



Round Robin Study Report

IP 570 'Determination of Hydrogen Sulfide in Fuel Oils – Rapid Liquid Phase Extraction Method'

**26th March 2009 version 2
(with editorial changes to Table 1)**

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Approved by: TMS SC-G-5

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**TMS SC-G-5 Working Group on H₂S in the Liquid Phase
H₂S Analyser Instrument: Round Robin
'Determination of Hydrogen Sulfide in Fuel Oils – Rapid Liquid Phase Extraction Method'**

1 Round Robin Study Report Summary

A round robin, organised by Christopher Roach (Stanhope-Seta), was held using 7 Seta Analytics H₂S Analyser Instruments and 15 samples in duplicate, to produce the repeatability and reproducibility of the test method. The samples used were marine fuel oils and blend stocks. Values of measured H₂S concentration varied from 0.01 to 15.3 mg/kg, and viscosities were measured from 30 to 3000 mm²/s.

The resulting calculated expressions of repeatability and reproducibility (valid from 0.40 to 15.0 mg/kg) were as follows:

$$\begin{aligned}\text{Repeatability} &= 0.2970 \times 0.6 \text{ mg/kg} \\ \text{Reproducibility} &= 0.5232 \times 0.6 \text{ mg/kg}\end{aligned}$$

The round robin results have shown that this new method is suitable for measuring very low levels of H₂S in the liquid phase. It is recommended that IP PM-DX is upgraded to IP 570 with the precision and be balloted for approval.

2 Introduction

This standard was developed in response to demand from industry for a quick and reliable test to determine the level of hydrogen sulfide present in fuel oils and blend stocks. H₂S is both toxic and is linked to corrosion, and it is therefore of considerable importance to be able to determine the levels present both quickly and accurately.

The current standard method for the determination of H₂S in fuel oils is IP 399, which requires the preparation of several solutions prior to testing, takes up a great deal of laboratory space, and is a time consuming and manually intensive test.

Therefore, this standard seeks to produce a test that will give a result in typically 15 minutes, does not require the preparation of solutions, frees the operator for other tasks while the instrument undertakes the test, and has a physically small footprint.

The information contained herein represents the finding of a round robin held at the Nalco laboratory, Fawley, on the 5th and 6th of March 2009. The trial compared the performance of 7 instruments testing 15 samples in duplicate and in a random order. In total 9 operators took part.

The purpose of this trial was to produce a statistically valid level of performance of the instrument. All the instruments were calibrated in accordance with the manufacturers instructions prior to the trial.

This is the second round robin that has been undertaken with this instrument. The first one compared seven instruments testing 10 samples in duplicate. The results from this round robin highlighted the importance of correct sample handling, and it was felt that further development

of the instrument would bring improved precision. In addition, there was an industry desire to extend the range of samples that were tested. This was in terms of viscosity, H₂S levels, as well as fuel types comprising as much as practicable all commercially available marine fuel grades and typical blend stock components, in order to demonstrate the suitability of the method over a wide set of materials.

3 Objectives

The objective of the study was to generate repeatability and reproducibility data for the test method, to give an estimate of the performance of the instrument under typical laboratory conditions.

4 Test Method

The test method used for this study was titled IP PM-DX ‘Determination of total hydrogen sulfide in fuel oils – Rapid liquid phase extraction method’, version 09 February 2009, and is attached as Appendix A.

5 List of Participating Laboratories and Operators

Owing to the unstable nature of H₂S in fuel oils, all testing was done at a single site over two days. The laboratory used in this study was at Nalco Ltd, Block 102 Cadland Road, Hardley, Southampton SO41 8FU. The primary contact name at the host facility is Ron Sharpe.

