filled in by the suveyor supervised by TNO.

3. SELECTION OF CRUDES AND SAMPLES

The cadmium concentration will be measured in ten different crude cargoes of crudes that are regularly processed in Dutch refineries. The ten crudes will be selected based on their relative weight in the total quantity of crude processed in the Netherlands. TNO will be informed by VROM about the crudes that have been selected for cargo sampling.

In addition, the two most frequently processed crudes will be sampled from five different cargoes to assess whether the different batches show any variation and to allow a judgement about any seasonal variation.
Consequently (8 x 1) + (2 x 5) = 18 cargoes will be sampled.

Samples will be taken from the 'Power Mixer' together with samples from the top (approximately one metre below the surface) and the bottom (as close as possible) layers of two, randomly chosen tanks. The first and last tanks loaded are to be excluded.

In summary, each cargo will yield 5 samples, resulting in a total of 90 samples.

The validation study will be reported in detail and the application of the method in the further studies will be decided upon in consultation with the Steering Committee.

6.4 Protocol for analysis

The analysis of the crude oil samples will be performed according to an analytical protocol in general agreement with the GLP guidelines. The protocol will be submitted to the Steering Committee after discussion and approval of the validation study.

6.5 Equipment and facilities

- Perkin-Elmer 5100 PC Atomic Absorption Spectrometer
- Fisons Instrument VG Plasma Quad ICP/MS
- Cold O_2 plasma ashing apparatus
- Ultra-trace laboratory
- Standard laboratory equipment and facilities

7. PERSONNEL

Project supervisor	:	Dr.Ir. E.W.B. de Leer
Project manager	:	S.J. Spijk
Supervision sampling	:	S.J. Spijk, Ing. J.M. Timmner
Responsible annalists	:	Ing E.M. Stofberg (Zeeman GFAAS) H.P.M. de Haan (Zeeman GFAAS, ICP/MS)
Quality assurance	:	Quality Assurance Unit IMW-TNO

8. REPORTING

All reports and correspondence will be in the English language.
TNO aims to report the results in a scientific journal.

9. LITERATURE

M.F. Ali, A. Bukhari, and M. Saleem
Ind. Eng. Chem. Prod. Res. Dev. 22, 691-694 (1983)
Trace Metals in Crude Oils from Saudi Arabia

H.M. Al-Swaidan
Analytical Letters 23(7), 1345-1356 (1990)
Trace Metal Determination by Wet Ashing ICP/MS in Saudi Arabian Crude Oils

C.J. Lord, III
Anal. Chem. 63(15), 1594-1599 (1991)
Determination of Trace Metals in Crude Oil by Inductively Coupled Plasma Mass Spectrometry with Microemulsion Sample Introduction

H.D. Narres, C. Mohl, and M. Stoeppler
Intern. J. Environ. Anal. Chem. 18, 267-279 (1984)
Metal Analysis in Difficult Materials with Platform Zeeman-Atomic Absorption Spectrometry

Annex 3: Drawing of the sampler

Annex 4: TNO Report: 'Protocol crude oil sampling' IMW-R 93/211

IMW - R 93/211 **Protocol Crude Oil Sampling**

Author : S.J. Spijk

Date : 31 August 1993

Order no. : 52213

Client : Dutch Ministry of Housing, Physical Planning and Environment (VROM), Directorate-General for Environmental Protection, Air & Energy/640, Industry Branch For the attention of Drs. C.P.A. Dekkers P.O. Box 30945 2500 GX The Hague The Netherlands

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APPROVAL OF THE PROTOCOL

For the client, Dutch Ministry of Housing, Physical Planning and Environment (VROM), Directorate-General for Environmental Protection, Air & Energy/640, Industry Branch:

Drs C.P.A. Dekkers date:
Deputy Head Industry Branch

For TNO Institute of Environmental Sciences
Department of Analytical Chemistry:

S.J. Spijk date:
Project Manager

Dr Ir E.W.B. de Leer date:
Head Department of Analytical Chemistry
Project Supervisor

DISTRIBUTION LIST

Copies of this protocol will be distributed as follows:

Client	(1 original)
Study file	(1 original)
Mr. C.P.A. Dekkers, VROM/DGM	(1 copy)
Mr. P. Spapens, VROM/DGM	(1 copy)
Mr. G. Stobbelaar, VROM/DGM/DWL	(1 copy)
Mr. F.O. Dorgelo, VROM/SVS/S	(1 copy)
Mr. M.L. Daane, KSLA, Shell Amsterdam	(1 copy)
Mr. A.R. Goddard, PB Research UK	(1 copy)
Mr. P. van Driesten, ESSO Nederland B.V.	(1 copy)
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Mr. A.W.F van Alphen, TEM	(1 copy)
Mr. C.A.P. Bakker, OCC	(1 copy)
Mr. J. van Zwieten, Saybolt & van Duyn	(1 copy)

1. INTRODUCTION AND OBJECTIVE OF THE STUDY

The Dutch Ministry of Housing, Physical Planning and Environment (VROM), Directorate-General for Environmental Protection, Air & Energy/640, Industry Branch, has requested the TNO Institute of Environmental Sciences to sample and analyze a selected number of crude oil cargoes for their cadmium content.

The Project is conducted under the guidance of a Steering Committee chaired by VROM and comprising representatives of VROM, Shell, ESSO, BP, and DCMR (Regional Environmental Authority).

The cadmium concentration will be measured in ten different types of crude regularly processed in Dutch refineries.
The ten crudes will be selected by the Steering Committee on basis of their proportion of the total amount of crude oil processed in the Netherlands.

In addition the two most frequently processed crudes will be sampled from five different cargoes to assess whether the different batches show any variations, e.g. seasonal variations.

Consequently (8 x 1) + (2 x 5) = 18 cargoes will be sampled

Samples will be taken from the 'Power Mixer', i.e. samples from the in-line sampler, as well as from the top (about one metre below the surface) and from as near as possible to the bottom of two randomly chosen tanks of the crude carrier.
The first and last tanks loaded are excluded.

In short, each cargo will yield five samples, resulting in a total of 90.

The actual sampling will be performed by Saybolt-Van Duyn*, a company of surveyors engaged by TNO.
TNO will be responsible for all sampling and for the storage of the samples.

This protocol describes the sampling procedure.

2. CLIENT

The study has been commissioned by the Dutch Ministry of Housing, Physical Planning and Environment (VROM), Directorate-General For Environmental Protection, Air & Energy/640, Industry Branch
P.O. Box 30945
2500 GX The Hague
The Netherlands

3. RESPONSIBLE STAFF

TNO

Project Supervisor : Dr. Ir. E.W.B. de Leer
Project Manager : S.J. Spijk
Supervising Sampling : S.J. Spijk, Ing. J.M. Timmner
Quality Assurance : Quality Assurance Unit IMW-TNO

Saybolt-Van Duyn

Project Manager : J. van Zwieten
Account Manager : J.C. Bronner
Assistant Project Manager : H. de Bruijn
Inspectors : C. Minderhout
W. Poppelier

4. RESPONSIBILITIES

The term 'Responsibilities' is in no way intended to confer or interfere with any legal and contractual obligations. The aim is to record certain general steps to be taken to ensure that the particular procedures specified herein may be carried out and to indicate who should be involved.

VROM:

- to compile a list of crudes that have to be sampled and passing it on to the Terminal Operator of T.E.M. Note: a copy of the list will be sent to TNO.
- to ask the Terminal Operator of T.E.M. to make all necessary arrangements for access by TNO and Saybolt-Van Duyn staff to the Terminal.
- to ask the Terminal Operator of T.E.M. to make all necessary arrangements with the master of the vessel to carry out the job, special attention being paid to permission to open butterworth holes.
- to ask the Terminal Operator of T.E.M. for the standard cleaning procedure for the 20-L receptacle of the 'in-line sampler' and to allow TNO/-Saybolt-Van Duyn to inspect the receptacle visually prior to its use.
- to ask the Terminal Operator of T.E.M. to provide TNO with the results of the analysis (content of water and sediment, API Gravity) of all samples taken from the 'Power Mixer'.

Terminal Operator of T.E.M.

- to announce the expected date of arrival of the crude carrier with a cargo of the selected crude. This announcement should be faxed to TNO and Saybolt-Van Duyn. Saybolt-Van Duyn should confirm receipt of the fax to the Terminal Operator of T.E.M.
- to make all the necessary arrangements with the master of the vessel to carry out the job, special attention being paid to permission to open butterworth holes.
- to arrange permission for taking a 2-litre subsample by TNO from the 'Power Mixer' at the laboratory involved.
- to specify the laboratory where the receptacle has been sent to, and the timing of the subsampling.
- to provide a computer print out on the functioning of the 'in-line sampler' during the unloading of the cargo.
- to make available to TNO the analytical data (content of water and sediment, API Gravity) of 'Power Mixer' samples of those crude oil cargoes, that are part of the sampling procedure in the project.

TNO

- to supervise all sampling activities of the surveyor.

- to send an advance copy of the sampling protocol to Saybolt-Van Duyn and Terminal Operator of T.E.M., to be signed by Saybolt-Van Duyn for acceptance.
- to make arrangements with Saybolt-Van Duyn for sampling the crude cargo on board.
- to take the 2-litre sample from the 'Power Mixer' at the laboratory involved.
- to prepare a checklist of all sampling activities. This checklist should be signed for each of the stated activities by both Saybolt-Van Duyn and TNO, in case of supervised activities, or by TNO.
- to send a copy of the checklists to VROM within 24 hours of all relevant data becoming available. .
- to supply pre-prepared borosilicate sample bottles to Saybolt-Van Duyn on the day of sampling.

Saybolt-Van Duyn

- to confirm by fax receipt of the announcement of arrival of the carrier and to confirm the sampling.
- to provide the sampling equipment and to gather all the necessary information (if available) as stated in the 'Registration of Crude Cargoes' checklist.
- to send to TNO with the least possible delay the completed 'Registration of Crude Cargoes' checklist.
- to perform the sampling of oil from the tanks of the crude carrier according to the procedures detailed in Section 8.
- to supply labels.

5. ACTION SCHEDULE

The following actions should be carried out in sequence

- *Terminal Operator of T.E.M* to announce (by fax) to TNO and Saybolt-Van Duyn the ETA of the crude carrier from which samples have to be taken.
- *TNO and Saybolt-Van Duyn* to consult on time of arrival at the T.E.M.
- *Saybolt-Van Duyn* to confirm by fax the receipt of the announcement of arrival of the carrier to the Terminal Operator of T.E.M. and to confirm the sampling. A copy of this fax should be sent to TNO.
- *TNO* to supply pre-prepared borosilicate sample bottles to T.E.M. on the day of sampling.
- *Saybolt-Van Duyn* to supply sampling equipment to T.E.M on the day of sampling.
- *Saybolt-Van Duyn* to perform sampling on board under TNO supervision.
- *Terminal Operator of T.E.M* to supply an estimate of the time of subsampling of the sample from the 'in-line' sample of the laboratory involved.
- *TNO/Saybolt-Van Duyn* to fill in checklists.
- *TNO* to take the 2-litre samples from the 'Power Mixer' at the laboratory involved.
- *TNO* to transport the samples to their laboratory and store them there.
- *TNO* to send a copy of the checklists to VROM within 24 hours of all relevant data becoming available.
- *Terminal Operator of T.E.M.* to provide TNO with a copy of the analytical data (content of water and sediment, API Gravity) of 'Power Mixer' samples of those crude oil cargoes, that are part of the sampling procedure in the project.
- *Terminal Operator of T.E.M.* to provide TNO with a copy of the computer print-out on the functioning of the in-line sampler during sampling.

6. SAMPLE BOTTLES AND LABELLING

2-Litre bottles made of colourless borosilicate glass will be used for samples taken from the 'Power Mixer'.

The samples taken one metre below the surface of the crude oil, and as near as possible to the bottom of the tanks will be collected in 1-litre bottles made of colourless borosilicate glass.

The sample bottles will be cleaned inside and out with nitric acid, followed by demineralised Milli-Q water. Before use each sample bottle is packed in a closed plastic bag.

After taking samples the sample bottles will be closed by a plastic screwcap with teflon inlay.

Immediately after being taken the samples will be labelled.
Labels will be filled in fully and will contain the following information:

- Sample taken from (Power Mixer/vessel)
- Before/during/after loading/discharge/transfer
- Product
- Installation
- Sample description (use definitions as given in Section 8.1)
- Date/hour of sampling
- Where applicable: vessel's cargo tank designation (PS1, C3, SB7 etc.)
- Name of inspector

An example of the label is shown in Annex 1.

7. SAMPLING EQUIPMENT AND PRECAUTIONS

A special device for horizontal sampling is developed by Saybolt-Van Duyn. It is made of stainless steel, coated with teflon and with movable parts made from 'Delrin'. Prior to sampling of a crude cargo the sampler is cleaned with xylene.
A drawing of the sampler including technical details is shown in Annex 2.

The sampler will be attached to a colourless cotton rope. A fresh rope will be used for each tank. The depth of the tank will be measured in advance. The predetermined length of the rope determines the depth of the sampler in the tank.

In view of the obstacles usually found under official hatches, samples should preferably be taken through butterworth holes.
In that case samples can only be taken when the tanks are depressurized (i.e after release of inert gas pressure). A second condition that has to be fulfilled is that the hydrogen sulphide content of the inert gas should not be dangerously high.

8. SAMPLING PROCEDURE

8.1 Definitions

In these procedures the following definitions will apply:

POWER MIXER SAMPLE : A subsample from the Power Mixer taken at the laboratory involved

TOP SAMPLE : A sample taken one metre below the surface of the product by means of the special device.

BOTTOM SAMPLE : A sample taken from as near as possible* to the bottom of that tank by means of a special device.

8.2 Registration

Upon arrival of the crude carrier, the representatives of Saybolt - Van Duyn B.V. (SAYBOLT) and TNO will board the vessel and complete registration of the incoming crude cargo in accordance with the 'Crude Oil Registration' checklist (see Annex 3).

If applicable the following definitions will apply:

Definitions:

Bill of Lading
A document which states the quantity of oil delivered to the vessel

Calibration Table
A table, often referred to as a tank table or tank capacity table, showing the capacity of, or volumes in a tank corresponding to various liquid levels measured from a reference point.

Datum Point
The point from which all measurements for the calibration of a tank are related.

Dip (Innage)

* The exact height depends on the construction of the sampling device.

The depth of a liquid in a tank, measured from the surface of the liquid to a fixed datum point. Note: Dip measurements are usually referred to the firmly fixed level plate located on or close to the tank bottom.

Free water (FW)
The water that exist as a separate layer from the oil, and typically lies beneath the oil.

Gross Standard Density of Oil
The mass per unit gross Standard Volume of oil (determined after homogenisation of the sample).

Gross Observed Volume (GOV)
The entire volume of all petroleum liquids, sediment and water, excluding free water, at measured temperature and pressure

Gross Standard Volume (GSV)
The entire volume of all petroleum liquids and sediments and water, excluding free water, corrected to a standard reference temperature and pressure.

Indicated Volume
The change in meter reading that occurs during transfer through a meter.

Indicated Volume with Factor
The indicated volume multiplied by the meter factor for the particular liquid and operating conditions under which the meter was proved.

In-Transit Difference
The difference between the Total Calculated Volume immediately after a loading and the Total Calculated Volume immediately before discharge.

On Board Quantity
Oil, water, sludge and sediment in cargo tanks and associated lines and pumps before loading

Quantity Remaining on Board (ROB)
Oil, water, sludge and sediment in cargo tanks and associated lines and pumps

Reference Height
The distance between the dip datum point and the upper reference point

Reference point
A point to which all measurements subsequent to calibration are related (see also, datum point).

Suspended Water
The water contained within the oil that is finely dispersed as small droplets.

Total Calculated Volume (TCV)
The entire volume of all petroleum liquids and suspended sediment and water, excluding free water, corrected by the appropriate volume correction factor (Cv) for the observed temperature and density to a standard reference temperature (15 °C, 20°C, or 60 °F), and also corrected by the applicable pressure factor (Cp) and meter factor, with all free water measured at observed temperature and pressure added back in (i.e. Gross Standard Volume plus Free Water)

Total Observed Volume (TOV)
The entire volume of material contained in a tank at the tank temperature.

Ullage (Outage)
The distance between the surface of a liquid in a tank and a fixed reference point on the top of the tank. Also, the capacity of a tank not occupied by liquid

Water Cut (Dip)
The procedure of locating the oil/water interface for the purpose of determining the volume of free water in a shore tank or vessel compartment.

The necessary data are to be obtained primarily by direct measurement activities by the designated party or parties. Indirect data sources should be clearly indicated

8.3 Selection of the tanks

The following tanks will be omitted from the selection in advance:

- the first tank that was loaded (in view of any possible line fills)
- the last tank that was loaded (in view of possible stripping)
- wing tanks (owing to possibly irregular bottom surfaces)*.

From the remaining centre tanks two will be selected at random for sampling

8.4 Data from the two selected tanks

For the two selected tanks the following data are required:

---

* If the carrier is a so-called Combi-carrier or Multiple-Cargo carrier, the crude to be sampled may be loaded in wing tanks only. In that case two randomly chosen wing tanks will be sampled. Furthermore, a Multiple-Cargo carrier may carry a load of different crude oils that have to be sampled.

- from the ship's calibration tables: the reference heights of the official hatches and their height above deck
- from the ship's OBQ report the OBQ data for the two tanks (liquid/non-liquid, free water).

8.5 Measurements

For the two selected tanks, measurements will be made of the actual reference height of the official hatches, of that of the butterworth holes, and of the ullage (free space) from deck-level to liquid surface at the butterworth hole.

From these data the theoretical reference height of butterworth hole is calculated.

Furthermore from these data the actual rope length necessary for both the top and the bottom sampling can be calculated.

The rope length for the top sample is the ullage from deck level near the butterworth hole to the liquid level, plus one metre.

The rope length for the bottom sample is the actual reference height near the butterworth hole corrected for the height of the sampling device.

8.6 Sampling

The sample from the Power Mixer at the laboratory involved will be taken in a 2-litre bottle.
From each of the two tanks the following samples will be taken:

- 1 litre top sample
- 1 litre bottom sample

Prior to its use for sampling a cargo, the sampler will be cleaned with xylene.
All sample bottles will be made of colourless borosilicate glass, closed with a plastic screwcap with teflon inlay.

The actual samples will be taken as follows:

POWER MIXER SAMPLE (from the 'in-line sampler')
Prior to sampling of the crude cargo, the receptacle of the in-line sampler should be checked for cleanness and dryness.
After sampling the crude cargo, the contents of the receptacle should be properly mixed before being subsampled at the laboratory involved. The first 100 ml has to be discarded.

- Place the sample bottle under the outlet of the receptacle.

- When the bottle is full, shut it at once.
- Label the sample.

TOP SAMPLE

- Place the sample bottle in the sampling device. It will then close automatically
- Lower the sampler to the desired level of one metre below the surface (ullage plus one metre) with the bottle in horizontal position, using a fresh rope.
- Open the lever by pulling a second rope attached to the lever. This lever operates a valve that allows the bottle to fill.
- Raise the bottle as soon as no more air bubbles appear at the surface of the oil. The bottle will then close automatically. When it is raised fully, pour off a small amount of oil and close it immediately with the plastic screwcap with Teflon inlay.
- Label the sample
- As the bottle is raised, the rope must be kept clear of any foreign material. Keep the rope in a clean plastic bucket before taking the bottom sample from the same tank.

BOTTOM SAMPLE (from the same tank):

- Place the sample bottle in the sampling device. It will then close automatically
- Submerge the sampling device to a depth of about 15 metres in the oil, raise it and check whether it has remained empty. If it has, submerge it again and continue the sampling. If it has not, replace the bottle in its holder and repeat the test
- Lower the sampling device to the desired level (total reference height corrected for height of sampling device) with the bottle in horizontal position.
- Bottle opens and fills automatically.
- Raise the bottle as soon as no more air bubbles appear at the surface of the oil. It then closes automatically and assumes an upright position as soon as it is clear of the bottom.
- When raised fully, pour off a small amount of oil and close the bottle immediately with the plastic screwcap with Teflon inlay.
- Label the sample
- Discard the rope.

9. REPORT

All reports and correspondence will be in the English language

10. DEVIATIONS FROM THE PROTOCOL

Deviations from the protocol are not likely to occur.

If, however, a situation occurs that necessitates unforseen actions, a formal amendment to the protocol will only be drawn up if, in the opinion of the Project Manager, the changes have a significant impact on the nature of the Study.

Otherwise, the situation and the action taken will be documented in the study file, reported in the 'Registration of Crude Cargoes' checklist and the final report.

11. TRANSPORT AND STORAGE OF SAMPLES

A TNO representative will take the samples to the TNO laboratory, where they will be stored in the dark at 4° C. All samples will be kept for three years after completion of the Study.