6 Test Specimens

Table 1: Samples used in the round robin

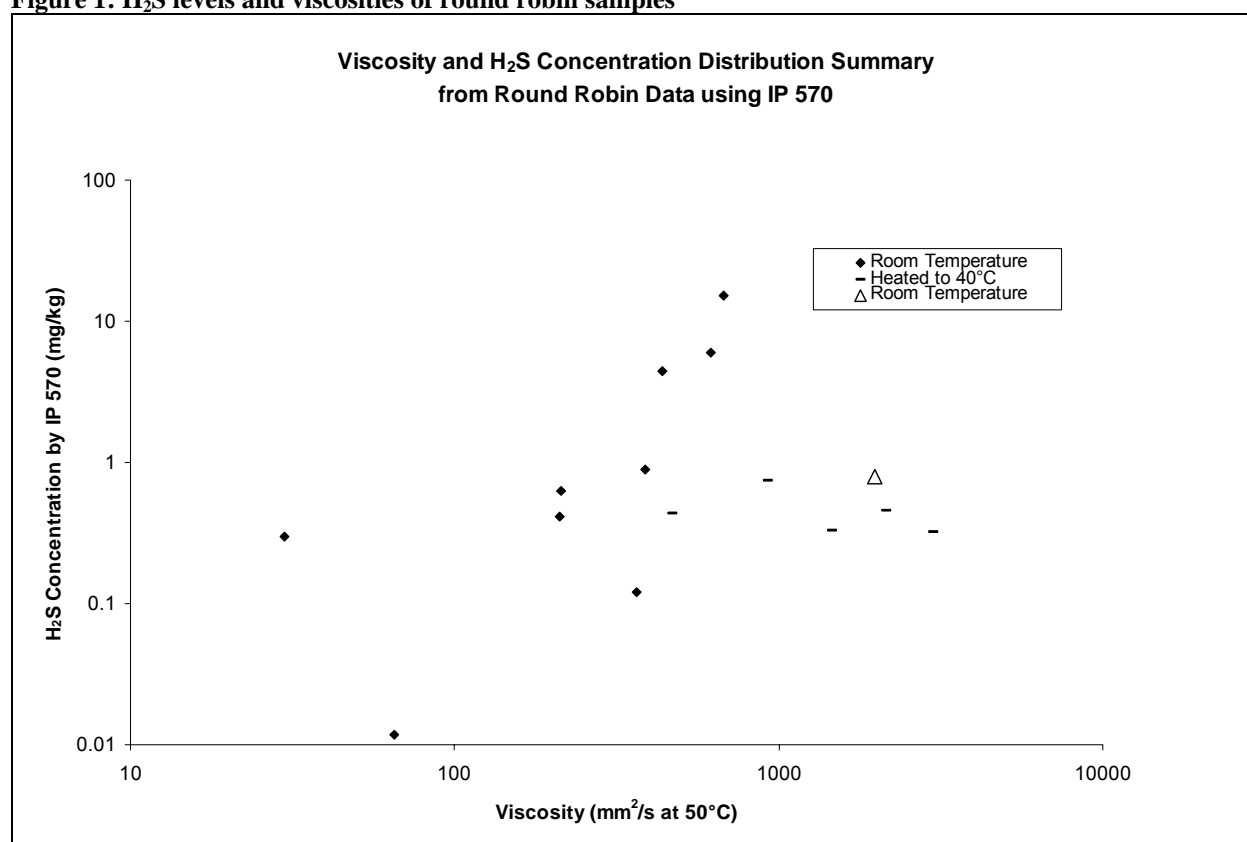
Sample No.	Sample Ref. (Blind Coded)	Description	Viscosity ¹ (mm ² /s at 50°C)	Density ¹ (kg/m ³ at 50°C)
1	3, 11	RFO Vacuum distillation unit feed	677	938
2	10, 14	RFO Vacuum distillation unit feed	620	939
3	7, 19	RFO High sulfur visbreaker residue	3000	983
4	5, 12	RFO Blend stock	927	976
5	2, 20	RFO Vacuum distillation unit feed	1455	959
6	4, 13	RFO Blend stock	438	973
7	6, 15	RFO with scavenger	2149	982
8	8, 17	RFO Cracked vacuum distillate	29.7	919
9	1, 16	RFO 380	389	947
10	9, 18	RFO 380	363	938
11	21, 30	RFO 500	471	967
12	25, 23	Diluent oil	65.4	852
13	27, 22	RFO 180	211	953
14	24, 26	RFO 200	213	951
15	29, 28	RFO vacuum residue with scavenger	1986	974

1: Measured by ASTM D7042 - 04

Table 1 above details the samples used in the round robin. In order to minimise the possibility of the concentration of H₂S altering significantly over the test period, on day 1 samples 1 to 10 were tested in duplicate in a random order, and on day 2, samples 11 to 15 were tested in duplicate in a random order. No samples were tested on more than one day. None of the samples were opened prior to testing, all were stored in an air-conditioned laboratory from the time of receipt until they were used. Some of the more viscous samples were warmed to 40° C to aid sample introduction into the syringe.