ANNEX 1: LABEL

Chemical Laboratories **SAYBOLT - VAN DUYN BV**
P.O. Box 151 Rotterdam

Sample from:..... Date:.....
Hour:.....

before/after/during * loading/discharge/transfer *

Into/from : .....

Product : .....

Installation : .....

Upper –*	Running –*	Bottom –*
Middle –	Pipeline –	Ship's sample :.....
Lower –	1st Foot –	Name inspector :.....

Sample description : .....

This sample to be retained for a period of 3 years * delete as necessary.

ANNEX 2: SAMPLER

ANNEX 3: CRUDE OIL REGISTRATION

SAYBOLT-VAN DUYN BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

SAYBOLT

Report no.: _____
Date : _____
Vessel : _____
Location : _____
Jetty : _____
Grade : _____

CRUDE OIL REGISTRATION
GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA	
Load port Bill of Lading G.S.V. Weight Bill of Lading Date	Bbls60°F/m³15°C/_____* Longtons/Mtons* vac/air*

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F		
Watercontent vol%/wt%*		
Sediments vol%/wt%*		
BS&W vol%		
Carbon residue wt%		
Sulphur wt%		

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume m³/bbls*	Dip cm/inch*	Volume m³/bbls*	Dip cm/inch*	Volume m³/bbls*
Sub-Totals						

Total OBQ Selected tanks	

HISTORY	
Previous Vessel Names	

Previous Cargoes	Date	API 60°F	Watercontent	Others

COPY of relevant LOADPORT PAPERS obtained YES/NO*

* delete as applicable

Post address
P.O. Box 151
3000 AD Rotterdam
The Netherlands

Tel. (010) 460 99 11
Telex 216 42
Fax (010) 435 36 00

All our activities are carried out under the terms lodged at the Arrondissementsrechtbank (County Court) in Rotterdam. Trade Register Rotterdam No 228.922.

ANNEX 4: 'SAMPLING ACTIVITIES' CHECKLIST

Name of vessel : _____
Date of sampling : _____
Name of TNO representative : _____
Name of representative of Saybolt-Van Duyn : _____

- Sample bottles visually dry and clean yes/no
- Plastic screw caps with Teflon inlay clean yes/no
- Sampling device clean yes/no
- Sampling device functions properly yes/no
- Cotton rope fresh yes/no
- Cotton rope visually dry and clean yes/no
- A fresh cotton rope to be used for each tank yes/no
- Plastic bucket for temporary storage clean yes/no
- Receptacle (20-litre) clean yes/no
- Length of rope noted for each sample taken from tanks yes/no
- Depth of tank noted yes/no
- Samples taken:
  Tank (1) Top sample yes/no
  Bottom sample yes/no
  Tank (2) Top sample yes/no
  Bottom Sample yes/no
  Power Mixer sample yes/no
- Sample bottles labelled properly yes/no
- All necessary information gathered from master of vessel yes/no
- Crude Oil Registration' checklist filled in yes/no
- Deviations from protocol yes/no
- Samples handed to TNO yes/no
- Samples stored at TNO yes/no

Signature: TNO representative Saybolt-Van Duyn representative

Date: _____

Annex 5: Data from ships' records

Annex 3 lists the data from ships' logs in the following order :

Name of ship	Type of oil
Mega Hawk	Iranian Heavy
Sereno	Ural
Astro Alpha	Arabian Light
ESSO Demetia	Iranian Heavy
ESSO Normandie	Arabian Light
Kristhild	Iranian Heavy
ESSO Demetia	Arabian Heavy
ESSO Demetia	Iranian Heavy
Bergina	Stattfjord
TV Irian	Iranian Heavy
Edin.Satsuma	Iranian Light
Vanadis, Stockholm	Arabian Light
Esso Hawaii	Arabian Light
Pollux	Arabian Light
Kristen	Kuwait
Sunetta	Oseberg

SAYBOLT NEDERLAND BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

Members ASTM/IP
Management Ir. F. Pluimers

SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 27-12-93
Vessel : MEGA HAWK
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA	
Load port	Kharg Island Iran
Bill of Lading G.S.V.	1.826.124 Bbls60 F
Weight	251.726 Mtons*air*
Bill of Lading Date	19-11-93

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	31.33	ASTM D 1298
Watercontent vol%/wt%*	0,05	ASTM D 4006/473
Sediments vol%/wt%*		
BS&W vol%		
Carbon residue wt%		
Sulphur wt%		

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume m^3/bbls*
Grade1		426		343		
Sub-Totals		426		343		

Total OBQ Selected tanks	778 Bbls

HISTORY	
Previous Vessel Names	JARE BELLA SOUTH SEA

Previous Cargoes	Date	API 60°F	Watercontent	Others
ARAB LIGHT/EXTRA LGHT	01/10	33,4/37	No info	N.A
I.H.C.O	21/08	31,0	No info	N.A
KUWAIT EXPORT C.O	16/08	31,0	No info	

COPY of relevant LOADPORT PAPERS obtained No

* delete as applicable

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 27-12-93
Vessel : MEGA HAWK
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil
Data to be measured:No Permission from the Master of the Vessel

CRUDE OIL REGISTRATION

MEASUREMENTS

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1.	2.
Measured ref.height ullage hatch **A** (mm/inch*)			
Observed ullage at ullage hatch **B** (mm/inch*)			
Observed ullage butterworth hole **C** (mm/inch*)			
Measured ref.height butterw. hole (mm/inch*)			
Theoretical reference height at butterworth hole **(A-B+C)** *(rope length 35 mtr)* (mm/inch*)			
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm/inch* Corrected ullage mm/inch*			
Total Observed Volume m^3/bbls*			
Observed water dip mm/inch* Corrected water dip mm/inch*			
Free water m^3/bbls*			
Gross Observed Volume m^3/bbls*			
Temperature °C/°F*			
Density/API*			
Volume Corr. Factor Table			
Gross Standard Volume m^3/bbls*			
Density/W.C.F Table			
Mass/Weight Ltons/Mtons vac/air*			
SUMMARY (Selected tanks)			
T.O.V. m^3/bbls* Free Water G.O.V. G.S.V. T.C.V. Mass/Weight Ltons/Mtons Vac/Air*			

* delete as applicable

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 27-05-94
Vessel : MEGA HAWK
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	N.A. (m^3/bbls)*

LOADING PLAN ex LOADPORT

No info the Chief Officer boarded vessel during voyage to Rotterdam
Load plan unknown

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Due to hihg H2S content (6200 ppm) TNO and Saybolt not allowed by loading master Mr.Hoogland to open the butterworth hole to sample the cargo not allowed to open and sample with breatthing app.

In agreement with Mr. J.v Spijk from TNO we accept inline samples from the parcel only.

Receptacle container from the inlinesampler No 14 inspected and accepted

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J. van Zwieten
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Quality Assurance Services
Chemical Laboratories

Members ASTM/IP
Management Ir. F. Pluimers

SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 27-12-93
Vessel : MEGA HAWK
Location : TEAM Terminal Europoort
Jetty : 3
Grade : Irian Heavy and Arabian Heavy C.O

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Type of Vessel	VLCC
Owners/Flag	Norway
Max.cap. mtons	257.227 Mt
Total cap. 98%	306.747 M3
Max. summer & draft	20.900 m
Type of coating	No coating
Ballast system Segregated tanks	F.P and Aft.P
Permanent tanks	D.B and W.3
(De-)ballast time	
Number of sea suction valves	
Equiped with Heating coils	in port slop
Inert gas system	Yes
Segregation possibility Capa-	2 grades
city of ship's decklines	116,4 M3
Capacity of ship's bottom lines	115,6 M3
No. of pumps	4
Type of pumps	Centrifugal
Total capacity (cbm/hr)	16,000 m3/hrs
Stripping pumps	1
Methode of gauging	Vapour lock MMC
Position of gauging point	Aft
Is trim correction available	Yes
Max rate/pressure	8,000 m3/hrs
Cargo tanks Centers	5
Cargo tanks Wings	4

Tank contents at 98% (^{3})

P 1	19,050	C 1	28,348	S 1	19,050
P 2	21,806	C 2	27,747	S 2	21,806
P 3	P.B	C 3	33,296	S 3	P.B.
P 4	23,976	C 4	33,296	S 4	23,976
P 5	20,925	C 5sl	12.547	S 5	20,925
P 6		C 6		S 6	
P 7		C 7		S 7	
P 8		C 8		S 8	
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks

Saybolt Nederland B.V.
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Chemical Laboratories

Members ASTM/IP
Management Ir. F. Pluimers

SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 27-12-93
Vessel : MEGA HAWK
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

SAMPLE REPORT

Tank	No	Size	Description/Type of sample	Seal	Distribution
Inline	1	2 L	Irian Heavy Crude Oil	Open	TNO
Total					

Samples drawn by	J.v.Spijk/J.v.Zwieten /W.Poppelier

Remarks:
No permission from the master to take samples from the ships tanks.
Receptacle container 14 samples drawn during power mixen.

Bij Nerefco Lab.with J.v.Spijk (T.N.O) and W.Poppelier Saybolt

Saybolt Nederland B.V.
J. van Zwieten
Field Manager

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S v D 4029

SAYBOLT-VAN DUYN BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

SAYBOLT

Report no.: 2439/94
Date : 14-02-1994
Vessel : SERENO
Location : T.E.M. Europoort
Jetty : 2
Grade : Russian Export Blend Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA		
Load port		Ventspils
Bill of Lading	G.S.V.	87,759.059 M3 15oC
	Weight	75,753.620 Mtons vac
Bill of Lading Date		11-02-94

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	32.34	
Watercontent vol%/wt%*	0,27	
Sediments vol%/wt%*	0,008	
BS&W vol%	0,278	Calculated
Carbon residue wt%	-	
Sulphur wt%	1,35	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm	Volume m³/	Dip cm/inch*	Volume m³/bbls*	Dip cm	Volume m³/
C-1	4	17.9				
C-2	4	26.6				
Sub-Totals		44.8				

Total OBQ Selected tanks	44.8 M3

HISTORY	
Previous Vessel Names	T.V. Eagle, and before Fina Belgica

Previous Cargoes	Date	API 60°F	Watercontent	
1.Brent Blend	02-02-94	38.47		

COPY of relevant LOADPORT PAPERS obtained	Yes.

* delete as applicable

Saybolt Nederland B.V.
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S.v.D 4000

SAYBOLT-VAN DUYN BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

SAYBOLT

Report no.: 2439/94
Date : 14/02/94
Vessel : SERENO
Location : T.E.M. - Europoort
Jetty : 2
Grade : Russian Export Blend Crude Oil

CRUDE OIL REGISTRATION

MEASUREMENTS

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1. C 1	2. C-2
Measured ref.height ullage hatch **A** (mm/inch*)		2061 cm	1993 cm
Observed ullage at ullage hatch **B** (mm/inch*)		478 cm	240.5 cm
Observed ullage butterworth hole **C** (mm/inch*)		415 cm	117.5 cm
Measured ref.height butterw. hole (mm/inch*)		1959 cm	1926 cm
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 30 mtr)* (mm/inch*)		1998 cm	1930 cm
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm/inch*	4780	2405	
Corrected ullage mm/inch*	4780	2405	
Total Observed Volume m^3/bbls*	8,844.06	14,827.97	23,672.03
Observed water dip mm/inch*	nil		
Corrected water dip mm/inch*	nil		
Free water m^3/bbls*	nil		nil
Gross Observed Volume m^3/bbls*	8,844.06	14,827.97	23,672.03
Temperature °C	4,3	4.1	
Density 15°C	0.8632	0,8632	
Volume Corr. Factor Table 54A	1.0088	1.0090	
Gross Standard Volume m^3	8,921.88	14,961.422	23,883.302
Density	0.8632	0.8632	
Mass Mtons vac	7,701.374	12,914.699	20,616.073

SUMMARY (Selected tanks)	
T.O.V. m^3	23,672.03
Free Water	-
G.O.V.	23,672.03
G.S.V.	23,883.31
T.C.V.	23,883.31
Mass Mtons Vac	20,616.073

* delete as applicable

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S.v.D 4000

SAYBOLT-VAN DUYN BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

SAYBOLT

Report no.: 2439/94
Date : 14/02/1994
Vessel : SERENO
Location : T.E.M. - Europoort
Jetty : 2
Grade : Russian Export Blend Crude Oil

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	50	(m^3*

LOADING PLAN ex LOADPORT

Commenced loading into wings 3 and completed in center 4

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

- Sludse and sediments in Center 1 and 2
- Samples taken from Center 2 and 1 at butterworth hole.
- Ullage, temperature, free water dipping done before sampling and reference height measurements
- reference height measurements at butterworth hole
- all activities in cooporation with TNO/VROM representatives.
- c.o.w. operations: a. topwash 90°/30°
  b. bottomwash 30°/zero

all cargotanks 100% c.o.w.

Saybolt/TNO/ repr.present at TEM		14/02/1994	19:00
Inspection of inline Sampler		14/02/1994	19:10
On board T.V.		14/02/1994	19:30
Sampling etc.	from 14/02/94 19:45 -		22:30
Left the Terminal		14/02/1994	23:00
Saybolt/TNO Repr.present at Nerefco Pernis to check distrubution of the inline Sampler	from 15/02/94 09:30 -		10:30

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SAYBOLT

Report no.: 2439/94
Date : 14-02-1994
Vessel : SERENO
Location : T.E.M. - Europoort
Jetty : 2
Grade : Russian Export Blend Crude Oil

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Type of Vessel	Motor Tanker
Owners/Flag	Inver Gargill/Liberian
Max.cap. mtons	89,500 mton sdwt
Total cap. 98%	101,415 M3
Max. summer & draft	S: 13.001/ W: 12.731
Type of coating	none
Ballast system Segregated tanks	-
Permanent tanks	wings 2,4,7 ,fore and aftpiek
(De-)ballast time	during load/discharging
Number of sea suction valves	2
Equiped with Heating coils	Yes
Inert gas system	yes
Segregation possibility	3
Capacity of ship's decklines	147.9 M3
Capacity of ship's bottom lines	160.1 M3
No. of pumps	3
Type of pumps steam centrifugal	2.750 m^3/hr
Total capacity (cbm/hr)	8.250 M3/Hr
Stripping pumps steam repric	1 x 250 M3 /hr
Methode of gauging	manual MMC
Position of gauging point	Varios
Is trim correction available	yes
Max rate/pressure	-
Cargo tanks Centers	5
Cargo tanks Wings	4

Tank contents at 98% (m^3)

P 1	5,749.9	C 1	10,782	S 1	5,741.1
P 2	Ballast	C 2	15,932	S 2	Ballast
P 3	5,932.0	C 3	12,404	S 3	5,930.4
P 4	Ballast	C 4	14,134	S 4	Ballast
P 5	3,378.2	C 5	13,584	S 5	3,377.9
P 6	2,233.9			S 6	2,234.5
P 7	Ballast			S 7	Ballast

Remarks

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SAYBOLT

Report no.: 2439/94
Date : 14-02-1994
Vessel : SERENO
Location : T.E.M. - Europoort
Jetty : 2
Grade : Russian Export Blend Crude Oil

CRUDE OIL REGISTRATION

SAMPLE REPORT

Tank	No	Size	Description/Type of sample	Seal	Distribution
C 1	1	ltr	top sample (1 m below surface)	-	T.N.O.
C 1	1	ltr	bottom sample (7 cm above bottom)	-	T.N.O.
C 2	1	Ltr	top sample (1 m below surface)	-	T.N.O.
C 2	1	ltr	bottom sample (7 cm above bottom)	-	T.N.O.
pipeline	1	2 ltr	Inline sample	-	T.N.O.
Total	5				

Samples drawn by	Saybolt
Remarks	

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SAYBOLT

Report no.: 3239/94
Date : 21-03-94
Vessel : ASTRA ALPHA
Location : Texaco Esso Maatschap Terminal R'dam
Jetty : 3
Grade : Arabian Light Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA		
Load port	Juahmah, Saudi Arabia	
Bill of Lading G.S.V.	1.916.491	Bbls 60 oF
Weight	261.671,56	Mtons* air*
Bill of Lading Date	12-02-94	

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	32,90	
Watercontent vol%/wt%*	not reported	
Sediments vol%/wt%*	not reported	
BS&W vol%	calculeted from B/L nil	
Carbon residue wt%	not reported	
Sulphur wt%	not reported	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip inch*	Volume bbls*	Dip inch*	Volume bbls*	Dip inch*	Volume bbls*
Ctr 2	nil		nil		5	111
Ctr 4					3	96
Sub-Totals						207
Total OBQ Selected tanks						

HISTORY				
Previous Vessel Names	No info			
Previous Cargoes	Date	API 60°F	Watercontent	Others
Arab light/medium	15-01-94	33,4/30,	not reported	
Irian Crude oil	30-10-94	31,0	not reported	

COPY of relevant LOADPORT PAPERS obtained YE*

* delete as applicable

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SAYBOLT

CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 3239/94
Date : 21-03-94
Vessel : Astro Alpha
Location : Texaco Esso Maatschap R'dam
Jetty : 3
Grade : Arabian Light Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1.Ctr 2	2 Ctr 4.
Measured ref.height ullage hatch **A** (mm/inch*)		91'09"	91'10"
Observed ullage at ullage hatch **B** (mm/inch*)		11'02"	07'11"
Observed ullage butterworth hole **C** (mm/inch*)		08'05"	05'01"
Measured ref.height butterw. hole (mm/inch*)		88'10"	88'10"
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)* (mm/inch*)		88'12"	89'00"
ULLAGE MEASUREMENTS AT ULLAGE HATCH	Ctr2	Ctr 4	
Observed ullage mm/inch*	11'02"	07'11"	
Corrected ullage mm/inch*	11'02,5"	07'11,5"	
Total Observed Volume m^3/bbls*	22.649,447	24.504,984	
Observed water dip mm/inch*	00,5"	02,5"	
Corrected water dip mm/inch*	00,5"	02,5"	
Free water m^3/bbls*	12,083	61,687	
Gross Observed Volume m^3/bbls*	22.637,364	24.443,297	
Temperature °C/°F*	19,6	20,9	
Density/API* Api = 32,90	0,8602	0,8602	
Volume Corr. Factor Table 54A	0,9962	0,9951	
Gross Standard Volume m^3/bbls*	22.551,342	24.323,525	
Density/W.C.F Table *	0,8602	0,8602	
Weight Mtons vac*	19.398,664	20.923,096	

SUMMARY (Selected tanks)	
T.O.V. bbls*	47.154,431
Free Water	73,770
G.O.V.	47.080,661
G.S.V.	46.874,867
T.C.V.	46.948,637
Weight Mtons Vac*	40.421,760

* delete as applicable

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SAYBOLT

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 3239/94
Date : 21-03-94
Vessel : Astro Alpha
Location : Texaco Esso Maatschap R'dam
Jetty : 3
Grade : Arabian Light Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	nil (m^3/bbls)*

LOADING PLAN ex LOADPORT

By commensed loading all cargotanks open

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

No

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CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 3239/94
Date : 21-03-94
Vessel : Astra Alpha
Location : Texaco Esso Maatschap R'dam
Jetty : 3
Grade : Arabian Light Crude Oil

Type of Vessel	VLCC
Owners/Flag	Kristen Navigation
Max.cap. mtons	117.265.39 B.Grt
Total cap. 98%	2.014.711 USBbls
Max. summer & draft	264.073 L.T
Type of coating	Yes,Epoxy
Ballast system Segregated tanks	W.4 For and Aft Piek
Permanent tanks	
(De-)ballast time	
Number of sea suction valves	2 Segreted line
Equiped with Heating coils	Only SB sloptank
Inert gas system	Yes
Segregation possibility	4 Grades
Capacity of ship's decklines	208 cu m
Capacity of ship's bottom lines	200 cu m
No. of pumps	4
Type of pumps	centrifucal
Total capacity (cbm/hr)	5.000 cu m each
Stripping pumps	two eductors
Methode of gauging	manual
Position of gauging point	aft
Is trim correction available	yes
Max rate/pressure	20.000 cu m 12 Bar
Cargo tanks Centers	7
Cargo tanks Wings	12 + 2 sloptanks

Tank contents at 98% (US BBls)

P 1	46.939	C 1	83.429	S 1	46.939
P 2	76.452	C 2	153.398	S 2	76.452
P 3	81.409	C 3	159.577	S 3	81.409
P 4	Ballast	C 4	159.554	S 4	Ballast
P 5	81.368	C 5	159.295	S 5	81.368
P 6	81.058	C 6	159.256	S 6	81.058
P 7	73.915	C 7	205.402	S 7	73.915
P 8slopt	26.259	C 8		S 8	26.259
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks Segregated Ballast Cap. 43.332 cu m

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SAYBOLT

CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 3239/94
Date : 21-03-94
Vessel : Astra Alpha
Location : Texaco Esso Maatschap R'Dam
Jetty : 3
Grade : Arabian Ligjt Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
Ctr.2	2	x 1	Upper and Bottom Sample	open	T.N.O.
Ctr.4	2	x 1	Upper and Bottom Sample	open	T.N.O.
Inline	2	X 2	Inline Sample	open	T.N.O
Total	6				

Samples drawn by	H. de Bruijn / W.J. Poppelier

Remarks

Saybolt and T.N.O arrived on the installation	21-03-94	13;30
Inline sample contianer no 15 checked and passed	21-03-94	14:00
Inline sampler checked : 50 grabs = 54 ml	21-03-94	14:00
Tank vessel completed mooring on jetty 3	21-03-94	14:20
Commenced measured and sampling Ctr. 2 and 4	21-03-94	14:45
Completed measured and sampling Ctr. 2 and 4	21-03-94	15:40
Inline sample contianer no 19 checked and passed	21-03-94	21;00
Claerensline sample take in contianer 20	22-03-94	10:00
Tank vessel has partly discharged to TEM and MOT T.N.O. J.v.Spijk informed after complition of Discharge operations.	23-03-94	09:00

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SAYBOLT

CRUDE OIL REGISTRATION

GENERAL DATA

Report no.:2439/94
Date :26-03-94
Vessel : Esso Demetia
Location : Texaco Esso Maatschap Terminal R'dam
Jetty : 2
Grade : Iranian Heavy Crude oil

Data below to be copied from ship's records.