Figure 1 combines the range of viscosities from the above table with the H₂S levels that were determined during the round robin for each of the samples. This graph plots the H₂S level as found by IP PM-DX against the viscosity of the sample. This illustration shows that there was no relationship between the sample type, viscosity, and recorded H₂S level. Those samples that were heated to 40° C are noted. It was found that samples over 500 mm²/s normally require heating to aid the sample handling. The single point on Figure 1 over this value of viscosity which was not heated is marked as Δ. This was due to the container supplied not readily fitting the oven used.

Figure 1: H₂S levels and viscosities of round robin samples



7 Round Robin Protocol

See Appendix B

8 Apparatus

Seven H₂S Analyser Instruments were used for testing. As part of the instrument apparatus, 10 ml disposable syringes were supplied and fitted with a short length of flexible silicon tubing. These were used for taking the oil sample, the length of tubing ensuring that the sample could be taken from below the surface of the fuel oil, thus ensuring a representative sample from the bulk material. A 1 ml positive displacement pipette and a supply of disposable tips were also supplied to ensure as much as practical that each test was undertaken with the same volume of sample, and the sample introduction was controlled. The size of the sample taken depended on the H₂S concentration of the sample, the table in section 11.7 of the method, repeated in section 5.6.3 of the test protocol provided guidance.

9 Software

The instruments used in the testing utilised software versions 3.01/2.00

10 Data Report Forms

Table 2 summarises the data generated by each of the instruments used in the trial.

Table 2: Results from each instrument

	L1		L2		L3		L4		L5		L6		L7	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
S1	14.7	13.9	14.4	14.1	15.3	13.7	15.8	15.2	16.6	16.6	16.4	15.3	16.0	15.5
S2	5.74	5.23	3.83	3.36	-999.9	6.96	5.75	6.08	7.12	6.40	5.59	5.53	6.93	5.36
S3	0.28	0.30	0.28	0.29	0.30	0.36	0.30	0.37	0.34	0.32	0.36	0.44	0.30	0.24
S4	0.77	0.71	0.60	-999.9	0.82	0.82	0.66	0.63	0.88	0.80	0.82	0.84	0.65	0.62
S5	0.45	0.34	0.29	0.30	0.26	0.25	0.31	0.21	0.41	0.32	0.33	0.46	0.40	0.30
S6	3.55	3.61	4.23	3.90	5.29	5.15	4.57	4.53	4.86	4.72	4.65	5.00	4.03	4.08
S7	0.37	0.34	0.41	0.40	0.55	0.50	0.40	0.41	0.49	0.46	0.55	0.54	0.46	0.48
S8	0.25	0.24	0.23	0.23	0.36	0.59	0.29	0.31	0.27	0.29	0.30	0.29	0.25	0.26
S9	0.64	0.55	0.89	0.83	1.08	1.11	0.77	0.81	0.85	0.78	1.10	1.13	0.97	0.90
S10	0.08	0.06	0.07	0.13	0.24	0.23	0.10	0.08	0.09	0.06	0.16	0.19	0.10	0.11
S11	0.35	0.29	0.35	0.41	0.51	0.61	0.39	0.35	0.35	0.35	0.58	0.59	0.48	0.48
S12	0.02	0.00	0.03	0.00	0.03	0.02	0.00	0.04	0.02	0.00	0.00	0.06	0.02	0.00
S13	0.26	0.26	0.42	0.40	0.47	0.44	0.33	0.35	0.38	0.37	0.62	0.59	0.45	0.41
S14	0.42	0.44	0.61	0.59	0.77	0.82	0.61	0.62	0.58	0.54	0.77	0.76	0.68	0.67
S15	0.59	0.62	0.83	0.80	1.01	0.95	0.71	0.75	0.71	0.74	0.91	0.91	0.83	0.83

In the above table L1, L2, etc., represent the different instruments, S1, S2, etc., represent the samples tested. 1 and 2 are the first and repeat results respectively, and all results are in mg/kg.

The two results recorded as -999.9, S2, L3, repeat 1, and S4, L2, repeat 2 were due to an operator error and instrument error respectively and were removed from the subsequent analysis.

11 Statistical Evaluation of the Data

The data was analysed according to ISO 4259 (IP 367) using the ASTM D2PP software package to generate values for repeatability and reproducibility. Full details of data used and the ASTM D2PP report can be found in Appendix C.