LOADPORT DATA	
Load port	Sidi Kerir Egypt
Bill of Lading N.S.V.	1.193.949 USBbls 60 oF
Weight	165.890,193 Mtons* vac/air*
Bill of Lading Date	16-03-94

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	30,90	ASTM D 1298
Watercontent vol%*	no info	
Sediments vol%*	no info	
BS&W vol%	0,520	ASTM D 4928/D4807
Carbon residue wt%	no info	
Sulphur wt%	no info	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm*	Volume m^3/*	Dip cm*	Volume m^3/*	Dip cm/*	Volume m^3/*
Ctr 3	4	2,067	nil		nil	
Ctr 5	8	6,359	nil		nil	
Sub-Totals		8,426				

Total OBQ Selected tanks	8,426 cu m liquid o.b.q

HISTORY	
Previous Vessel Names	None

Previous Cargoes Ctr.3 and 5	Date	API 60°F	Watercontent	Others
Arabian light C.O	no info	32,63	0,179 KF V%	
Arabian Light C.O	no info	36,39	0,218 KF V%	
Irian Heavy C.O	no info	30,83	0,539 KF V%	

COPY of relevant LOADPORT PAPERS obtained YES/*

* delete as applicable

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CRUDE OIL REGISTRATION
MEASUREMENTS

Report no.: 2439/94
Date : 26-03-94
Vessel : Esso Dementia
Location : Texaco Esso Maatschap Terminal R'dam
Jetty : 2
Grade : Irian Heavy Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)				
Tank description			1.Ctr.3	2.Ctr.5
Measured ref.height ullage hatch **A**	(mm*)		27700	27800
Observed ullage at ullage hatch **B**	(mm*)		3700	3140
Observed ullage butterworth hole **C**	(mm*)		2660	2080
Measured ref.height butterw. hole	(mm*)		26660	26730
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)*	(mm*)		26660	26740
ULLAGE MEASUREMENTS AT ULLAGE HATCH				
Observed ullage Corrected ullage	mm* mm*	3700 2840	3140 2280	
Total Observed Volume	m^3*	30.793,079	15.743,847	
Observed water dip Corrected water dip	mm* mm*	100 100	180 180	
Free water	m^3*	127,985	113,994	
Gross Observed Volume	m^3/bbls*	30.665,094	15.629,853	
Temperature	°C*	19,10	18,80	
Density/*		0,8708	0,8708	
Volume Corr. Factor Table 54 A		0,9967	0,9969	
Gross Standard Volume	m^3*	30.563,899	15.581,400	
Density/		0,8708	0,8708	
Mass/Weight Mtons vac*		26.615,043	13.568,283	

SUMMARY (Selected tanks)		
T.O.V.	m^3/*	46.536,926
Free Water		241.979
G.O.V.		46.294,947
G.S.V.		46.145,299
T.C.V.		46.387,278
Mass/Weight	Mtons Vac*	40.183,326

* delete as applicable

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CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 2439/94
Date : 26-03-94
Vessel : Esso Demetia
Location : Texaco Esso Maatschap R'dam
Jetty : 2
Grade : Irian Heavy Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	no info	(m^3/*

LOADING PLAN ex LOADPORT

TV loaded two parcel at Sidi Kerir
A) Arabian Heavy into Ctr.2,4/wing 4 not discharged at TEM distination Fawley UK
B) Irian Heavy Crude oil Ctr 1,3,5 /Wing 1,2,5,6 and sloptanks Partly discharged at TEM

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Due to H2S 7650 ppm at the Irian heavy parcel Surveyors used breathing equiment during sampling of ctr 3 and 5

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SAYBOLT

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/94
Date : 26-03-94
Vessel : Esso Demetia
Location : Texaco Esso Maatschap Terminal R'dam
Jetty : 2
Grade : Irian Heavy Crude Oil

Type of Vessel		V.L.C.C.
Owners/Flag		Esso Bermuda
Max.cap. mtons		258.970 sdtwt
Total cap. 98%		310,791 cu m
Max. summer & draft		S20.07m
Type of coating		none
Ballast system	Segregated tanks	Fp./W.3/Ap
	Permanent tanks	
	(De-)ballast time	During load/dischar
Number of sea suction valves		2 sea /1 overboard
Equiped with	Heating coils	only sloptank
	Inert gas system	Yes
	Segregation possibility	3 grades
Capacity of ship's decklines		4x 26,5 cu m
Capacity of ship's bottom lines		294,8 cu m
No. of pumps		4
Type of pumps		centrifugal
Total capacity (cbm/hr)		4 x 4,000 cu m/hr.
Stripping pumps		1 x 200 cu m/hr
Methode of gauging		Manual
Position of gauging point		MMC stand pipe aft
Is trim correction available		yes
Max rate/pressure		16,000 cu m 10 Bar
Cargo tanks	Centers	5
Cargo tanks	Wings	6 and slopt

Tank contents at 98% ( )

P 1	14667	C 1	23948	S 1	14667
P 2	24334	C 2	33113	S 2	24334
P 3		C 3	33113	S 3	
P 4	12168	C 4	33113	S 4	12168
P 5	23912	C 5	16548	S 5	23912
P 6	6777	C 6		S 6	6777
P 7	3620	C 7		S 7	3620
P 8		C 8		S 8	
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks

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SAYBOLT

CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 2439/94
Date : 26-03-94
Vessel : Esso Demetia
Location : Texaco Esso Maatschap Terminal R'dam
Jetty : 2
Grade : Irian Heavy Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
Ctr.3	2	x 1	Upper,Bottom (15 cm)	open	T.N.O
Ctr 5	2	x 1	Upper,Bottom (15 cm)	open	T.N.O
Inline	2	x 2	Automatic inline sampler	open	T.N.O
Total	6				

Samples drawn by	H. d . Bruijn /W.J.Poppelier

Remarks

Saybolt and T.N.O arrived at the Terminal	26-03-94 15:00
Inline Sample contianer 31 and 11 inspected and passed	26-03-94 15:40
Sampler checked 50 graps = 50 ml	26-03-94 15:40
Vessel all vast	26-03-94 15:50
H2S Check by Inscape 7650 ppm at the Irian Heavy	26-03-94 16:00
Permission voor sampling with Breathing equipment	26-03-94 17:50
Completed sampling center 3 and 5	26-03-94 18:25
Sample contianer no 29 inspected and passed for clearens sample	27-03-94 10:00
Sample of M.O.T. Party to N,R.C Pernis and info to T.N.O Hr. J.v.Spijk	27-03-94 16:00
Vessel completed discharging to T.E.M.	28-03-94 09:30
Info to T.N.O Hr. J.v.Spijk voor inline sample	28-03-94 10:00

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SAYBOLT-VAN DUYN BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

SAYBOLT

Report no.: 2439/94 :
Vessel : ESSO NORMANDIE
Location : TEAM Terminal Europoort Rotterdam
Jetty : 2
Grade : Arabian Extra Light Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA			
Load port			
Bill of Lading	G.S.V.	341,080	Bbls60°F/
	Weight	45,587.332	Mton* air*
Bill of Lading Date		14-04-1994	

CRUDE DATA ON LOADING			
PROPERTY		RESULT	METHOD
API Gravity at 60°F		36,43	ASTM D 1298
Watercontent	vol%	0,093	ASTM D 4928
Sediments	vol%	not reported	ASTM D 4807
BS&W	vol%	" "	
Carbon residue	wt%	" "	
Sulphur	wt%	" "	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm	Volume bbls*	Dip cm/*	Volume bbls*	Dip cm*	Volume bbls*
Ctr 1	6	48	nil		nil	
Ctr 3	nil		nil		nil	
Sub-Totals		48				
Total OBQ Selected tanks			48 bbls			

HISTORY				
Previous Vessel Names				
Previous Cargoes	Date	API 60°F	Watercontent	Others
Forties C.O.	08-04-94	39,90		
Arab Light C.O.	09-02-94	32,80		
Arab Medium	04-01-94	29,00		
COPY of relevant LOADPORT PAPERS obtained			YES*	

* delete as applicable

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SAYBOLT

CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 2439/94
Date : 24-04-94
Vessel : Esso Normandie
Location : Team Terminal Europoort Rotterdam
Jetty : 2
Grade : Arab Extra Light Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1.Ctr 1	2.Ctr 3
Measured ref.height ullage hatch **A**	(mm*)	29860	29610
Observed ullage at ullage hatch **B**	(mm*)	1990	7510
Observed ullage butterworth hole **C**	(mm*)	1100	6280
Measured ref.height butterw. hole	(mm*)	28970	28380
Theoretical reference height at butterworth hole **(A-B+C)** *(rope length 35 mtr)*	(mm*)	28970	28380
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage Corrected ullage	mm* mm*	1990 1995	7510 7525
Total Observed Volume	m^{3*}	39,321.142	28,816.871
Observed water dip Corrected water dip	mm* mm*	nil	nil
Free water	m^{3*}	nil	nil
Gross Observed Volume	m^3/bbls*	39,321,142	28,816,871
Temperature	°C*	21,8	21,6
Density/API*		0,8422	0,8422
Volume Corr. Factor Table 54 A		0,9941	0,9943
Gross Standard Volume	m^{3*}	39,089,147	28,652,615
Density		0,8422	0,8422
Mass	Mtons vac*	32,920.880	24,131.232

SUMMARY (Selected tanks)		
T.O.V.	m^{3*}	68,138,013
Free Water		0
G.O.V.		68,138,013
G.S.V.		67,741,762
T.C.V.		67,741,762
Mass	Mtons Vac*	57,052.112

* delete as applicable

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CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.:2439/94
Date :24-04-94
Vessel :Esso Normandie
Location :Team Terminal Europoort Rotterdam
Jetty : 2
Grade : Arab Extra Light Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	(m^3/bbls)*

LOADING PLAN ex LOADPORT

TV loaded 3 grades of cargo :

A) Arab Extra Light Crude Oil into Ctr. 1,3,4 and 5
commenced loading in ctr 5,completed loading in Ctr 4
B) Arab Heavy Crude Oil into Wings 1 and 5
C) Ras Badran Crude Oil into Wings 3,4, and 6

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Samples taken from Ctr. 1 and 3 .
H2s content 130 ppm.
Smal lekkages of the sampler before taken the bottom samples.
Discharge plan : Part cargo discharge of the Arab Extra Light Crude Oil
at TEAM Terminal approx 54,000 M3 at 15 oC

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CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/94
Date : 24-04-94
Vessel : Esso Normandie
Location : TEAM Terminal Europoort Rotterdam
Jetty : 2
Grade : Arab Extra Light Crude Oil

Type of Vessel	V.L.C.C
Owners/Flag	ESSO France,Le Havre
Max.cap. mtons	SDWT 314.238
Total cap. 98%	326,930 M3
Max. summer & draft	S= 21.378 m
Type of coating	No
Ballast system Segregated tanks	FP,Wing 2 AFP
Permanent tanks	
(De-)ballast time	During loading ore
Number of sea suction valves	discharing. 2
Equiped with Heating coils	only in sloptanks
Inert gas system	Yes
Segregation possibility	3 grades
Capacity of ship's decklines	2 x 61 M3
Capacity of ship's bottom lines	210 M3
No. of pumps	4
Type of pumps	Centrifugal
Total capacity (cbm/hr)	4 x 3000 M3 /hrs
Stripping pumps	2 x 350 M3,
Methode of gauging	Manual
Position of gauging point	Aft
Is trim correction available	Yes
Max rate/pressure	
Cargo tanks Centers	4
Cargo tanks Wings	10

Tank contents at 98% (Cu. M)

P 1	25,250	C 1	39,539	S 1	25,250
P 2		C 2		S 2	
P 3	13,246	C 3	36,287	S 3	13,246
P 4	26,487	C 4	36,284	S 4	26,487
P 5	19,097	C 5	36,217	S 5	19,097
P sl	5,288	C 6		S 6	5,288
P 7		C 7		S 7	
P 8		C 8		S 8	
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks

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CRUDE OIL REGISTRATION
SAMPLE REPORT

Report no.: 2439/94
Date : 24-04-94
Vessel : Esso Normandie
Location : Team Terminal Europoort Rotterdam
Jetty : 2
Grade : Arab Extra Light Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
Ctr 1	2	1	Upper and Lower sample	open	T.N.O
Ctr 3	2	1	Upper and Lower sample	open	T.N.O
Total	4				

Samples drawn by	H. de Bruijn ,W.Poppelier

Remarks

15 ltr sample take at the manifold due to cleaning oil for i.l.s. mixer.Delvered at Nerefco Pernis Lab.

For T.N.O during sampling Hr. J.Spijk and Hr J.Timmer.

CRUDE OIL REGISTRATION
GENERAL DATA

Report no.: 2439/94 :
Vessel : ESSO NORMANDIE
Location : TEAM Terminal Europoort Rotterdam
Jetty : 2
Grade : Arabian Extra Light Crude Oil

Data below to be copied from ship's records.

LOADPORT DATA			
Load port			
Bill of Lading	G.S.V.	341,080	Bbls60°F/
	Weight	45,587.332	Mton* air*
Bill of Lading Date		14-04-1994	

CRUDE DATA ON LOADING			
PROPERTY		RESULT	METHOD
API Gravity at 60°F		36,43	ASTM D 1298
Watercontent	vol%	0,093	ASTM D 4928
Sediments	vol%	not reported	ASTM D 4807
BS&W	vol%	" "	
Carbon residue	wt%	" "	
Sulphur	wt%	" "	

Saybolt Nederland B.V.
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O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid	Non-liquid	Free Water

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 30-04-94
Vessel : KRISTHILD
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA		
Load port	Kharg Island Iran	
Bill of Lading G.S.V.	1,944,279	BBls 60 oF
Weight	268,942	Mtons*air*
Bill of Lading Date	21-03-94	

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	30,77	No info
Watercontent vol%/wt%*	Zero	
Sediments vol%/wt%*	Zero	
BS&W vol%	Zero	
Carbon residue wt%	no info	
Sulphur wt%	no info	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume m^3/bbls*
C.3	1	36				
C.5		nil				
Sub-Totals		36				

Total OBQ Selected tanks	36 Bbls

HISTORY	
Previous Vessel Names	No previos names

Previous Cargoes	Date	API 60°F	Watercontent	Others
Arab.Light/Iran Light	24-12-93	32/34	nil	
Iran Heavy/Iran Light	23-11-93	30/33	nil	
Iran Heavy Crude Oil	02-08-93	30,33	nil	

COPY of relevant LOADPORT PAPERS obtained	Yes

* delete as applicable

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 30-04-94
Vessel : KRISTHILD
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

MEASUREMENTS

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1.	2.
Measured ref.height ullage hatch **A** (mm/*)		28.900	28.900
Observed ullage at ullage hatch **B** (mm/*)		2.040	1.760
Observed ullage butterworth hole **C** (mm/*)		1.280	1.000
Measured ref.height butterw. hole (mm/*)		28.030	28.080
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)* (mm/*)		28.140	28.140
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm/*	2.790	2.510	
Corrected ullage mm/*	2.790	2.510	
Total Observed Volume Bbls*	100,645	101,695	202,340
Observed/corrected water dipmm/	Nil	Nil	
Free water bbls/*			
Gross Observed Volume bbls/*	100,645	101,695	202,340
Temperature F*	69,3	69,3	
API*	30,77	30,77	
Volume Corr. Factor Table 6A	0,9958	0,9958	
Gross Standard Volume Bbls/*	100,222	101,268	201,490
W.C.F Table 13	0,13833	0,13833	
Weight /Mtons /air*	13,863.709	14,008.402	27,872.111

SUMMARY (Selected tanks)	
T.O.V. bbls*	202,340
Free Water	
G.O.V.	202,340
G.S.V.	201,490
T.C.V.	201,490
Weight Mtons Air*	27,872.111

* delete as applicable

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SAYBOLT

T.N.O. Order No: 52213

Report no.: 2439/94
Date : 30-04-94
Vessel : KRISTHILD
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	N.A. (m^3/bbls)*

LOADING PLAN ex LOADPORT

Commenced loading into P/S 2 and 5 than all other tanks.
Completed loading into Center 4

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Inert Gas pressure released ex C3 and C.5
Smal lekages from the sampler during bottom sampling
H2S content during sampling 30 ppm.

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 08-01-94
Vessel : STENA CONDUCTOR
Location : TEAM Terminal Europoort
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Type of Vessel	VLCC
Owners/Flag	Panama
Max.cap. mtons	274,732 SDWT
Total cap. 98%	326,464 cu.m.
Max. summer & draft	21.076 m
Type of coating	none
Ballast system Segregated tanks	Wings 3/Fore and Aftp
Permanent tanks	none
(De-)ballast time	During
Number of sea suction valves	Loading/discharg
Equiped with Heating coils	Only sloptanks
Inert gas system	Yes
Segregation possibility Capa-	4 Grades
city of ship's decklines	approx 130 cu.m
Capacity of ship's bottom lines	no info
No. of pumps	4 x 4000 cu.m/hrs
Type of pumps	Centrifugal
Total capacity (cbm/hr)	16.000 cu.m/hrs
Stripping pumps	1 x 350 cu.m./hrs
Methode of gauging	Manual
Position of gauging point	Tankhatch
Is trim correction available	Yes
Max rate/pressure	12.5 Bar
Cargo tanks Centers	6
Cargo tanks Wings	5

Tank contents at 98% (326,464 M3)

P 1	10,845	C 1	16,604	S 1	10,845
P 2	26,771	C 2	32,786	S 2	26,771
P 3	P.B.	C 3	16,393	S 3	P.B
P 4	26,845	C 4	32,786	S 4	26,845
P 5	23,754	C 5	16,393	S 5	23,754
P 6sl	6,471	C 6	22,123	S 6sl	6,471
P 7		C 7		S 7	
P 8		C 8		S 8	
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks
Volume are giving in cubic meters

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 08-01-94
Vessel : STENA CONDUCTOR
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

SAMPLE REPORT

Tank	No	Size	Description/Type of sample	Seal	Distribution
C.3	1	1	Top	open	T.N.O
C.3	1	1	Bottom	open	T.N.O
C.5	1	1	Top	open	T.N.O
C.5	1	1	Bottom	open	T.N.O
Container	1	15	Line sample for cleaning 15	open	Nerefco Pernis Lab
Totaal	5				

Samples drawn by	C.Minderhout and J.v.Zwieten

Remarks:

29-04-94 at	22:00	End of seapassage
30-04-94	05:20	Arrival Hoek of Holland
30-04-94	06:48	first line ashore
30-04-94	07:48	All fast
30-04-94	08:05	Inline samplercontainer Nr.25 checked and oke 50 grabs = 51 milliltre
30-04-94	08:30	H2S test by Dr.Verwey
30-04-94	08:30	Measurments and sampling by Ipechem till 10:30
30-04-94	10:45	Sampling by Saybolt and T.N.O. with pressed air
30-04-94	11:25	Completed sampling by Saybolt
30-04-94	11:30	Calculation ready by Ipechem
30-04-94	16:00	Take line sample in container 15 and send it to Nerefco Pernis Lab.for clearings purpus.

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SAYBOLT

Report no.: 2439/94
Date : 07-05-94
Vessel : ESSO DEMENTIA
Location : TEAM Terminal Europoort, Rotterdam
Jetty : 2
Grade : Irian Heavy and Arabian Heavy C.O

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA	
Load port	Sidi Kerir Egypt
Bill of Lading G.S.V.	122,311 and 107,171 /m315°C/*
Weight	105,478 and 94,889 Mtons*air*
Bill of Lading Date	25-04-94

CRUDE DATA ON LOADING			
PROPERTY	RESULT		METHOD
API Gravity at 60°F	30.58 and	28.03	ASTM D 1298
Watercontent vol%/wt%*			
Sediments vol%/wt%*			
BS&W vol%	0,631	0,22	ASTM D 4928/D4807
Carbon residue wt%			
Sulphur wt%	1,00	1,00	ASTM D 1551

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume m^3/bbls*
Grade1		103		21		
Grade2		30				
Sub-Totals		133		21		

Total OBQ Selected tanks	154 Bbls

HISTORY

Previous Vessel Names

Previous Cargoes	Date	API 60°F	Watercontent	Others
Brent Blend	13/04	38.3	0,29	N.A
I.H.C.O	16/03	30.9	0,52	N.A

COPY of relevant LOADPORT PAPERS obtained No

* delete as applicable

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CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 2439/94
Date : 07-05-94
Vessel : ESSO DEMENTIA
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 2
Grade : Irian Heavy and Arabian Heavy C.O.

Data to be measured:No Permission from the Master of the Vessel

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1.	2.
Measured ref.height ullage hatch **A** (mm/inch*)			
Observed ullage at ullage hatch **B** (mm/inch*)			
Observed ullage butterworth hole **C** (mm/inch*)			
Measured ref.height butterw. hole (mm/inch*)			
Theoretical reference height at butterworth hole **(A-B+C)** *(rope length 35 mtr)* (mm/inch*)			
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm/inch* Corrected ullage mm/inch*			
Total Observed Volume m^3/bbls*			
Observed water dip mm/inch* Corrected water dip mm/inch*			
Free water m^3/bbls*			
Gross Observed Volume m^3/bbls*			
Temperature °C/°F*			
Density/API*			
Volume Corr. Factor Table			
Gross Standard Volume m^3/bbls*			
Density/W.C.F Table			
Mass/Weight Ltons/Mtons vac/air*			

SUMMARY (Selected tanks)	
T.O.V. m^3/bbls* Free Water G.O.V. G.S.V. T.C.V. Mass/Weight Ltons/Mtons Vac/Air*	

* delete as applicable

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CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 2439/94
Date : 07-05-94
Vessel : ESSO DEMENTIA
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 2
Grade : Irian Heavy and Arabian Heavy C.O.

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	N.A. (m^3/bbls)*

LOADING PLAN ex LOADPORT

Irian Heavy Crude Oil is stored in Wing 1,4,6,slop and Center 2,4

Arabian Heavy Crude Oil is stored in Center 1,3 and 5

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

H2S check Arabian Heavy Crude Oil 2500 ppm and Irian Heavy Crude Oil 90 ppm, the Master giving no permission to open the tanks for sampling

In agreement with Mr. J.v Spijk from TNO we accept inline samples from both parcels only.

Receptacle container from the inlinesampler No 14 for the Irian Heavy and No. 32 for the Ariabian Heavy inspected and accepted.

Receptacle containers No 5 and 17 inspected and accepted for flussing the power mixers.Filling on the line during disscharging of the parcels.

06-05-94 at 07:30 The vessel moored alongside the terminal All vast
06-05-94 at 08:30 No permisson from the master for sampling.
07-05-94 at 01:48 Commenced Discharge Irian Heavy Crude Oil
07-05-94 at 10:00 Filling Receptacle container 5
08-05-94 at 08:45 Completed Discharge Irian Heavy Crude Oil
08-05-94 at 09:00 Commenced Discharge Arabian Heavy Crude Oil
08-05-94 at 15:45 Filling Receptacle container 17
09-05-94 at 05:00 Completed Discharge Arabian Heavy Crude Oil
09-05-94 at 11:35 Deleverd all receptacle containers at the laboratories of Nerefco Pernis.

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CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/94
Date : 07-05-94
Vessel : ESSO DEMENTIA
Location : TEAM Terminal Europoort
Jetty : 2
Grade : Irian Heavy and Arabian Heavy C.O

Type of Vessel	VLCC
Owners/Flag	Esso Int.Sh.Bermuda
Max.cap. mtons	258,970 Mt
Total cap. 98%	310,787 M3
Max. summer & draft	20.071 m
Type of coating	No coating
Ballast system Segregated tanks	F.P and Aft.P
Permanent tanks	D.B and W.3
(De-)ballast time	
Number of sea suction valves	
Equiped with Heating coils	in port slop
Inert gas system	Yes
Segregation possibility Capa-	4 grades
city of ship's decklines	141,4 M3
Capacity of ship's bottom lines	319,6 M3
No. of pumps	4
Type of pumps	Centrifugal
Total capacity (cbm/hr)	16,000 m3/hrs
Stripping pumps	1
Methode of gauging	Vapour lock MMC
Position of gauging point	Aft
Is trim correction available	Yes
Max rate/pressure	7,000 m3/hrs
Cargo tanks Centers	4
Cargo tanks Wings	7

Tank contents at 98% (M3)

P 1	14,666	C 1	23,948	S 1	14,666
P 2	24,334	C 2	33,113	S 2	24,334
P 3	P.B	C 3	33,113	S 3	P.B.
P 4	12,168	C 4	33,113	S 4	12,168
P 5	23,912	C 5	16,548	S 5	23,912
P 6	6,777	C 6		S 6	6,777
P 7	3,619	C 7		S 7	3,619
P 8		C 8		S 8	
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks

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CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 2439/94
Date : 09-05-94
Vessel : ESSO DEMENTIA
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 2
Grade : Irian Heavy and Arabian Heavy C.O.

Tank	No	Size	Description/Type of sample	Seal	Distribution
Inline	2	2 L	Irian Heavy Crude Oil	Open	TNO
Inline	2	2 L	Arabian Heavy Crude Oil	Open	TNO
Total					

Samples drawn by	J.v.Spijk/H. de Bruijn

Remarks:
No permission from the master to take samples from the ships tanks.

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Report no.: 2439/94
Date : 20-05-94
Vessel : BERGINA
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Stadfjord Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA	
Load port	Stadfjord offshore
Bill of Lading G.S.V.	858,208 Bbls60°F
Weight	112,988 Mtons*/air*
Bill of Lading Date	18-05-94

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	38,98	
Watercontent vol%/wt%*	0,11	
Sediments vol%/wt%*		
BS&W vol%		
Carbon residue wt%		
Sulphur wt%		

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm	Volume m^3	Dip cm/inch*	Volume m^3/bbls*	Dip cm/inch*	Volume m^3/bbls*
C 2	5	5,36				
C 4	4	3,18				
Sub-Totals		8,54				

Total OBQ Selected tanks	8,54 M3

HISTORY	
Previous Vessel Names	JARENA

Previous Cargoes	Date	API 60°F	Watercontent	Others
Statfjord C.O	14-05-94	38,04	0,12	
HoindPoint C.O	06-05-94	39,70	0,04	
Statfjord C.O	29-04-94	38,18	0,06	

COPY of relevant LOADPORT PAPERS obtained * YES

* delete as applicable

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CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 2439/94
Date : 20-05-94
Vessel : BERGINA
Location : TEAM Terminal Europoort, Rotterdam.
Jetty : 3
Grade : Statfjord Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1. Center 2	2.Center 4
Measured ref.height ullage hatch **A**	(mm*)	23300	23300
Observed ullage at ullage hatch **B**	(mm/)	1583	1623
Observed ullage butterworth hole **C**	(mm	883	923
Measured ref.height butterw. hole	(mm/	22600	22600
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)*	(mm	22600	22600
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage/Corrected ullage	mm*	1583	1623
Total Observed Volume	m^3/*	24,776.6	24,379.9	49,156.5
Observed water dip Corrected water dip	mm/* mm/*	0 0	0 0
Free water	m^3/*	0	0
Gross Observed Volume	m^3/*	24,776.6	24,379.9	49,156.5
Temperature C		32.6	33.1
Density		0,8296	0,8296
Volume Corr. Factor Table 54 A		0,98450	0,98378
Gross Standard Volume	m^3/*	24,392.5	23,984.4	48,376.9
Density/W.C.F Table		0,8285	0,8285
Weight	Mtons/air*	20,209.2	19,871.1	40,080.3

SUMMARY (Selected tanks)		
T.O.V.	m^3/*	49,156.5
Free Water		0
G.O.V.		49,156.5
G.S.V.		48,376.9
T.C.V.		48,376.9
Weight	/Mtons /Air*	40,080.3

* delete as applicable

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CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 2394/94
Date : 20-05-94
Vessel : BERGINA
Location : TEAM Terminal Europoort Rotterdam
Jetty : 3
Grade : Statfjord Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	N.A	(m^3/bbls)*

LOADING PLAN ex LOADPORT

Commenced loading in center 1 and 3 ,completed loading in center 3

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Incase of the slugse on the bottom we have used a roop to open the sampler on the bottom for both tanks.

No h2s was presend in the tanks.

Inspected and accepted the receptacle containers 14 and 21 for the inline sampler

Receptacle container 6 used for flussing the power mixer.

19-05-94 at 23:35 The vessel moored alongsite terminal
20-05-94 at 00:30 Permision for sampling center 2 and 4
20-05-94 at 01:30 Completed sampling
20-05-94 at 11:00 filling container 6 and the line.
21-05-94 at 10:30 Samples delivered at Nerefco Pernis laboraories.

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CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/94
Date : 20-05-94
Vessel : BERGINA
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Statfjord Crude Oil

Type of Vessel	VLCC
Owners/Flag	Bergehavne/Norwegian
Max.cap. mtons	134,089 Mt
Total cap. 98%	156,864 M3
Max. summer & draft	15.018 m
Type of coating	no
Ballast system Segregated tanks	Yes
Permanent tanks	Yes
(De-)ballast time	N.a
Number of sea suction valves	One
Equiped with Heating coils	Sloptans only
Inert gas system	Yes
Segregation possibility	Two
Capacity of ship's decklines	117 M3
Capacity of ship's bottom lines	114 M3
No. of pumps	4
Type of pumps	Centrifucal
Total capacity (cbm/hr)	12,000 M3 /hrs
Stripping pumps	2,000 M3 /hrs
Methode of gauging	Manual
Position of gauging point	Aft
Is trim correction available	Yes
Max rate/pressure	10 bar/10,000 M3
Cargo tanks Centers	4
Cargo tanks Wings	5

Tank contents at 98% (M3)

P 1 7,067	C 1 25,264	S 1 7,067
P 2 7,183	C 2 25,266	S 2 7,183
P 3 7,183	C 3 25,266	S 3 7,183
P 4 4,964	C 4 24,922	S 4 4,964
P 5Sl1,676	C 5	S 5sl1,676
P 6	C 6	S 6
P 7	C 7	S 7
P 8	C 8	S 8
P 9	C 9	S 9
P10	C10	S10
P11	C11	S11

Remarks

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CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 2439/94
Date : 20-05-94
Vessel : BERGINA
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Statfjord Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
Center 2	1	1 l.	Bottom sample	open	TNO
Center 2	1	1 l	Top sample	open	TNO
Center 4	1	1 l	Bottom sample	open	TNO
Center 4	1	1 l	Top sample	open	TNO
Cont. 14	2	2 l	Receptacle to TEAM	open	TNO
Cont. 21	2	2 l	Receptacle to MOT	open	TNO
Total	8				

Samples drawn by	J.v.Spijk,J.v.Zwieten and H.d Bruijn
Remarks	

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CRUDE OIL REGISTRATION

GENERAL DATA

Report no.: 2439/94
Date : 21-05-94
Vessel : IRIAN
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Iranian Heavy Crude Oil

Data below to be copied from ship's records.

LOADPORT DATA	
Load port	Kharg Island,Iran
Bill of Lading G.S.V.	2,019,478 Bbls60°F *
Weight	279,870 Mtons*/air*
Bill of Lading Date	17-04-94

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	30.47	ASTM D 1298
Watercontent vol%/wt%*	Zero	ASTM D 4006 /D 473
Sediments vol%/wt%*		
BS&W vol%		
Carbon residue wt%		
Sulphur wt%		

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume ^{3}/bbls*
All Tanks		220		81		40
Sub-Totals						
Total OBQ Selected tanks		341 Bbls				

HISTORY	
Previous Vessel Names	None

Previous Cargoes	Date	API 60°F	Watercontent	Others
Arab X L and Arab Heavy	01-03-94	36.8/27.	Not reported	
Lower Zakum UmnShaif C.O	26-02-94	37.45	0,05	
Iran Light and Iran Heavy	29-01-94	40.22	Zero	

COPY of relevant LOADPORT PAPERS obtained YES*

* delete as applicable

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CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 2439/94
Date : 21-05-94
Vessel : IRIAN
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Iranian Heavy Crude Oil

Data to be measured:No permission from the Master for Sampling and tobe measured.

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1.	2.
Measured ref.height ullage hatch **A** (mm/inch*)			
Observed ullage at ullage hatch **B** (mm/inch*)			
Observed ullage butterworth hole **C** (mm/inch*)			
Measured ref.height butterw. hole (mm/inch*)			
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)* (mm/inch*)			
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm/inch* Corrected ullage mm/inch*			
Total Observed Volume m^3/bbls*			
Observed water dip mm/inch* Corrected water dip mm/inch*			
Free water m^3/bbls*			
Gross Observed Volume m^3/bbls*			
Temperature °C/°F*			
Density/API*			
Volume Corr. Factor Table			
Gross Standard Volume m^3/bbls*			
Density/W.C.F Table			
Mass/Weight Ltons/Mtons vac/air*			

SUMMARY (Selected tanks)	
T.O.V. m^3/bbls*	322,282.389
Free Water	7.790
G.O.V.	322,274.599 at 22,1 oC
G.S.V.	320,437.634 at 15 oC
T.C.V.	320,282.380
Mass/Weight Ltons/Mtons Vac/Air*	279,774.098

* delete as applicable

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CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 2439/94
Date : 21-05-94
Vessel : IRIAN
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Iranian Heavy Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	No info (m^3/bbls)*

LOADING PLAN ex LOADPORT

Tankvessel commenced loading into Center 4 and completed loading at Center 4.

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

The master give no permission to open the butterworthing holes for Sampling with the special sampler.He was not informed by the agents.

In agrement with Mr.J.v.Spijk we accept only the inline samples.

We inspected and accepted receptacle container 1 and 19

The Vessel wil discharged to MOT and TEAM for the parcel to MOT ussing container 1 and for the parcel to TEAM container 19.

The Parcel to MOT into Shoretanks 16 and 19
The Parcel to TEAM into Shoretanks 962,963,964,965,966 and 967

21-05-94 at 13:00 Tankvessel moored alongside terminal
21-05-94 at 14:30 The master give no permission to open the butterworthing hole.He was not informed by the agents
21-05-94 at 14:45 Mr.J.v.Spijk will accept inline samples only
21-05-94 at 15;00 Commenced Discharging to MOT
22-05-94 at 08:10 Completed to MOT
22-05-94 at 08:35 Commenced Discharging to TEAM
22-05-94 at 09:45 Filling container nr.28 from the line for flussing
23-05-94 at 16:30 Completed Discharging to TEAM
23-05-94 at 20:15 Inform Mr.J.Timmer the samples will arrived 24/05 at 09:00 at the laboratories of Nerefco Pernis.

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CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/94
Date : 21-05-94
Vessel : IRIAN
Location : TEAM Terminal Europoort, Rotterdam
Jetty : 3
Grade : Iranian Heavy Crude Oil

Type of Vessel	VLCC
Owners/Flag	Madura/Monrovia, Liberia
Max.cap. mtons	285,715 MT
Total cap. 98%	324,180 M3
Max. summer & draft	20.82 m/20.39 m
Type of coating	Epoxy
Ballast system — Segregated tanks	F.P.Wings 2,3,5
Permanent tanks	
(De-)ballast time	
Number of sea suction valves	-
Equiped with — Heating coils	Only sloptanks
Inert gas system	Yes
Segregation possibility	3 grades
Capacity of ship's decklines	120 m3
Capacity of ship's bottom lines	
No. of pumps	3
Type of pumps	Centrifucal
Total capacity (cbm/hr)	15,000 M3
Stripping pumps	350 M3
Methode of gauging	Saab Radar, Manual MMC
Position of gauging point	Center
Is trim correction available	Yes
Max rate/pressure	10 Bar
Cargo tanks — Centers	6
Cargo tanks — Wings	3 + slopt

Tank contents at 98% (M3)

P 1	22,212	C 1	39,008	S 1	22,212
P 2	P.B	C 2	26,007	S 2	P.B.
P 3	P.B	C 3	26,007	S 3	P.B.
P 4	22,774	C 4	39,011	S 4	22,774
P 5	P.B.	C 5	26,007	S 5	P.B.
P 6	19,320	C 6	30,338	S 6	19,320
P 7	4,595	C 7		S 7	4,595
P 8		C 8		S 8	
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks

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CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 2439/94
Date : 21-05-94
Vessel : IRIAN
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Iranian Heavy Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
Not allowed to manual sampling					
Cont.1	2	2 l	Parcel MOT receptacle 1	open	TNO
Cont.19	2	2 l	Parcel TEAM receptacle 19	open	TNO
Total					

Samples drawn by	J.Timmer,H.de Bruijn,W.Poppelier

Remarks
In case that we no permission voor manual sampling we have accept only the inline receptacle containers.

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S.v.D. 4029

SAYBOLT NEDERLAND BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

SAYBOLT

Report no.: 02439/94
Date : 20-06-1994
Vessel : EDINBURGH SATSUMA
Location : TEAM TERMINAL EUROPOORT, ROTTERDAM
Jetty : 2
Grade : IRIAN LIGHT CRUDE OIL

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA		
Load port		Kharg Island Iran
Bill of Lading	G.S.V.	1.566.026 Bbls60°F
	Weight	212,022 Mtons* air*
Bill of Lading Date		13-05-1994

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	34,29	ASTM D 1298
Watercontent vol%/wt%*	Zero	ASTM D 4006
Sediments vol%/wt%*	Zero	ASTM D 473
BS&W vol%		
Carbon residue wt%	No info	
Sulphur wt%	No info	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm*	Volume bbls*	Dip cm*	Volume bbls*	Dip cm*	Volume bbls*
C.3 C.5	3	163				
Sub-Totals		163				
Total OBQ Selected tanks						

HISTORY	
Previous Vessel Names	Satsuma Maru, Satsuma.

Previous Cargoes	Date	API 60°F	Watercontent	Others
Arabian Extra Light C.O.	22-04-94	No info		
Arabian Extra Light C.O.	21-03-94	No info		
Arabian Extra Light C.O.	15-02-94	No info		

COPY of relevant LOADPORT PAPERS obtained YES *

* delete as applicable

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SAYBOLT

Report no.: 2439/94
Date : 20-06-94
Vessel : EDENBURGH SATSUMA
Location : TEAM TERMINAL EUROPOORT ,ROTTERDAM
Jetty : 2
Grade : IRIAN LIGHT CRUDE OIL

CRUDE OIL REGISTRATION

MEASUREMENTS

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1. Center 3	2.Center 5
Measured ref.height ullage hatch **A** (mm*)		28200	28190
Observed ullage at ullage hatch **B** (mm*)		1910	1870
Observed ullage butterworth hole (mm*)		27700	27690
Measured ref.height butterw. hole C (mm*)		1410	1370
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)* (mm*)		27700	27690
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm*	1910	1870	
Corrected ullage mm*	1900	1855	
Total Observed Volume bbls*	161,269	215,270	376,539
Observed water dip mm*		20	
Corrected water dip mm*		20	
Free water bbls*		42	42
Gross Observed Volume bbls*	161,269	215,228	376,497
Temperature °F*	74,3	75	
API*	34,29	34,29	
Volume Corr. Factor Table A 6	0,9954	0,9929	
Gross Standard Volume bbls*	160,724	213,699	373,871.4
W.C.F Table 13	0,13538	0,13538	
Mtons/air*	21,684.139	28,930.570	50,614.709

SUMMARY (Selected tanks)	
T.O.V. bbls*	376,539
Free Water	42
G.O.V.	376,497
G.S.V.	373,871.4
T.C.V.	373,913.4
Weight Mtons /Air*	50,614.709

* delete as applicable

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SAYBOLT

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 02439/94
Date : 20-06-94
Vessel : EDENBURGH SATSUMA
Location : TEAM TERMINAL EUROPOORT,ROTTERAM
Jetty : 2
Grade : IRIAN LIGHT CRUDE OIL

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	no info (m³/bbls)*

LOADING PLAN ex LOADPORT

Commenced loading into wings 5 and completed loading center 4.for the Irian Light Crude Oil.
In the Center 1 and wings 6 and sloptank Port was loaded Irian Heavy Crude Oil.