The repeatability and reproducibility were found to be:

$$\text{Repeatability} = 0.2970 \times 0.6 \text{ mg/kg (DF 100)}$$

$$\text{Reproducibility} = 0.5232 \times 0.6 \text{ mg/kg (DF 38)}$$

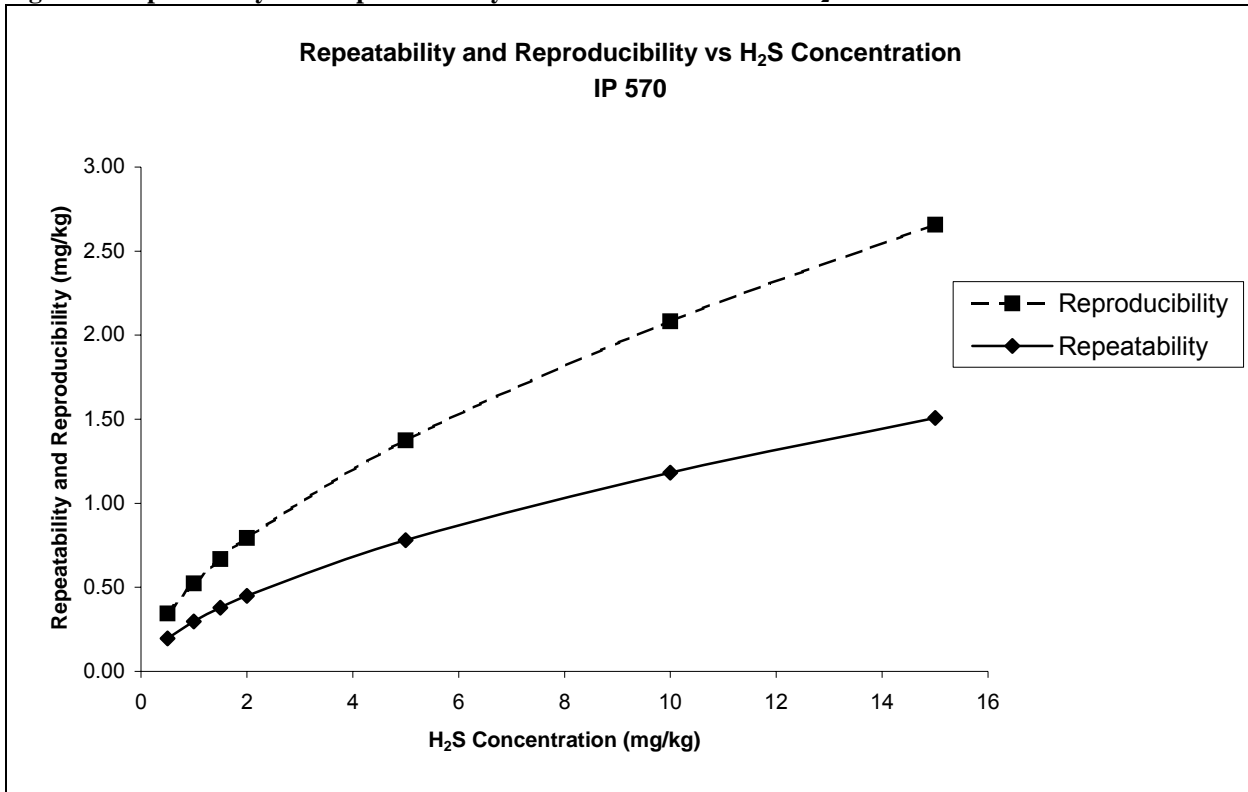
The pooled limit of quantitation limit was found to be 0.41 mg/kg.

These relationships are summarised in Table 3 and Figure 2.

Table 3: Summary of repeatability and reproducibility

H₂S Concentration mg/kg	Calculated Repeatability mg/kg	Calculated Reproducibility mg/kg
0.5	0.20	0.35
1	0.30	0.52
1.5	0.38	0.67
2	0.45	0.79
5	0.78	1.37
10	1.18	2.08
15	1.51	2.66

Figure 2: Repeatability and Reproducibility of IP 570 as a function of H₂S concentration



12 Comparison with IP 399

As a further task the samples that were tested as part of the round robin were subsequently passed onto a third party laboratory for testing to IP 399. The results are illustrated in Figure 2 and a linear best-fit line has been added to show the relationship between the two methods.

The IP 399 result data was an average of two determinations, and the method used cadmium sulfate for the absorbing solution.

The error bars that have been added to the IP 399 data represent $\pm R/(\sqrt{2})$, where R is the reproducibility as published for IP 399/94 (2009).