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

On the bottom of Center 3 and 5 was a lot of sediments its make the sampling difficult.We have open the sampler with a roop also for the bottomsample.
Sampling with Breathing equipment.

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SAYBOLT

Report no.: 02493/94
Date : 20-06-94
Vessel : EDENBURGH SATSUMA
Location : TEAM TERMINAL EUROPOORT,ROTTERDAM.
Jetty : 2
Grade : IRIAN LIGHT CRUDE OIL

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Type of Vessel	VLCC
Owners/Flag	Edenburgh Tankers
Max.cap. mtons	261,918 mt
Total cap. 98%	312,973 m3
Max. summer & draft	20.577 m 20.334
Type of coating	N.A
Ballast system Segregated tanks	No
Permanent tanks	Wings 4 F/A Peek
(De-)ballast time	no info
Number of sea suction valves	two
Equiped with Heating coils	N.A.
Inert gas system	Yes
Segregation possibility	Yes
Capacity of ship's decklines	80 m3
Capacity of ship's bottom lines	120 m3
No. of pumps	4
Type of pumps	Centrifucal
Total capacity (cbm/hr)	4 x 4500 m3 /hrs
Stripping pumps	Eductor
Methode of gauging	MMC
Position of gauging point	Aft
Is trim correction available	Yes
Max rate/pressure	18.000 M3 /hrs
Cargo tanks Centers	6
Cargo tanks Wings	6 and wingsloptanks

Tank contents at 98% (312,973 m3)

P 1	12,324	C 1	17,368	S 1	10,824
P 2	13,469,5	C 2	29,131	S 2	13,469,5
P 3	15,820	C 3	26,198	S 3	15,820
P 4	P.B.	C 4	17,466	S 4	P.B
P 5	13,560	C 5	34,931	S 5	13,560
P 6	13,538,5	C 6	10,925	S 6	13,538.5
P 7	12,844			S 7	12,884
P sl	6,881			S Sl	3,440

Remarks

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SAYBOLT

Report no.: 2439/94
Date : 20-06-94
Vessel : EDENBURG SATSUMA
Location : TEAM TERMINAL EUROPOORT ROTTERDAM
Jetty : 2
Grade : IRIAN LIGHT CRUDE OIL

CRUDE OIL REGISTRATION

SAMPLE REPORT

Tank	No	Size	Description/Type of sample	Seal	Distribution
Center 3	2	1	Bottom and Top sample	open	TNO
Center 5	2	1	Bottom and Top sample	open	TNO
Inline	1	2	Inline sample to MOT	open	TNO
Inline	1	2	Inline sample to MOT	open	TNO
Total					

Samples drawn by	
Remarks	
Saybolt and T.N.O. arrived at the Terminal	20-06-94 15:00
Inline Sample contianer 20 and 1 inspected and passed	20-06-94 15:15
Sampler checked 50 graps =49ml	20-06-94 15:20
Vessel all vast	20-06-94 15:42
H2S Check by Verwey 10.00 ppm at the Irian Light	20-06-94 16:15
Permision voor sampling with Breathing equipment	20-06-94 18:00
Completed sampling center 3 and 5	20-06-94 18:55
Vessel discharge first Irian Heavy parcel	20-06-94 19:10
Commenced discharge Irian Light to M.O.T.	21-06-94 05:55
Completed to M.O.T	22-06-94 08:00
Commenced discharge to TEAM	22-06-94 08:05
Completed discharge	23-06-94 17:00
Samples delivered to Nerefco Pernis	24-06-94 08:00
Info to T.N.O.Hr.J. v. Spijk voor inline sample	24-06-94 09:00

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 20-07-94
Vessel : VANADIS
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Light Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA		
Load port	Ras Tanura	
Bill of Lading G.S.V.	1,590.625	BBls 60 oF
Weight	268,942	Mtons*air*
Bill of Lading Date	18-06-1994	

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	32,40	No info
Watercontent vol%/wt%*	0,05%	
Sediments vol%/wt%*	Not reported	
BS&W vol%	" "	
Carbon residue wt%	" "	
Sulphur wt%	" "	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume m^3/bbls*
C.4	8	208				
Sub-Totals		208				

Total OBQ Selected tanks	33.069 Ltrs

HISTORY	
Previous Vessel Names	No previos names

Previous Cargoes	Date	API 60°F	Watercontent	Others
Arab.Light C.O	05-04-94	32,50	Zero	
Arab.Medium C.O	20-01-93	31,50	0,025	
Arab.Medium C.O	08-04-93	31,10	0,05	

COPY of relevant LOADPORT PAPERS obtained	Yes

* delete as applicable

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 20-07-94
Vessel : VANADIS
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Heavy Crude Oil

CRUDE OIL REGISTRATION

MEASUREMENTS

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1.	2.
Measured ref.height ullage hatch **A** (mm/*)		32.090	
Observed ullage at ullage hatch **B** (mm/*)		1.950	
Observed ullage butterworth hole **C** (mm/*)			
Measured ref.height butterw. hole (mm/*)			
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)* (mm/*)			
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm/*	1.950		
Corrected ullage mm/*	1.950		
Total Observed Volume M3 *	38.388,6		38.388,6
Observed/Corrected water dipmm/	Nil	Nil	
Free water bbls/*			
Gross Observed Volume M3 /*	38.388,6		38.388,6
Temperature C*	24,7		
Density*	0,8629		
Volume Corr. Factor Table 54 A	0,9920		
Gross Standard Volume M3 /*	38.081,4		38,081,4
Density	0,8629		
Weight /Mtons /air*	32.860,519		32.860,519

SUMMARY (Selected tanks)	
T.O.V. M3 *	38.388,600
Free Water	
G.O.V.	38.388,600
G.S.V.	38.081,491
T.C.V.	
Weight Mtons Air*	32.860,519

* delete as applicable

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SAYBOLT

T.N.O. Order No: 52213

Report no.: 2439/94
Date : 20-07-94
Vessel : VANADIS
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Irian Light Crude Oil
Data to obtained from ship's officer:

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Estimation of ROB (SELECTED TANKS ONLY)	N.A.	(m^3/bbls)*

LOADING PLAN ex LOADPORT

B) First loaded Arab Extra Light Crude Oil Ctr.1,5
A) Second loading Arab light crude oil ctr 2,3,4,6 and wings 1,4,6 sloptanks
Commenced loading : Ctr 2,3,6
Completed loading : wings 1,4

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Ch/off. Depressurrized Ctr. 4,5 for sampling.
Only Ctr. 4 used for sampling (Arab light Crude Oil)
All other tanks under i.g.pressure = =/- 900 mm/wg
Vessel not fitted with butterworth hole's
Actual sampling carried out on tank hatch
During sampling problems to open the sampler at the bottom of the tank after for try's result.

Discharge plan :
A) Arab light 184.000 M3 to Team tanks 923,924,925 Balance to MOT tank 31
B) Arab extra light to MOT tanks 2 and 25

During discharging to I.L. sample containers used (Arab light)
Container Nr.19 for TEAM parcel
Container Nr.14 for MOT parcel.

1 I.L. sample container Nr.2 used for taken cleaning oil for I.S. mixer at jetty manifolt.

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 20-07-1994
Vessel : VANADIS
Location : TEAM Terminal Europoort
Jetty : 3
Grade : Arab light Crude Oil

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Type of Vessel	VLCC
Owners/Flag	Sweden
Max.cap. mtons	285.872 SDWT
Total cap. 98%	326,464 cu.m.
Max. summer & draft	S20.82 W 20.39
Type of coating	none
Ballast system Segregated tanks	Wings 2,3,5 FP,AP
Permanent tanks	none
(De-)ballast time	During Loading/discharg
Number of sea suction valves	Only sloptanks
Equiped with Heating coils	Yes
Inert gas system	4 Grades
Segregation possibility Capa-city of ship's decklines	approx 71,7cu.m
Capacity of ship's bottom lines	94,2
No. of pumps	3 x 4000 cu.m/hrs
Type of pumps	Centrifugal
Total capacity (cbm/hr)	12.000 cu.m/hrs
Stripping pumps	2 x 350 cu.m./hrs
Methode of gauging	Manual
Position of gauging point	Tankhatch
Is trim correction available	Yes
Max rate/pressure	12.5 Bar
Cargo tanks Centers	6
Cargo tanks Wings	5

Tank contents at 98% (326,464 M3)

P 1	22,212	C 1	39,009	S 1	22,212
P 2	P.B.	C 2	26,007	S 2	P.B
P 3	P.B.	C 3	26,007	S 3	P.B
P 4	22,774	C 4	39,010	S 4	22,774
P 5	P.B	C 5	26,007	S 5	P.B
P 6	19,320	C 6	30,338	S 6	19,320
P 7	4,595	C 7		S 7	4,595
P 8		C 8		S 8	
P 9		C 9		S 9	
P10		C10		S10	
P11		C11		S11	

Remarks
Volume are giving in cubic meters

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SAYBOLT

T.N.O. order No: 52213

Report no.: 2439/94
Date : 20-07-94
Vessel : VANADIS
Location : TEAM Terminal Europoort, Rotterdam
Jetty : 3
Grade : Arab light Crude Oil

CRUDE OIL REGISTRATION

SAMPLE REPORT

Tank	No	Size	Description/Type of sample	Seal	Distribution
C.4	2	1	Top and Bottom sample	open	T.N.O
inline	1	15	Inline sample	SVD	T.N.O
Manifold	1	15	Manifold sample	SVD	T.N.O
Totaal	5				

Samples drawn by	W.J.Poppelier and R.Luycx

Remarks:
15 Ltr. sample taken at the manifold due to cleaning for I.L.S. mixir.

Hr.J v, Spijk on behalf of TNO onboard TV for sampling.

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SAYBOLT

CRUDE OIL REGISTRATION

GENERAL DATA

Report no.: 02439/94
Date : 25-08-94
Vessel : ESSO HAWAII
Location : T.E.A.M. Rotterdam Europoort
Jetty : 2
Grade : Arab.Light Crude Oil

Data below to be copied from ship's records.

LOADPORT DATA			
Load port		Sidi Kerir	
Bill of Lading	G.S.V.	571,093	Bbls60°F
	Weight	78.331,977	Mtons* air*
Bill of Lading Date		14-08-1994	

CRUDE DATA ON LOADING			
PROPERTY		RESULT	METHOD
API Gravity at 60°F		32,58	ASTM D 1298
Watercontent	vol%	0,265	ASTM D 4928
Sediments	vol%		
BS&W	vol%	0,265	ASTM D 4807
Carbon residue	wt%	Not reported	
Sulphur	wt%	" "	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume m^3/bbls*	Dip cm*	Volume bbls*	Dip cm/inch*	Volume m^3/bbls*
C-2			0,03	38		
C-4			0,03	38		
Sub-Totals						

Total OBQ Selected tanks	76 Bbls

HISTORY	
Previous Vessel Names	None

Previous Cargoes	Date	API 60°F	Watercontent	Others
Arab.Heavy	12-07-94	30,81	No info	No info
Arab.Extra light	03-06-94	36,31	" "	" "
Arab.Light	14-05-94	32,50	" "	" "

COPY of relevant LOADPORT PAPERS obtained	YES

* delete as applicable

Saybolt Nederland B.V.
J. van Zwieten
Field Manager

SAYBOLT

CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 02439/94
Date : 25-08-94
Vessel : ESSO HAWAII
Location : T.E.A.M. Rotterdam Europoort
Jetty : 2
Grade : Arab.Light Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1. C-2	2.
Measured ref.height ullage hatch **A** (mm*)		30.377	30.377
Observed ullage at ullage hatch **B** (mm*)		1.770	1.830
Observed ullage butterworth hole **C** (mm*)		800	835
Measured ref.height butterw. hole (mm*)		29.350	29.370
Theoretical reference height at butterworth hole **(A-B+C)** *(rope length 35 mtr)* (mm*)		29.407	29.382
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage mm*	1770	1830	
Corrected ullage mm*	1770	1830	
Total Observed Volume bbls*	196,916	196,503	393.419
Observed/encorrected water dipmmh*	100	60	
Free water bbls*	688	413	1.101
Gross Observed Volume bbls*	196.228	196.090	392.318
Temperature °F*	88.9	88.7	
API*	32.58	32.58	
Volume Corr. Factor Table 6 A	0,98666	0,98676	
Gross Standard Volume bbls*	193.610	193.494	387.104
Density/W.C.F Table	0,13680	0,13680	
Mass Mtons/air*	26.485,848	26.469,979	52.955,827

SUMMARY (Selected tanks)	
T.O.V. bls*	393,419
Free Water	1,101
G.O.V.	392,318
G.S.V.	387,104
T.C.V.	388,205
Mass/Weight Ltons/Mtons Vac/Air*	52.955,827

* delete as applicable

Saybolt Nederland B.V.
J. van Zwieten
Field Manager

SAYBOLT

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 02439/94
Date : 25-08-94
Vessel : SIDI KERIR
Location : T.A.E.M.Rotterdam Europoort
Jetty : 2
Grade : Arab.Light Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	Unknown (m^3/bbls)*

LOADING PLAN ex LOADPORT

A) First loaded Arab Extra Light Crude Oil into Wings,1,2,3,4 and 5

B) Second Loading Arab Light Crude Oil into Center 1,2 and 4

C) Irian Heavy Crude Oil Loading into center 3,5 and Port Sloptank

Commenced en completed loadig of Arab.Light Crude Oil Ceneter 1.

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Ch/off Depressurized Center 2 and 4 for sampling.
On the bottom of center 2 and 4 was a lot of sediments its make the sampling difficult.we have open the sampler with a roop also for the bottomsample.
Sampling with breathing equipment in case of H2S 200 ppm.

Discharge plan:
A) Arab.Extra Light into shoretank 966,914 and 962.
B) Iran Heavy into shoretank 963,964 and 913
C) Arab Light Crude Oil into shoretank 968 and 967

Container 17 use for inline sample
Container 18 use for manifold sample

Saybolt Nederland B.V.
J. van Zwieten
Field Manager

SAYBOLT

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 02439/94
Date : 25-08-1994
Vessel : ESSO HAWAII
Location : T.E.A.M. Rotterdam Europoort
Jetty : 2
Grade : Arab.Light Crude Oil

Type of Vessel		V.L.C.C.
Owners/Flag		Exxon Comp.Int.Bahamas
Max.cap. mtons		283.274 Mt
Total cap. 98%		334.192 M3
Max. summer & draft		22.09 m
Type of coating		None
Ballast system	Segregated tanks	fore and aft peak
	Permanent tanks	N.A
	(De-)ballast time	In between
Number of sea suction valves		2
Equiped with	Heating coils	No
	Inert gas system	Yes
	Segregation possibility	Four
Capacity of ship's decklines		120 M3
Capacity of ship's bottom lines		135 M3
No. of pumps		4
Type of pumps		MC PS Mitsubischi
Total capacity (cbm/hr)		16.000 M3
Stripping pumps		2 x 400 M3
Methode of gauging		manuel
Position of gauging point		aft
Is trim correction available		Yes
Max rate/pressure		12.000 M3 8 Bar
Cargo tanks	Centers	5
Cargo tanks	Wings	6

Tank contents at 98% (334.192 M3)

P 1	19.700	C 1	31.401	S 1	19.700
P 2	21.620	C 2	31.401	S 2	21.620
P 3	10.810	C 3	31.401	S 3	10.810
P 4	21.495	C 4	31.401	S 4	21.495
P 5	16.554	C 5	15.701	S 5	16.554
P sl	6.266			S sl	6.266

Remarks

Saybolt Nederland B.V.
J. van Zwieten
Field Manager

SAYBOLT

CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 02439/94
Date : 25-08-94
Vessel : ESSO HAWAII
Location : T.E.A.M. Rotterdam
Jetty : 2
Grade : Arab.Light Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
Center 2	2	1 L	Bottom and Top Sample	open	TNO
Center 4	2	1 L	Bottom and Top Sample	open	TNO
Inline	1	15L	Inline Sample Container 17	SVD	TNO
Manifold	1	15L	Manifold sample Container 18	SVD	TNO
Total					

Samples drawn by	H.de Bruijn ,M.Storm Saybolt

Remarks
15 Ltr sample taken at the manifold due to cleaning I.L.S. mixer in container 18.
Delivered at NRC Lab.Pernis.

Hr.J.Timmer on behalf of TNO onboard TV for sampling.

Saybolt Nederland B.V.
J. van Zwieten
Field Manager

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Report no.: 2439/94
Date : 07-12-94
Vessel : POLLUX
Location : TEAM Terminal Europoort, Rotterdam
Jetty : 3
Grade : Arabian Light Crude Oil

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA	
Load port	Ras Tanura ,Saudi Arabia
Bill of Lading G.S.V.	314,148 Bbls60°F *
Weight	46.693,65 Mtons*/air*
Bill of Lading Date	25-10-1994

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	32.50	no info
Watercontent vol%/wt%*	Zero	no info
Sediments vol%/wt%*	no info	
BS&W vol%	no info	
Carbon residue wt%	no info	
Sulphur wt%	no info	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume /bbls*	Dip cm/inch*	Volume ^{3}/bbls*
SB 3		nil		nil		nil
SB 7		nil		nil		nil
Sub-Totals						
Total OBQ Selected tanks			nil			

HISTORY	
Previous Vessel Names	Builded name: Happy Enterprice

Previous Cargoes	Date	API 60°F	Watercontent	Others
Arab Light	09-07-94	33,00	Nill	only Wings
Arab. Heavy	28-02-94	27.50	no info	3 and 7
Arab. Heavy	07-09-93	30.77	0,05	

COPY of relevant LOADPORT PAPERS obtained YES*

* delete as applicable

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CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 2439/94
Date : 07-12-94
Vessel : POLLUX
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Arabian Light Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1. SB 3	2 SB 7
Measured ref.height ullage hatch **A**	(mm*)	30.870	30.870
Observed ullage at ullage hatch **B**	(mm*)	3.180	3.260
Observed ullage butterworth hole **C**	(mm*)	2.400	2.480
Measured ref.height butterw. hole	(mm*)	30.090	30.090
Theoretical reference height at butterworth hole **(A-B+C)** *(rope length 35 mtr)*	(mm*)	30.090	30.090
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage Corrected ullage	mm* mm*	3180 2400	3260 2480
Total Observed Volume	bbls*	85.435	85.210	170.645
Observed water dip Corrected water dip	mm* mm*	nil	nil
Free water	bbls*		
Gross Observed Volume	bbls*	85.435	85.210	170.645
Temperature	°F*	63,9	64,0
API*		32,50	32,50
Volume Corr. Factor Table	6A	0,9982	0,9982
Gross Standard Volume	bbls*	85.281	85.057
W.C.F Table		0,13687	0,13687
Mass/Weight Ltons/Mtons vac/air*		11.672,410	11.641,752	23.314,162

SUMMARY (Selected tanks)		
T.O.V.	bbls*	170.645
Free Water		
G.O.V.		170.645
G.S.V.		170.338
T.C.V.		
MassMtons Air*		23.314,162

* delete as applicable

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CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.: 2439/94
Date : 07-12-94
Vessel : POLLUX
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Arabian Light Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	No info (m^3/bbls)*

LOADING PLAN ex LOADPORT

Tankvessel commenced loading first Arabian Extra Light
Second commenced loading Arabian light into wings 3 and 7
Started and stopped at wings 3
Completed loading with Arabian heavy crude oil.

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

The master give permission to open the butterworthing holes for Sampling with the special sampler.
The produkt are stored in:
A) Arabian Extra Light stored in center,1 till 8 and wing 2,4,6,8,9,11
B) Arabian Light stored in wings 3 and 7
C) Arabian Heavy stored in wings 1 and 10

We inspected and accepted receptacle container 8 and 17

The Vessel wil discharged the parcel Arabian light into shoretank 965 and the balance in shoretank 926.

The is started with the Arabian extra Light into Shoretank 37 and 34 at MOT.

07-12-94 at	18:00	Saybolt inspectors H. de Bruijn and W.Poppelier , TNO J.Timmer arrived at TEAM Terminal
	18:30	Inspected contaner 8
	19:24	Tankvessel moored alongside terminal
	19:35	Permission from the master to open the butterworthing holes for sampling SB 3 and SB 7
	20:15	Completd sampling SB 3 and SB 7
09-12-94	02:00	Commenced discharging Arabian Light C.O
	04:15	Take line sample in container 17 for flussing
	12:00	Completed discharging.
	15:00	Inform TNO that the wil be arrived at Nerefco Pernis at 10-12-94 08:00

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SAYBOLT

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/94
Date : 07-12 94
Vessel : POLLUX
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Arabian Light Crude Oil

Type of Vessel		VLCC
Owners/Flag		Norway
Max.cap. mtons		357.147 MT
Total cap. 98%		433.393 M3
Max. summer & draft		22.36 m/21.90 m
Type of coating		
Ballast system	Segregated tanks	Wings 5
	Permanent tanks	-
	(De-)ballast time	During
Number of sea suction valves		Loading/Discharging
Equiped with	Heating coils	only sloptanks
	Inert gas system	Yes
	Segregation possibility	Yes
Capacity of ship's decklines		3 grades
Capacity of ship's bottom lines		N.A
No. of pumps		4 x 5.500 cu/hrs
Type of pumps		Centrifucal
Total capacity (cbm/hr)		22,000 M3
Stripping pumps		Vacuum stripping
Methode of gauging		systeem
Position of gauging point		Saab Radar,Manual MMC
Is trim correction available		Center
Max rate/pressure		Yes
Cargo tanks	Centers	9
Cargo tanks	Wings	20

Tank contents at 98% (M3)

P 1	12,574	C 1	18,394	S 1	12,574
P 2	13,645	C 2	29,459	S 2	13,645
P 3	13,884	C 3	14,725	S 3	13,884
P 4	13,887	C 4	14,725	S 4	13,887
P 5	P.B.	C 5	29,459	S 5	P.B.
P 6	13,888	C 6	14,725	S 6	13,888
P 7	13,887	C 7	29,459	S 7	13,887
P 8	13,882	C 8	8,367	S 8	13,882
P 9	13,736	C 9	5,698	S 9	13,736
P10	12,869	C10		S10	12,869
P11	11,940	C11		S11	11,940

Remarks

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CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 2439/94
Date : 07-12-94
Vessel : POLLUX
Location : TEAM Terminal Europoort,Rotterdam
Jetty : 3
Grade : Iranian Heavy Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
S.B 3	2	1 l	Top and bottom	open	TNO
S.B.7	2	1 l	Top and bottom	open	TNO
Cont.8	2	2 l	From inline Sample	open	TNO TNO
Total					

Samples drawn by	J.Timmer,H.de Bruijn,W.Poppelier
Remark:	

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Report no.: 2439/94
Date : 19-12-94
Vessel : KRISTEN
Location : MOT Terminal Europoort Rotterdam
Jetty : 2
Grade : Kuwait Export Crude Oil.

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA			
Load port	Mina Al Ahmadi		
Bill of Lading G.S.V.	2,300,209	BBls 60 oF	
Weight	317,064	Mtons*	air*
Bill of Lading Date	11-11-94		

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	31,30	no info
Watercontent vol%/wt%*	Zero	
Sediments vol%/wt%*	Zero	
BS&W vol%	Zero	
Carbon residue wt%	no info	
Sulphur wt%	no info	

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm/inch*	Volume m³/bbls*	Dip cm/inch*	Volume m³/bbls*	Dip cm/inch*	Volume bbls*
C.2	nil		nil		3"	73
C.3	nil		nil		2"	40
Sub-Totals						113

Total OBQ Selected tanks	113 Bbls

HISTORY	
Previous Vessel Names	KIRSTEN MAERSK

Previous Cargoes	Date	API 60°F	Watercontent	Others
Lavan		no info	no info	
No info				

COPY of relevant LOADPORT PAPERS obtained YES*

* delete as applicable

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CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 2439/94
Date : 19-12-94
Vessel : KRISTEN
Location : MOT Terminal Europoort,Rotterdam
Jetty : 2
Grade : Kuwait Export Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1 C.2	2. C.3
Measured ref.height ullage hatch **A** (Inch*)		100'01"	100'01"
Observed ullage at ullage hatch **B** (inch)		15'05,5"	8'02"
Observ d ullage butterworth hole **C** (inch)		12'05,5"	5'02"
Measured ref.height butterw. hole (inch)		97'01"	97'01"
Theoretical reference height at butterworth hole (**A-B+C**) (*rope length 35 mtr*) (inch*)		97'01"	97'01"
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage inch Corrected ullage inch	17'06" 15'05,5"	10'03" 8'02"	
Total Observed Volume /bbls*	146,771	120,170	266,941
Observed water dip mm Corrected water dip mm	nil	nil	
Free water /bbls*			
Gross Observed Volume bbls*	146,771	120,179	266,941
Temperature °F*	70,2	69,6	
/API*	31,30	31,30	
Volume Corr. Factor Table 6A	0,9954	0,9957	
Gross Standard Volume bbls*	146,096	119,662	265,758
Density/W.C.F Table 13	0,13788	0,13788	
Weight Mtons air*	20,143.716	16,498.977	36,642.713

SUMMARY (Selected tanks)	
T.O.V. bbls*	266,950
Free Water	
G.O.V.	266,950
G.S.V.	265,758
T.C.V.	265,758
Weight Mtons Air*	36,642.713

* delete as applicable

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CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/94
Date : 19-12-94
Vessel : KRISTEN
Location : MOT Terminal Europoort,Rotterdam
Jetty : 2
Grade : Kuwiat Export Crude Oil

Type of Vessel		VLCC
Owners/Flag		Greek
Max.cap. mtons		339.005 SDWT
Total cap. 98%		402,099 cu m.
Max. summer & draft		22.475 M
Type of coating		none
Ballast system	Segregated tanks	P/S 3 /Fore and Aftp
	Permanent tanks	None
	(De-)ballast time	During
Number of sea suction valves		Loading/Discharg.
Equiped with	Heating coils	Only sloptanks
	Inert gas system	Yes
	Segregation possibility	4 grades
Capacity of ship's decklines		approx.130 cu m
Capacity of ship's bottom lines		no info
No. of pumps		4 x 4500 cu m/hr
Type of pumps		Centrfugal
Total capacity (cbm/hr)		16000 cu m./hr
Stripping pumps		1 x 350 cu.m/hr
Methode of gauging		UTI
Position of gauging point		Ullage plug
Is trim correction available		Yes
Max rate/pressure		12,5 bar
Cargo tanks	Centers	6
Cargo tanks	Wings	5

Tank contents at 98% (326,464 cu.m)

P 1	15,123	C 1	26,528	S 1	15,123
P 2	20,570	C 2	25,993	S 2	20,570
P 3	P.B	C 3	19,576	S 3	P.B
P 4	23,018	C 4	29,365	S 4	23,018
P 5	20,570	C 5	25,992	S 5	20,570
P 6	17,501	C 6	22,838	S 6	17,501
P 7	10,950	C 7	26,085	S 7	10,950
P sl	5,127	C 8		S sl	5,127
		C 9		S 9	
		C10		S10	
		C11		S11	

Remarks
Volume are giveing in cubic meters

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CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 2439/94
Date : 19-12-94
Vessel : KRISTEN
Location : MOT Terminal Europoort,Rotterdam
Jetty : 2
Grade : Kuwiat Export Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
C.2	1	1	Top	open	T.N.O.
C.2	1	1	Bottom	open	T.N.O
C.3	1	1	Top	open	T.N.O
C.3	1	1	Bottom	open	T.N.O
Total	–				

Samples drawn by	C.Minderhout and H.de Bruijn
Remarks	

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CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.:2439/94
Date :30-04-94
Vessel :KRISTEN
Location :MOT Terminal Europoort,Rotterdam
Jetty : 2
Grade : Kuwiat Export Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	Nil	(m^3/bbls)*

LOADING PLAN ex LOADPORT

Commenced loading into Center 1 all other tanks
Completed loading into Center 4

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Inert Gas pressure released from all cargo tanks

H2S content during sampling 600ppm.

During sampling using breathing unit.

Sampling with J.Timmer (TNO),J. Spijk (TNO) C.Minderhoud (Saybolt NL)
H.de Bruijn (Saybolt NL)

19-12-1994 at 12:15 Tankvessel moorde alongside terminal.
19-12-1994 at 13:15 We inspected and accepted receptacle containers.
19-12-1994 at 13:25 Discussed with the master incase to open the butterworthing hole incase of the H2S content.
19-12-1994 at 15:00 The master give permision for sampling after he received a letter of Saybolt and signed by the loading master.
19-12-1994 at 15:00 Commenced sampling
19-12-1994 at 16:00 Completed sampling
20-12-1994 at 06:30 Filling container froom the line for flussing.
20-12-1994 at 08;30 Info to J.v.Spijk the first container is in the laboratoruim of MOT
22-12-1994 at 06:40 Vessel completed Discharging .
The vessel have discharge into Shoretank 12,3,11,30 28 and to Shell Europoort .

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SAYBOLT

Report no.: 2439/95
Date : 09-02-95
Vessel : SUNETTA
Location : Shell Europoort , Rotterdam
Jetty : 102
Grade : Oseberg Crude Oil.

CRUDE OIL REGISTRATION

GENERAL DATA

Data below to be copied from ship's records.

LOADPORT DATA				
Load port	Sture Crude Oil Terminal			
Bill of Lading G.S.V.	99,890.000	M3 15 oC		
Weight	84,117.000		Mtons*	air*
Bill of Lading Date	06-02-95			

CRUDE DATA ON LOADING		
PROPERTY	RESULT	METHOD
API Gravity at 60°F	36,20	ASTM D 4052
Watercontent vol%/wt%*	0,19	ASTM D 4377
Sediments vol%/wt%*	Zero	
BS&W vol%	0,19	
Carbon residue wt%		
Sulphur wt%	0,25	IP 336

O.B.Q. DATA ON LOADING (SELECTED TANKS ONLY)

Tank	Liquid		Non-liquid		Free Water	
	Dip cm*	Volume m^3*	Dip cm*	Volume m^3*	Dip cm*	Volume M3 *
C.2	3	4.30	nil			
C.4	4	5.70	nil			
Sub-Totals		10.00				113

Total OBQ Selected tanks	10.00 M3

HISTORY	
Previous Vessel Names	Caroline Jane

Previous Cargoes	Date	API 60°F	Watercontent	Others
Forties	24-01	41.0	0,03	
Brent blend	15-01	38.4	0,35	
Oseberg	02-01	36.2	0,20	

COPY of relevant LOADPORT PAPERS obtained YES*

* delete as applicable

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SAYBOLT

CRUDE OIL REGISTRATION

MEASUREMENTS

Report no.: 2439/95
Date : 09-02-95
Vessel : SUNETTA
Location : Shell Europoort , Rotterdam
Jetty : 102
Grade : Oseberg Crude Oil

Data to be measured:

REFERENCE HEIGHTS (SELECTED TANKS ONLY)			
Tank description		1 C.2	2. C.4
Measured ref.height ullage hatch **A** (Cm *)		1994	1991
Observed ullage at ullage hatch **B** (Cm)		303	204
Observ d ullage butterworth hole **C** (Cm)		189	93
Measured ref.height butterw. hole (Cm)		1880	1880
Theoretical reference height at butterworth hole (**A-B+C**) *(rope length 35 mtr)* (Cm *)		1880	1880
ULLAGE MEASUREMENTS AT ULLAGE HATCH			
Observed ullage inch Corrected ullage inch	303 303,5	204 204,5	
Total Observed Volume M3 *	10,902.580	11,543.480	22,446.060
Observed water dip mm Corrected water dip mm	nil	nil	
Free water /bbls*			
Gross Observed Volume bbls*	10,902.580	11,543.480	22,446.060
Temperature °C*	11.0	10.8	
Density*	0,8432	0,8432	
Volume Corr. Factor Table 54A	1.0035	1,0036	
Gross Standard Volume M3 *	10,940.739	11,585.037	22,525.776
Density	0,8432	0,8432	
Weight Mtons vac*	9,225.231	9,768.503	18,993.734

SUMMARY (Selected tanks)	
T.O.V. M3 *	22,446.060
Free Water	
G.O.V.	22,446.060
G.S.V.	22,525.776
T.C.V.	22,525.776
Weight Mtons vac*	18.993,734

* delete as applicable

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SAYBOLT NEDERLAND BV

Independent Inspectors
Quality Assurance Services
Chemical Laboratories

Members ASTM/IP
Management Ir. F. Pluimers

SAYBOLT

CRUDE OIL REGISTRATION

ADDITIONAL INFORMATION

Report no.:2439/95
Date :09-02-94
Vessel :SUNETTA
Location :Shell Europoort , Rotterdam
Jetty :102
Grade :Oseberg Crude Crude Oil

Data to obtained from ship's officer:

Estimation of ROB (SELECTED TANKS ONLY)	10	(m^3)*

LOADING PLAN ex LOADPORT

Commenced loading into Center 3 all other tanks
Completed loading into Center 1 and 5

OBSERVATIONS MADE DURING THE ACTUAL SAMPLING

Inert Gas pressure released from all cargo tanks

Sampling with J.Timmer (TNO), C.Minderhoud (Saybolt NL)
H.de Bruijn (Saybolt NL)

08-02-1995 at 19:45 Tankvessel moorde alongside terminal.
08-02-1995 at 19:50 We inspected and accepted receptacle containers. of the portable inline sampler
08-02-1995 at 20:00 The master give permision for sampling.
08-02-1995 at 20:00 Commenced sampling
08-02-1995 at 20:45 Completed sampling
08-02-1995 at 21:55 Commenced Discharge
09-02-1995 at 16:00 Filling container from the line for flussing.
10-02-1995 at 01:20 Completed Discharge
10-02-1995 at 01:30 Info to J.v.Spijk for filling the inline sample from portable inline sampler by Shell Europoort.
10-02-1995 at 04:00 Power mixing by J. Spijk and C.Minderhoud.

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SAYBOLT

CRUDE OIL REGISTRATION

VESSEL INFORMATION

Report no.: 2439/95
Date : 09-02-95
Vessel : SUNETTA
Location : Shell Europoort , Rotterdam .
Jetty : 102
Grade : Oseberg Crude Oil

Type of Vessel	Crude Tanker
Owners/Flag	Shell /Liberian
Max.cap. mtons	85.813 SDWT
Total cap. 98%	101.196 cu m.
Max. summer & draft	13.852 M
Type of coating	none
Ballast system Segregated tanks	none
Permanent tanks	P/S 3 Fore ballas
(De-)ballast time	
Number of sea suction valves	2
Equiped with Heating coils	sloptanks only
Inert gas system	Yes
Segregation possibility	
Capacity of ship's decklines	approx.64 cu m
Capacity of ship's bottom lines	approx 103 cu m
No. of pumps	3 x 2750 cu m/hr
Type of pumps	Centrfugal
Total capacity (cbm/hr)	8250 cu m./hr
Stripping pumps	1 x 200 cu.m/hr
Methode of gauging	MMC
Position of gauging point	Ullage plug
Is trim correction available	Yes
Max rate/pressure	12,5 bar
Cargo tanks Centers	5
Cargo tanks Wings	5

Tank contents at 98% (101,196 cu.M)

P 1	2,557	C 1	6,528	S 1	2,557
P 2	7,067	C 2	12,074	S 2	7,067
P 3	P.B	C 3	12,072	S 3	P.B
P 4	7,203	C 4	12,074	S 4	7,203
P 5	5,155	C 5	12,061	S 5	5,155
P 6	1,470			S 6	1,470

Remarks
Volume are giveing in cubic meters

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S v D 4029

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Management Ir. F. Pluimers

SAYBOLT

CRUDE OIL REGISTRATION

SAMPLE REPORT

Report no.: 2439/95
Date : 09-02-95
Vessel : SUNETTA
Location : Shell Europoort ,Rotterdam
Jetty : 102
Grade : Oseberg Crude Oil

Tank	No	Size	Description/Type of sample	Seal	Distribution
C.2	1	1	Top	open	T.N.O.
C.2	1	1	Bottom	open	T.N.O
C.4	1	1	Top	open	T.N.O
C.4	1	1	Bottom	open	T.N.O
Total	_				

Samples drawn by	C.Minderhout and H.de Bruijn
Remarks	

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S v D 4029

Annex 6: Sample description and TNO sample codes

Name of ship	Type of oil	Date	Sample	Sample code TNO
Mega Hawk	Iranian Heavy	27 December 1993	PM-TEM	AF 001
Sereno	Ural	14 February 1994	PM-TEM T1	AF 422
			T2	AF 423
			B1	AF 425
			B2	AF 424
				AF 426
Astro Alpha	Arabian Light	21 March 1994	PM-TEM	AF 446
			PM-MOT	AF 447
			T1	AF 442
			T2	AF 444
			B1	AF 443
			B2	AF 445
ESSO Demetia	Iranian Heavy	24 March 1994	PM-TEM	AF 488
			PM-MOT	AF 489
			T1	AF 490
			T2	AF 492
			B1	AF 491
			B2	AF 493
ESSO Normandie	Arabian Light	25 April 1994	PM-TEM	AF 853
			T1	AF 849
			T2	AF 850
			B1	AF 848
			B2	AF 851
Kristhild	Iranian Heavy	2 May 1994	PM-MOT	AF 852
			PM-TEM	AF 864
			T1	AF 844
			T2	AF 846
			B1	AF 845
			B2	AF 847
ESSO Demetia	Arabian Heavy	9 May 1994	PM-TEM	AF 865
ESSO Demetia	Iranian Heavy	9 May 1994	PM-TEM	AF 866
Bergina	Stattfjord	21 May 1994	PM-MOT	AF1161
			PM-TEM	AF1162
			T1	AF1157
			T2	AF1159
			B1	AF1158
			B2	AF1160
TV Irian	Iranian Heavy	22 May 1994	PM-MOT	AF1163
			PM-TEM	AF1164
Edin.Satsuma	Iranian Light	22 June 1994	PM-MOT	AF2032
			PM-TEM	AF2033
			T1	AF2444
			T2	AF2446
			B1	AF2445
			B2	AF2447

Vanadis, Stock-holm	Arabian Light	20 July 1994	PM-TEM	AF2129
			PM-MOT	AF2128
			T1	AF2156
			B1	AF2157
Esso Hawaii	Arabian Light	25 August 1994	PM-TEM	AF2299
			T1	AF2300
			T2	AF2302
			B1	AF2301
			B2	AF2303
Pollux	Arabian Light	07 December 1994	PM-TEM	AF3023
			T1	AF3024
			T2	AF3026
			B1	AF3025
			B2	AF3027
Kristen	Kuwait	10 December 1994	PM-MOT	AG 287
			T1	AF1567
			T2	AF1568
			B1	AF1569
			B2	AF1570
Sunetta	Oseberg	9 February	PM-Shell	AG 286
			T1	AF 316
			T2	AF 317
			B1	AF 315
			B2	AF 318

Annex 7: Sample label

Chemical Laboratories **SAYBOLT - VAN DUYN BV**
P.O. Box 151 Rotterdam

Sample from:.....

Date:.....
Hour:.....

before/after/during * loading/discharge/transfer *

Into/from :.....

Product :.....

Installation:.....

Upper –*	Running –*	Bottom –*
Middle –	Pipeline –	Ship's sample :.....
Lower –	1st Foot –	Name inspector :.....

Sample description :.....

This sample to be retained for a period of 3 years * delete as necessary.

Annex 8: TNO Report: 'Determination of cadmium in crude oil. Validation protocol for the graphite furnace AAS method of Narres et al.' IMW-R93/170

IMW - R 93/170

Determination of Cadmium in Crude Oil
Validation protocol for the graphite furnace AAS method of Narres et al.

Author : S.J. Spijk

Date : 16 July 1993

Order no. : 52213

Client : Ministry of Housing, Physical Planning and Environment
Directorate-General for Environmental Protection, Air & Energy/640,
of Industry
For the attention of Drs. C.P.A. Dekkers
P.O. Box 30945
2500 GX The Hague
The Netherlands

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11. REFERENCES

1. INTRODUCTION

At the request of The Dutch Ministry of Housing Physical Planning and Environment (VROM), Directorate-General for Environmental Protection, Air & Energy/640, Department of Industry, TNO is developing a method for the sampling of crude oil from crude carriers and for the determination of cadmium in samples of crude oil.

The project is conducted under the guidance of a Steering Committee chaired by VROM and comprising representatives of VROM, SHELL, ESSO, BP and DCMR (Regional Environmental Authority).

For the determination of cadmium in crude oil no standard methods are available. There are, however, several publications on ad hoc methods and their results. These results show wide variations in cadmium content in crude oils up to a factor of 7000!

Three reasons have been advanced to explain these variations:
1) Incorrect and unrepresentative sampling
2) Contamination of samples during sampling or analysis
3) Incorrect method of analysis

The method of sampling to be applied by TNO will be described separately in the protocol 'Sampling of Crude Oil'.
The protocol details all those measures that have to be taken to ensure that the samples are representative and uncontaminated.

The sampling protocol as well as the analytical protocol derived from the validation study are given in accordance with GLP guidelines, whereas the actual sampling and analysis are carried out under the Quality Assurance system operated by TNO, a system which meets STERLAB as well as GLP criteria.

The determination of cadmium in crude oil in principle involves two operations: dry or wet ashing and the actual measurement (with the aid of, e.g. Atomic Absorption Spectrometry).

In order to prevent contamination, direct methods skipping off-line dry or wet ashing are to be preferred. At the Steering Committee's recommendation it has been decided to take as a starting point the method described by Narres et al. (1) (which involves on-line ashing of a diluted sample) and to validate it by a procedure to be laid down in a protocol. In addition the method will be also validated for undiluted samples.

As a check on the accuracy of these methods TNO will use an additional different method.

A main feature of the validation study is to assess the performance and ruggedness of the method. By ruggedness is meant the insensitivity of the method to the inevitable variations of temperature which attend the drying and ashing of the oil sample. Other important features of the study are such performance criteria as intralaboratory repeatability and reproducibility, linearity, detection limit, sensitivity, accuracy and method blank value.

As soon as the method has been laid down in an analytical protocol, any alterations that may need to be made to it will be put before the Steering Committee for approval.

All raw data, correspondence, reports, etc., will be filed under the STERLAB Quality Assurance System.

2. EXPERIMENTAL DETAILS

- Original Test Sample (no.1)
This is the sample of crude oil (Arabian Heavy) taken by TNO on 23 March 1993 at NEREFCO, Rotterdam Pernis, in a 2-litre borosilicate-glass bottle, previously cleaned with nitric acid.

- Test sample no. 2
This consists of 25 grammes of oil taken from the undisturbed upper layer of the 'Original Test Sample', plus 75 grammes of carbon tetrachloride. To this mixture was added 1 µg/kg of ionic cadmium. If it is assumed that any water or sediment has settled to the bottom of the undisturbed 'Original Test Sample', Test Sample no. 2 can be regarded as relatively homogeneous and uncontaminated.

- Test Sample no. 3
Test Sample no. 3 is identical to no. 2, except for the addition of cadmium.

- Test Sample no. 4
Test Sample no. 4 consists of 100 grammes of 'Original Test Sample' to which 4 µg/kg of ionic cadmium has been added.

- Methods :
  - Direct introduction after dilution with carbon tetrachloride in GFAAS with Zeeman correction (GFZAAS) (1)
  - Wet ashing with sulphuric acid, followed by GFZAAS and/or ICP-MS (2)
  - Cold oxygen plasma ashing, followed by GFZAAS and/or ICP-MS (3)

- Equipment & facilities :
  - Perkin Elmer 5100 PC Atomic Absorption Spectrometer
  - Fisons Instrument VG Plasma Quad ICP-MS
  - Cold oxygen plasma ashing apparatus
  - Clean room facilities
  - Utra Turrax Mixer with a titanium shaft, type T25 IKA, 8000 - 24000 RPM. This is used to homogenise oil samples for 10 seconds
  - Standard laboratory equipment and facilities. All glassware that comes into contact with crude oil is cleaned with nitric acid and then rinsed with demineralised Milli-Q water until acid-free. The glassware is dried and stored in a clean room

3. SAMPLE STORAGE

3.1 Outline of the problem

As part of the project, samples of oil are taken from crude carriers during a period of several months. The samples are collected in glass bottles (colourless borosilicate) and stored in darkness at 4 °C(range 2-8 °C) prior to analysis. The analysis of samples is begun after the last crude carrier has been sampled. This means that the duration of storage is variable. It therefore need to be established whether the duration of storage affects the concentration of cadmium in the oil. It is not inconceivable that cadmium is adsorbed by the glass of the storage bottles, or settles to the bottom. In case of adsorption, the effectiveness of the homogenisation of the samples (with the Ultra Turrax Mixer) is in doubt.

If the results of the experiments show that adsorption may have taken place, it will be necessary to analyse the samples immediately after having been taken.

3.2 Experimental part

One hundred grammes of 'Original Test Sample' is transferred to a 125 ml glass bottle (colourless borosilicate). To the sample is added an amount of ionic cadmium up to a final concentration of 10 µg Cd/kg of oil, upon which the sample is homogenised and analysed at once. The time when the result is known is defined as t = 0. The sample is then stored in the dark at 4 °C (range 2-8 °C). At t = one week, the sample is again homogenised and subsampled for analysis. This procedure is repeated at t = 2 weeks, 4 weeks, 16 weeks, 32 weeks etc.

4. NON-UNIFORM DISTRIBUTION OF CADMIUM IN CRUDE OIL

4.1 Outline of the problem

The crude oil is sampled at three different locations:

1) from the so- called 'Power Mixer', which affords a representative sample of the entire cargo,
2) from one metre below the surface of the oil in two tanks (resulting in two samples) and
3) from the bottoms of the same two tanks (also resulting in two samples). The oil normally contains small amounts of water and sediment, most of wich settles to the bottom of the tanks during the voyage.

The bottom samples are likely to be rather inhomogeneous, with relatively large amounts of water and sediment. The fractions of water, sediment and oil will be analysed separately.

The other samples are not fractionated before analysis.

If the Power Mixer samples are found to contain a significant amount of cadmium, the other samples taken from the same carrier will also be analysed. Accordingly, the analytical method is dovetailed to this type of sample. It is then certain to be also applicable to the samples taken one metre below the surface and the oil fraction of the bottom samples.

The analytical protocol will specify that the oil sample should be homogenised with the aid of an Ultra Turrax Mixer. Experiments caried out by ESSO have shown that the Ultra Turrax method affords good results as far as the homogeneous distribution of water in samples is concerned. Whether this is also true for cadmium has yet to be established.

4.2 Experimental part

The Original Test Sample is homogenised for ten seconds with an Ultra Turrax Mixer and at once subsampled for analysis from ten positions within the sample. These positions are evenly distributed over the volume of the sample.

5. TESTING OF THE RUGGEDNESS OF THE GRAPHITE FURNACE TEMPERATURE PROGRAMME

5.1 Outline of the problem

In the method described by Narres et al. (1), cadmium is determined directly, with the aid of GFZAAS, in the oil sample diluted with carbon tetrachloride. The applied temperature programme needs to be checked for its suitability for the equipment used by TNO. The effect of the ashing and atomisation conditions should be established.

The method of Narres et al. involves injection into a graphite tube of 10 µl of the diluted sample. After drying and ashing, the adsorption signal is measured during the atomisation stage. The intensity of the signal depends on the instantaneously vapourised amount of cadmium. Clearly, the drying and ashing stages should cause no substantial losses of cadmium. If the temperature programmme for the graphite furnace is to be of any use, the temperature margins for ashing and atomisation stages should not be to narrow, because individual graphite tubes may vary in thickness. Likewise the aging of a single graphite tube may cause the same effect. This is particularly true for elements with a low atomisation temperature, such as cadmium.

As the atomisation temperature rises, the absorption signal increases and then levels off. The optimum atomisation temperature is the lowest temperature that produces the greatest signal.

The ashing temperature is taken as high as possible, to avoid ashing products being given off during the atomisation stage.

5.2 Experimental part

In the temperature programme described by Narres et al.(1), the ashing and atomisation temperature is optimised in steps of 25 °C for Test Sample no. 2.

When the final temperature programme for the graphite furnace has been decided upon, it is tested for suitability on two different days with two fresh graphite tubes.

6. REPEATABILITY

6.1 Outline of the problem

The repeatability is assessed in order to gain an insight into the experimental error under 'constant' conditions. This means that the variance of the method is determined within the course of a day for the same equipment, the same operator and the same type of sample. The repeatability is determined for two different cadmium concentrations.

6.2 Experimental part

In order to make a distinction between, on one hand, signal fluctuations caused by the measuring procedure and, on the other, fluctuations caused by inhomogenity of samples, the measuring repeatability is first assessed using Test Sample no. 2. This sample is analysed in tenfold, using the temperature selected. Under normal conditions, the relative standard deviation is less than 5%.

The repeatability of the analysis as a whole (including homogenisation and subsampling) is calculated from the results of experiment 4.2 (Original Test Sample) and Test Sample no. 4. The last mentioned sample is also analysed in tenfold.

7. REPRODUCIBILITY

7.1 Outline of the problem

The reproducibility is assessed in order to gain an insight into the experimental error under non-constant conditions. The variable is taken to be the day on which the analysis is carried out.

7.2 Experimental part

The experiments to assess the repeatability of the method as a whole (see section 6.2) are repeated on three different days.

8. LINEARITY, LIMIT OF DETECTION, LIMIT OF QUANTITATION

8.1 Outline of the problem

All quantitative analytical methods are subject to a lower and an upper detection limit. Within these limits there is either a linear or a non-linear correspondence between concentration and the signal it gives rise to. The in-built computer programme may underestimate concentrations exceeding the upper detection limit. Accordingly, the range within which the equipment processes the measuring signals correctly should be determined. The lower detection limit should preferably be determined by analysis of a comparable sample of oil containing no cadmium. In the absence of such a sample, that limit is defined as three times the standard deviation of the cadmium content of the 'Original Test Sample'. Consequently the limit of quantitation is defined as 10 times the standard deviation of the cadmium content of the 'Original Test Sample'.

8.2 Experimental part

Test Sample no. 3 is spiked with ionic cadmium in amounts of 0, 2, 4, 6, 8 and 10 µg/kg of sample. Each of these mixtures is analysed in duplicate. The results of the measurments reveal the upper detection limit. Oil samples exceeding that limit are pre-diluted.

The lower detection limit follows from the scatter of the analytical results described in Section 4.2. The limit of quantitation will be calculated by multiplying the result of the lower detection limit by 3.3.

9. SENSITIVITY

9.1 Outline of the problem

In general the GFZAAS method affords optimum sensitivity in the analysis of 'clean' aqueous solutions. Matrix effects may reduce the measuring signal for crude oils. The resulting effect can be assessed by comparison with the results for a clean solution. A reduction of the signal means that the lower detection limit is raised.

9.2 Experimental part

The sensitivity of the Narres's method will be assessed on basis of a comparison of the gradients of the calibration curves for the 'Original Test Sample' and Milli-Q water, both spiked with known amounts of cadmium.

10. ACCURACY, BIAS

10.1 Outline of the problem

The accuracy of a method can be determined by comparing it with another method preferably differing from it both in sample pre-processing and in measuring method. Two such methods involve cold oxygen ashing and wet ashing, followed by dissolution of the ashing residue in acid. The cadmium content of the resulting solutions is measured with the aid of GFZAAS or ICP/MS as an alternative. These alternative methods are not exhaustively validated. A rough agreement with the results of Narres's method is taken to be satisfactory.

10.2 Experimental part

- Wet ashing
A sample of crude oil is pre-ashed with concentrated sulphuric acid and the residue is then ashed in a muffle furnace at 550 °C. The ashing residue is then dissolved in dilute nitric acid upon which the cadmium concentration of the solution is determined with the aid of GFZAAS or ICP/MS or both.

The method will be validated to a limited extent by analysis of a sample of oil spiked with a known amount of ionic cadmium. The experiment will be repeated several times, with inclusion of a blank.

For each experiment, 5 grammes of oil are weight out in a quartz crucible. To each sample 5 grammes of concentrated sulphuric acid is added, and the mixture is slowly heated up on a hot plate. When it is charred, the crucible is placed in a muffle furnace and further ashed at 550 °C.

- Cold oxygen ashing
A sample of crude oil is 'cold'-ashed at reduced pressure in ozonised oxygen. The ashing temperature being relatively low, the loss of cadmium attending the ashing stage is likely to be less.
The ashing residue is taken up in dilute acid, and the cadmium concentration of the resulting solution determined with the aid of GFZAAS or ICP/MS or both.

The method will be validated to a limited extent by analysis of a sample of oil spiked with a known amount of ionic cadmium. The experiment will be repeated several times, with inclusion of a blank.

11. REFERENCES

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Spectrochimica Acta Vol. 4613, No 10, pp. 1403-1411, 1991
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Annex 9: TNO Report: 'Determination of cadmium in crude oil. Results of the validation study' IMW-R 93/225

IMW - R 93/225

Determination of cadmium in crude oil
Results of the validation study

Author : S.J. Spijk
Ing. E.M. Stofberg
Dr. Ir. E.W.B. de Leer

Date : September 7, 1993

Order no. : 52213

Client : Ministry of Housing, Physical Planning and Environment
Directorate-General for Environmental Protection, Air & Energy/640,
Industry Branch
For the attention of Drs. C.P.A. Dekkers
P.O. Box 30945
2500 GX The Hague
The Netherlands

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12. REFERENCES

Annex 1 Cadmium ZETA-AAS signals as a function of the ashing temperature at a fixed atomisation temperature of 1900 °C
Annex 2 Cadmium ZETA-AAS signals as a function of the atomisation temperature at a fixed ashing temperature of 650 °C
Annex 3 Atomatisation profile of ZETA-AAS, using the temperature programme of Narres
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AUTHENTICATION

Name and address of the commissioner

Ministry of Housing, Physical Planning and Environment
Directorate General for Environmental Protection, Air & Energy/640
Industry Branch
P.O. Box 30945
2500 GX The Hague
The Netherlands

Names and functions of the cooperators

S.J. Spijk	Research coordinator
Ing. E.M. Stofberg	Researcher
H.P.M. de Haan	Researcher
Dr ir E.W.B. de Leer	Project Supervisor

Period in which the research took place
from 25-05-1993 until now

Signatures

S.J. Spijk	E.W.B. de Leer
Research coordinator	Head of department
Date:	Date:

SUMMARY

The Dutch Ministry of Housing, Physical Planning and Environment has commissioned TNO to develop a method for determining cadmium in crude oil.

The method is based on one described by Narres *et al.*, which is a direct method of determination, using graphite furnace AAS involving a single dilution as the only pre-preparation of the sample.

The method has been tested for ruggedness of the graphite furnace, suitability of the temperature programme, repeatability, reproducibility, linearity, limit of detection, limit of quantitation, sensitivity, accuracy and bias.

On basis of these tests we drew up a temperature programme and applied it to samples of a given type of crude oil
The results were in good agreement with those obtained from a (standard) wet chemical method.

Attempts to apply direct method to undiluted samples resulted in a very time-consuming temperature programme, and were therefore abandoned.

The foremost performance data of the direct method applied to diluted samples are:

- Linearity : 0 - 60 µg Cd/kg oil
- limit of detection : 0.4 µg Cd/kg oil
- limit of quantitation : 1 µg Cd/kg oil

The method presented in this report (section 11) will be used to determine the cadmium content of several types of crude oil.

1. INTRODUCTION

At the request of The Dutch Ministry of Housing, Physical Planning and Environment (VROM), TNO has developed methods for sampling of crude oil from crude carriers and for determining cadmium in samples of crude oil.

The project is being conducted under the guidance of a Steering Committee chaired by VROM and comprising representatives of VROM, SHELL, ESSO, BP and DCMR (Regional Environmental Authority).

The method of sampling to be applied by TNO has been described separately in the protocol 'Sampling of Crude Oil'.
That protocol details all measures that have to be taken to ensure that the samples are representative and uncontaminated.

For the determination of cadmium in crude oil no standard methods are available. There are, however, several publications on ad hoc methods and their results. These results show wide variations in cadmium content in crude oils up to a factor of 7000!

Three reasons have been advanced to explain these variations:
1) Incorrect and unrepresentative sampling
2) Contamination of samples during sampling or analysis
3) Incorrect method of analysis

Both the 'Sampling Protocol' and the analytical method for the determination of cadmium in crude oil (based on the Validation Study (1)) are given in accordance with GLP guidelines, whereas the actual sampling and analysis are carried out under the Quality Assurance system operated by TNO, a system that meets STERLAB as well as GLP criteria.
All raw data, correspondence, reports, etc., will be filed under the STERLAB Quality Assurance System.

In principle, the determination of cadmium in crude oil involves two operations: dry or wet ashing and the actual measurement (with the aid of, e.g., Atomic Absorption Spectrometry).

In order to prevent contamination, direct methods skipping off-line dry or wet ashing are to be preferred. At the Steering Committee's recommendation it has been decided to take as a starting point the method described by Narres *et al.* (2) (which involves on-line ashing of a diluted sample) and to validate it by a procedure to be laid down in a protocol.

As a check on the accuracy of the method, TNO has used an additional different method (wet ashing).

A main purpose of the validation study (1) is to assess the performance and ruggedness of the method. By ruggedness is meant the insensitivity of the method to the inevitable variations of temperature that attend the drying and ashing of the oil sample. Other important features of the study are such performance criteria as intralaboratory repeatability and reproducibility, linearity, detection limit, sensitivity, accuracy and method blank value.

2. EXPERIMENTAL DETAILS

2.1 Samples

In the validation study we used the following types of samples:

- *Original Test Sample (no.1)*

This is the sample of crude oil (Arabian Heavy) taken by TNO on 23 March 1993 at NEREFCO, Rotterdam Pernis, in a 2-litre borosilicate-glass bottle, previously cleaned with nitric acid.

- *Test sample no. 2*

This consists of 25 grammes of oil taken from the undisturbed upper layer of the 'Original Test Sample', plus 75 grammes of carbon tetrachloride. To this mixture was added 1 µg/kg of ionic cadmium (the benzenesulphonic acid salt of cadmium). If it is assumed that any water or sediment has settled to the bottom of the undisturbed 'Original Test Sample', Test Sample no. 2 can be regarded as relatively homogeneous and uncontaminated.

- *Test Sample no. 3*

This consists of 25 grammes of oil taken from the undisturbed upper layer of the 'Original Test Sample', plus 75 grammes of carbon tetrachloride.
No cadmium salt was added.

- *Test Sample no. 4*

Test Sample no. 4 consists of 100 grammes of 'Original Test Sample', to which 4 µg/kg of ionic cadmium salt was added.

2.2 Methods

- Direct injection of sample diluted with carbon tetrachloride into graphite furnace atomic absorption spectroscopy with Zeeman correction (ZETA-AAS) (1)
- Ashing with sulphuric acid, followed by ZETA-AAS and/or ICP-MS (2)
- Cold oxygen plasma ashing, followed by ZETA-AAS and/or ICP-MS (3)

2.3 Equipment & facilities

- Perkin Elmer 5100 PC Atomic Absorption Spectrometer
- Fisons Instrument VG Plasma Quad ICP-MS
- Cold oxygen plasma ashing apparatus
- Clean room facilities

- Ultra Turrax Mixer with a titanium shaft, type T25 IKA, 8000 - 24000 RPM. This is used to homogenise oil samples.
- Standard laboratory equipment, facilities and reagents. All glassware that comes into contact with crude oil is cleaned with 7 M nitric acid and then rinsed with demineralised Milli-Q water until acid-free. The glassware is dried and stored in a clean room.

Wherever possible we used the procedure described in Section 11.

3. SAMPLE STORAGE

3.1 Introduction

As part of the project, samples of oil will be taken from crude carriers during a period of several months. The samples will be collected in glass bottles (colourless borosilicate) and stored in the dark at 2 - 8 °C prior to analysis. The analysis of samples will begin after the last crude carrier has been sampled. This means that the duration of storage is variable. It therefore needs to be established whether that duration affects the concentration of cadmium in the oil. Conceivably, cadmium may be adsorbed by the glass of the storage bottles, or settle to the bottom. In case of adsorption, the effectiveness of the homogenisation of the samples (with the Ultra Turrax Mixer) is in doubt.

If the results of the experiments show that adsorption may have taken place, it will be necessary to analyze the samples immediately after having been taken.

3.2 Experimental part

One hundred grammes of 'Original Test Sample' is transferred to a 125 ml glass bottle (colourless borosilicate). To the sample is added an amount of ionic cadmium up to a final concentration of 10 µg Cd/kg of oil, upon which the sample is homogenised and analyzed at once. The time when the homogenisation and measurement took place is defined as T = 0. The sample is then stored in the dark at 4 °C (range 2-8 °C). At T = one week, the sample is again homogenised and subsampled in duplicate. Each subsample is analyzed in duplicate. This procedure is repeated at T = 2 weeks, 4 weeks, 16 weeks, 32 weeks, etc.

3.3 Results

The results that have become available so far are listed in Table 1.

Table 1 *Cadmium content of the Original Test Sample after addition of approximately 10 µg Cd/kg oil (diluted 4 times) and storage. The measured values have been converted into values for undiluted oil.*

Week	Cd concentration in µg/kg*)	
	subsample 1	subsample 2
0	11.8-12.2	11.9-13.6
1	15.7-17.3	14.6-15.3
2	15.9-13.7	14.0-15.4
4**)	15.7-15.4	16.6-16.0
8	18.7-18.2	17.1-16.7
16		
32		

*) Each subsample analyzed in duplicate
**) Homogenised at t = 4 weeks and measured at t = 6 weeks

3.4 Conclusions

So far we have found no evidence that (prolonged) storage of samples causes any loss of cadmium. The results for t=8, t=16, and t=32 weeks will be reported in due course.

4. NON-UNIFORM DISTRIBUTION OF CADMIUM IN CRUDE OIL

4.1 Introduction

Crude oil will be sampled at three different locations:
1) from the so-called 'Power Mixer', which affords a representative sample of the entire cargo,
2) from one metre below the surface of the oil in two tanks (resulting in two samples) and
3) from the bottoms of the same two tanks (also resulting in two samples). The oil normally contains small amounts of water and sediment, most of which settles to the bottom of the tanks during the voyage.

The bottom samples are likely to be rather inhomogeneous, with relatively large amounts of water and sediment. The fractions of water, sediment and oil will be analyzed separately, using 'standard' methods.

The other samples are not fractionated before analysis.

If the Power Mixer samples are found to contain a significant amount of cadmium, the other samples taken from the same carrier will also be analyzed. Accordingly, the analytical method is dovetailed to this type of sample. It is then certain to be also applicable to the samples taken one metre below the surface and the oil fraction of the bottom samples.

The analytical protocol has to specify that the oil sample should be homogenised with the aid of an Ultra Turrax Mixer. Experiments carried out by ESSO have shown that the Ultra Turrax method affords good results as far as the homogeneous distribution of water in samples is concerned. Whether this is also true for the distribution of cadmium has yet to be established.

4.2 Experimental part

The Original Test Sample is homogenised for ten seconds with an Ultra Turrax Mixer and at once subsampled for analysis from ten positions within the sample. These positions are evenly distributed over the height of the sample bottle. The subsamples are diluted 4 times with carbon tetrachloride.

4.3 Results

The results are summarized in Table 2.

Table 2 *Distribution of cadmium in homogenised crude oil*

Position	Cd content in µg/kg*
top	0.95
1 cm	1.02
2 cm	0.99
3 cm	1.02
4 cm	1.43
5 cm	1.04
6 cm	1.44
7 cm	0.89
8 cm	1.15
bottom	1.91
average	1.18±0.32

* converted into Cd content of undiluted oil

4.4 Conclusions

Dixon's outlier test (5) has shown that none of the values listed above is an outlier. This means that the proposed method of homogenisation is satisfactory.

5. TESTING OF THE RUGGEDNESS OF THE GRAPHITE FURNACE TEMPERATURE PROGRAMME

5.1 Introduction

In the method described by Narres *et al.* (1), cadmium is determined directly, with the aid of ZETA-AAS, in the oil sample diluted with carbon tetrachloride. The applied temperature programme has been checked for its suitability for the equipment used by TNO. The effect of the ashing and atomisation conditions has been established.

The method of Narres *et al.* involves injection of 10 µl of the diluted sample into a graphite tube . After drying and ashing, the adsorption signal of cadmium is measured during the atomisation stage. The intensity of the signal depends on the instantaneously vaporised amount of cadmium. Clearly, the drying and ashing stages should cause no substantial losses of cadmium. If the temperature programme for the graphite furnace is to be of any use, the temperature margins for the ashing and atomisation stages should not be too narrow, because individual graphite tubes may vary in thickness. Likewise the aging of a single graphite tube may cause the same effect. This is particularly true for elements with a low atomisation temperature, such as cadmium.

As the atomisation temperature rises, the absorption signal increases and then levels off. The optimum atomisation temperature is the lowest temperature that produces the strongest signal.

The ashing temperature is taken as high as possible, to avoid ashing products being given off during the atomisation stage.

5.2 Experimental part

In the temperature programme described by Narres *et al.*(1), we optimised the ashing and atomisation temperature in steps of 25 °C for Test Sample no. 2.
When the final temperature programme for the graphite furnace had been decided upon (see 11.6), it was tested for suitability on different days with fresh graphite tubes.

5.3 Results

The results are summarized in Table 3 (optimisation of ashing temperature for a fixed atomisation temperature of 1900 °C) and in Table 4 (optimisation of the atomisation temperature for a fixed ashing temperature of 650 °C).
The results are shown in graphs in Annexes 1 and 2, respectively. In addition Annexes 3 and 4, show two atomisation profiles before and after optimisation of the temperature programme.

Table 3 *Cadmium ZETA-AAS signals as a function of the ashing temperature at a fixed atomisation temperature of 1900 °C*

Temperature [°C]	Corrected signal	Background signal
500	–	>2
550	0.222±0.0012	0.17
600	0.230±0.0022	0.05
650	0.227±0.0005	0.05
700	0.223±0.0077	0.05
750	0.215±0.0028	0.05
800	0.200±0.0128	0.05
850	0.150±0.0092	0.04

Table 4 *Cadmium ZETA-AAS signals as a function of the atomisation temperature at a fixed ashing temperature of 650 °C*

Temperature [°C]	Corrected signal	Background signal
1200	0.01±0.002	0.010
1250	0.025±0.002	0.010
1300	0.044±0.003	0.015
1350	0.077±0.005	0.021
1400	0.101±0.001	0.027
1450	0.122±0.002	0.035
1500	0.140±0.015	0.040
1550	0.153±0.010	0.042
1600	0.146±0.005	0.041
1650	0.145±0.0002	0.041
1700	0.145±0.0018	0.040
1750	0.151±0.006	0.040
1800	0.142±0.005	0.037
1850	0.144±0.008	0.037
1900	0.143±0.005	0.037
1950	0.140±0.003	0.038
2000	0.137±0.001	0.035
2050	0.146±0.005	0.036
2100	0.140±0.004	0.034
2150	0.138±0.005	0.041
2200	0.131±0.007	0.035

5.4 Conclusions

On basis of the results listed above, we selected the final temperature programme as described in Sect. 11.

The results of the test for suitability on different days with fresh graphite furnace tubes are given in Table 5 in Sect. 6.3.

6. REPEATABILITY AND REPRODUCIBILITY

6.1 Introduction

The repeatability is assessed in order to gain an insight into the experimental error under 'constant' conditions. This means that the variance of the method is determined within the course of a day for the same equipment, the same operator and the same type of sample. The repeatability is determined for two different cadmium concentrations.

The reproducibility is assessed in order to gain an insight into the experimental error under non-constant conditions. The variable is taken to be the day on which the analysis is carried out.

6.2 Experimental part

In order to make a distinction between, on one hand, signal fluctuations caused by the measuring procedure and, on the other, fluctuations caused by inhomogeneity of samples, the repeatability is first assessed using Test Sample no. 2.
This sample is analyzed in tenfold, using the optimised temperature programme selected. Under normal conditions, the relative standard deviation is less than 5%.

The repeatability of the analysis as a whole (including homogenisation and subsampling) is calculated from the results of experiment 4.2 (Original Test Sample) and Test Sample no. 4. The last mentioned-sample is also analyzed in tenfold.

To assess the reproducibility of the method as a whole the above experiments are repeated on four different days.

6.3 Results

The results of the experiments to asses repeatability and reproducibility are summarized in Table 5.

Table 5 *Measuring results from which repeatability and reproducibility are estimated*

Cd content in µg/kg, Test Sample 2*				
	day 1	**day 2****	**day 3**	**day 4**
	-	5.04-5.14	4.84	5.88
	4.92	5.97-5.06	5.08	5.84
	5.52	5.38-5.26	5.00	5.76
	5.12	5.36-5.32	5.04	5.72
	4.96	5.98-6.30	4.88	5.56
	5.36	7.15-5.22	5.04	5.76
	5.04	6.28-5.92	4.92	5.88
	5.28	6.32-5.90	5.56	5.64
	5.40	6.91-7.18	4.96	5.96
	5.52	5.90-6.05	4.92	5.72
average	5.24±0.23	5.88±0.67	5.02±0.20	5.77±0.12

* Amount of Cd added converted into Cd content of undiluted oil
** Measurements in duplicate

6.4 Conclusions

The results for a single day afford an insight into the repeatability. The relative standard deviation for a successive days is:

day 1: 4%
day 2: 11%
day 3: 4%
day 4: 2%

These results show that the relative standard deviation on three out of four days is less than 5%, and so does not deviate from that under standard conditions.
We have no explanation for the high standard deviation on day 2.

The reproducibility (measured on four different days) is 5.54±0.58 µg Cd/kg oil. Accordingly, the spread for a single sample analyzed on four different (not necessarily consecutive) days is 10%.

7. ANALYSIS OF UNDILUTED SAMPLES

An experiment on Test Sample no. 4 (undiluted oil with 4 ppb of Cd added) gives rise to a background signal that cannot be processed with the Zeeman background-correcting system.

The amount of oil injected is four times the amount used in Narres's method (2). It may be possible to obtain better results by modification of the temperature programme, although this may thereby be unduly lengthened.

The lower detection limit for diluted samples being satisfactory, such modification of the temperature programme has been abandoned (see Sect. 8.3).

8. LINEARITY, LIMIT OF DETECTION, LIMIT OF QUANTITATION

8.1 Introduction

All quantitative analytical methods are subject to a lower and an upper detection limit. Within these limits there is either a linear or a non-linear correlation between concentration and analytical response. The built-in computer programme may underestimate concentrations exceeding the upper detection limit. Accordingly, the range within which the equipment processes the measuring signals correctly should be determined.

The lower detection limit should preferably be determined by analysis of a comparable sample of oil containing no cadmium.
In the absence of such a sample, that limit is defined as three times the standard deviation of the cadmium content of Test sample no. 3.

Consequently, the limit of quantitation is defined as 10 times the standard deviation of the cadmium content of the 'Original Test Sample'.

8.2 Experimental part

- Linearity

Test Sample no. 3 is spiked with cadmium salt in amounts of 0, 2, 4, 6, 8 and 10 µg/kg of sample. A calibration curve has been made for concentrations of 0 and 4 ppb of cadmium in aqueous solution. This curve was used to measure the cadmium content of the samples.
Each of these samples is analyzed in duplicate (two sub-samples). The results of the measurements reveal the upper detection limit. Oil samples exceeding that limit have to be pre-diluted.

- Limit of detection

To determine the lower detection limit, Test Sample no 3 is analyzed in 10-fold on two different days.

- Limit of quantitation

The limit of quantitation is calculated by multiplying the result of the lower detection limit by a factor of 3.3.

8.3 Results

- Linearity

The results are collected in Tables 6 en 7.

Table 6 *Measured results from which the linearity is estimated*

Cd content in µg/kg, Test Sample 3		
	subsample 1	**subsample 2**
+ 0 ppb Cd:	0.13	0.13
+ 2 ppb Cd:	2.17	1.91
+ 4 ppb Cd:	5.40	3.78
+ 6 ppb Cd:	5.98	6.08
+ 8 ppb Cd:	7.80	9.02
+10 ppb Cd:	9.93	8.91

The regression coefficient calculated from the duplicate results is 0.9849 (R-squared: 0.9699)

The equation of the calibration curve, calculated from results listed in Table 6, is:
Y= 0.96X+0.32

Since the experiment gave no clear-cut deviation from linearity, further additions of 0, 5, 10, 15, 20, 25 and 30 µg Cd/kg were made to Test Sample 3. The results are given in Table 7.

Table 7 *Measured results from which the linearity is estimated (contd)*

Cd content in µg/kg, Test Sample 3		
	subsample 1	**subsample 2**
+ 0 ppb Cd	0.14- 0.15	0.13- 0.15
+ 5 ppb Cd	5.7 - 6.4	6.8 - 6.8
+ 10 ppb Cd	12.0 -13.1	11.6 -11.0
+ 15 ppb Cd	16.7 -16.7	14.4 -14.4
+ 20 ppb Cd	15.9 -16.1	19.5 -19.0
+ 25 ppb Cd	18.0 -18.1	19.0 -19.9
+ 30 ppb Cd	21.0 -19.0	-

The regression coefficient calculated from the duplicate results up to 30 ppb is 0.94404 (R-squared: 0.8912).
For concentrations in excess of 15 ppb, the calibration curve is no longer linear.
Re-calculation for values up to 15 ppb gives the following results:
r=0.9856 (R-squared 0.9714).

The equation of the curve then becomes:
Y=1.03X + 0.75.

The results listed above are shown in graphs in Annexes 5 and 6.

- *Limit of detection*

The results from which the lower limit of detection was estimated are listed in Table 8.

Table 8 *Results of Cd in oil in µg/kg obtained by the procedure described in Sect. 11. (converted into Cd contents for the undiluted sample)*

	Cd content in µg/kg, Test Sample 3	
	day 1	day 2
	0.34	0.46-0.48
	0.72	0.42-0.48
	0.53	0.66-0.76
	0.32	0.55-0.46
	0.44	0.45-0.46
	0.47	0.42-0.55
	0.46	0.56-0.53
	0.46	0.62-0.55
	0.50	0.44-0.58
	0.44	0.64-0.95
average	0.46±0.11	0.55±0.09

The lower detection limit, calculated as three times the standard deviation for Cd content of the undiluted oil sample, is 0.4 µg Cd/kg oil.

8.4 Conclusions

The results for linearity, lower limit of detection and limit of quantitation are as follows:

- Linearity : 0 - 60 µg Cd/kg oil (undiluted sample)
- limit of detection : 0.4 µg Cd/kg oil („)
- limit of quantitation : 1 µg Cd/kg oil („)

9. SENSITIVITY

9.1 Introduction

In general the ZETA-AAS method affords optimum sensitivity in the analysis of 'clean' aqueous solutions. Matrix effects may reduce the measuring signal for crude oils. The resulting effect can be assessed by comparison with the results for a clean solution. A reduction of the sensitivity implies that the lower detection limit is raised.

9.2 Experimental part

The sensitivity of Narres's method is assessed on basis of a comparison of the gradients of the calibration curves for the 'Original Test Sample' and Milli-Q water, both spiked with known amounts of cadmium.

9.3 Results

The results of this experiment are listed in Table 9.

Table 9 *Measured results from which the sensitivity was estimated*

Matrix		Absorbance
Water	+ 0 ppb Cd	auto zero
	+ 2	0.132
	+ 4	0.287
	+ 6	0.411
	+ 8	0.542
	+ 10	0.679
Oil*	+ 0 ppb Cd	0.012
	+ 2	0.201
	+ 4	0.349
	+ 6	0.562
	+ 8	0.721
	+ 10	0.824

*) diluted four times

The results listed above are shown in graph in Annex 7.

Note: The temperature programme for analysis of crude oil is less satisfactory than for aqueous samples (distorted peak shape), as shown in Annex 8.

9.4 Conclusions

The results show that an oil matrix does not suppress the cadmium signal.

10. ACCURACY, BIAS

10.1 Introduction

The accuracy of a method is normally determined by the analysis of certified reference materials. However, for cadmium in crude oil, no such materials are available. We therefore determined the accuracy by comparing the method with another differing from it both in sample pre-processing and measuring method, viz. wet ashing followed by dissolution of the ashing residue in acid. An alternative might be cold oxygen ashing, which is being studied.
The cadmium content of the resulting solution is measured with the aid of ZETA-AAS or, alternatively, ICP/MS. This method has not been exhaustively validated. A rough agreement with the results of Narres's method is taken to be satisfactory.

10.2 Wet ashing

A sample of crude oil is pre-ashed with concentrated sulphuric acid and the residue is then ashed in a muffle furnace at 550 °C. The ashing residue is then dissolved in dilute nitric acid, upon which the cadmium concentration of the solution is determined with the aid of ZETA-AAS or ICP/MS or both.

The method is validated to a limited extent by analysis of a sample of oil spiked with a known amount of ionic cadmium. The experiment is repeated several times, with inclusion of a blank.

- *Experimental*

For each experiment, 5 grammes of oil are weighed out in a quartz crucible. To each sample 5 grammes of concentrated sulphuric acid is added, and the mixture is slowly heated up on a hot plate. When it is charred, the crucible is placed in a muffle furnace and further ashed at 550 °C.

- *Results*

The results of the wet ashing method are listed in Table 10.

Table 10 *Analytical results for wet ashing method*

Sample	Cd content in µg/kg	
	ICP-MS	ZETA-AAS
crude oil no.1	1 12*	1.3 10*
crude oil no.1 + 1000 ppb Cd**	1130 1190	1230 1310
detection limit***	1.0	0.5

*) Contaminated ?
**) The applied cadmium standard (Conastan) contains the cadmium salt of benzenesulphonic acid in oil.
***) The detection limit is defined as three times the standard deviation of the Cd signal of a blank solution.

- *Conclusions*

The results of the wet ashing method corroborate Narres's method.

Note: The dilution preceding wet ashing causes the cadmium content to approach the lower detection limit.
The results can be improved by conducting all 'open air' manipulations in a dust-free laboratory, and using a smaller dilution factor.

10.3 Cold oxygen ashing

The experiments carried out so far with 5-gramme amounts of oil have failed to produce suitable ashing residues. They will in due course be repeated with smaller amounts of oil.

11. PROCEDURE FOR THE DETERMINATION OF CADMIUM IN CRUDE OIL

11.1 Scope

This procedure describes a method for determination of cadmium in crude oil, in concentrations of up to 10 µg/kg.

11.2 Principle

The cadmium content in crude oil is determined after dilution with carbon tetrachloride. The diluted sample is injected into a graphite furnace with L'VoV-platform and oxygen addition during the charring step. The spectrometer is equipped with Zeeman background compensation.

11.3 Reagents

11.3.1 Oxygen 99.9999%
11.3.2 Argon 99.999%
11.3.3 Carbon tetrachloride (reagent grade).
11.3.4 Cyclohexanol (reagent grade)
11.3.5 Solution of cadmium benzenesulphonate, 5000 mg Cd/l
11.3.6 Cadmium standard solution I, 10 mg Cd/l
Weigh out 0.2 g of the cadmium solution (3.5) into a conical flask, nominal capacity 200 ml, and make up to 100 g with cyclohexanol.
The solution is stable for at least a month.
11.3.7 Cadmium standard solution II, 100 µg Cd/l
Weigh out 1 g of the cadmium solution (3.6) into a conical flask, nominal capacity 200 ml, and make up to 100 g with cyclohexanol.

11.4 Equipment

11.4.1 An atomic absorption spectrometer adjusted to a wavelength of 228.8 nm, connected to a graphite furnace and provided with a facility for simultaneous correction of the background signal with the aid of a Zeeman correction system.
11.4.2 A hollow cathode tube or an electrodeless discharge tube for cadmium.
11.4.3 Diluter-dispenser, adjustable pipettes.
11.4.4 Standard laboratory glassware.
Immediately before use, clean all glassware with warm, dilute nitric acid and rinse with water. Then rinse with acetone and let the glassware dry.

11.5 Pre-preparation of sample

Dilute the sample four times: weigh out 2 grammes of oil in a conical flask and add 6 grammes of carbon tetrachloride. Homogenise the mixture.

11.6 Procedure

Adjust the atomic absorption spectrometer (11.4.1) for the measurement of cadmium in accordance with the user's manual. Prepare a calibration curve (11.3.6) for a cadmium content of 0 tot 10 µg Cd/ kg oil, using a sample of oil with a low concentration of cadmium.

Set up the following temperature programme, and optimise the ashing and atomisation temperatures for the spectrometer

Temperature Programme for ZETA-AAS analysis of Cd in crude oil

Step	Temperature (ºC)	Ramp time (s)	Hold time (s)	Int. gas flow (ml/min)
1	150	10	0	300 O_2
2	250	60	0	300 O_2
3	450	100	0	50 O_2
4	650	100	100	50 O_2
5	650	1	39	300 Ar
6	650	1	5	0 Ar
7	1900	1	5	0 Ar
8	2400	1	3	300 Ar
9	20	1	9	300 Ar

The injection volume is 10 µl. Determine the atomic absorption at 228.8 nm, preferably as a peak surface area. All injections should be carried out at least in duplicate. Correct the calibration curve for the natural cadmium content of the oil matrix. (The software incorporated in some types of equipment enables use of a 'method of addition calibration').

11.7 Calculation

Calculate the cadmium content of the oil sample as follows:

$$C = c \times d, \text{ where}$$

C = Cd concentration in undiluted sample (µg/kg)
c = measured Cd concentration in diluted sample (µg/kg)
d = dilution factor (w/w)

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ANNEX 1 CADMIUM ZETA-AAS SIGNALS AS A FUNCTION OF THE ASHING TEMPERATURE AT A FIXED ATOMISATION TEMPERATURE OF 1900 °C

ANNEX 2 CADMIUM ZETA-AAS SIGNALS AS A FUNCTION OF THE ATOMISATION TEMPERATURE AT A FIXED ASHING TEMPERATURE OF 650 °C

ANNEX 3 ATOMISATION PROFILE OF ZETA-AAS, USING THE TEMPERATURE PROGRAMME OF NARRES

ANNEX 4 ATOMISATION PROFILE OF ZETA-AAS, AFTER MODIFICATION OF THE TEMPERATURE PROGRAMME OF NARRES

ANNEX 5 LINEARITY TEST UP TO 10 PPB

ANNEX 6 LINEARITY TEST UP TO 30 PPB

ANNEX 7 SENSITIVITY TEST

ANNEX 8 DISTORTED PEAK SHAPE Cd IN AQUEOUS SAMPLES