Finished fuel grades (RFO) are differentiated from blend stock materials (IFO).

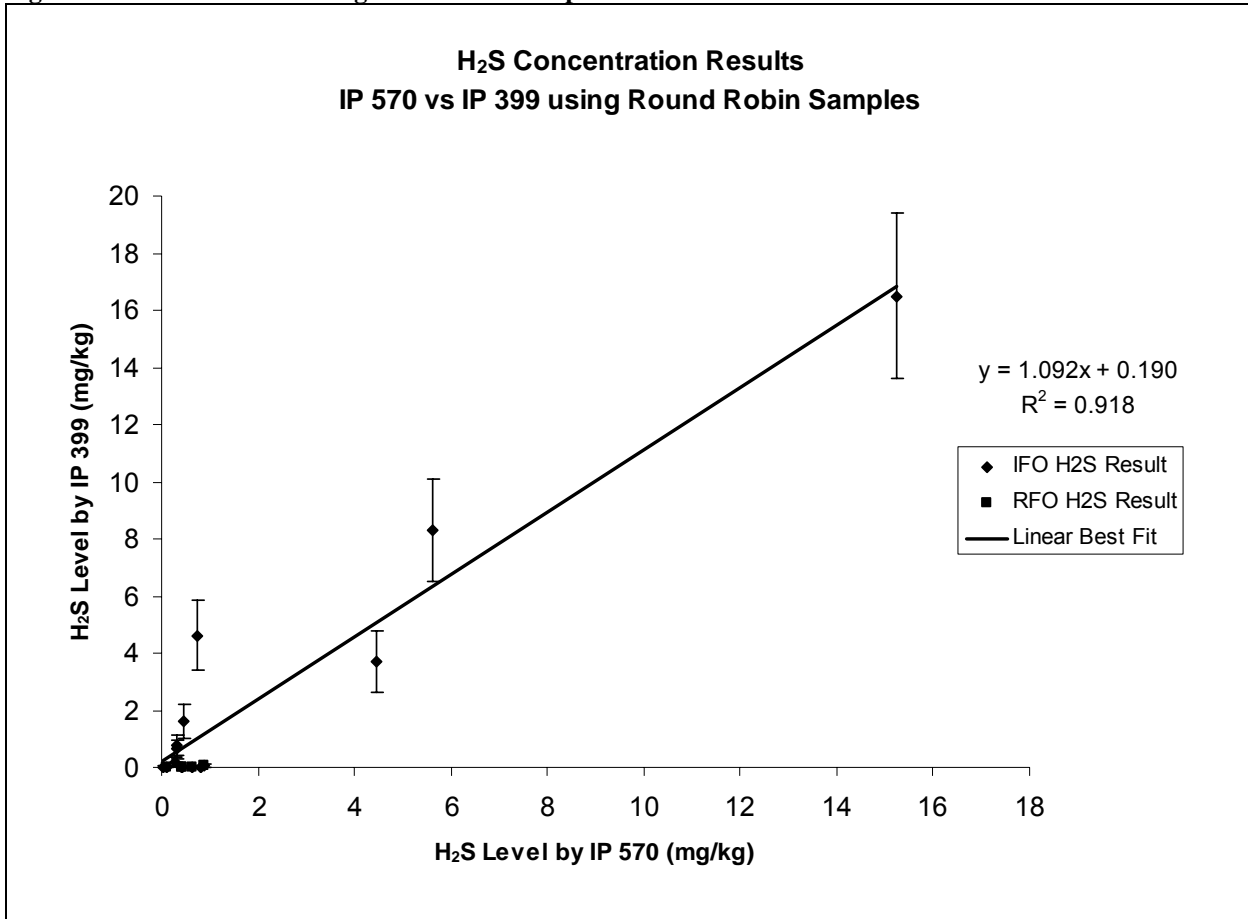
The graph indicates that there is a general agreement between the two methods, but as this is based on a small data set, caution is advised in the wider use of this result.

Repeatability and reproducibility for IP 399/94 (2009) are defined as:

$$\text{Repeatability} = 0.411 \times^{(2/3)} \text{ mg/kg}$$

$$\text{Reproducibility} = 0.627 \times^{(2/3)} \text{ mg/kg}$$

Figure 3: IP 570 vs IP 399 using round robin samples



13 Thanks and acknowledgements

Thanks to the members of the TMS SC-G-5 Working Group and to the participants of the round robin who represented Infineum, Esso Norway, the Energy Institute, Nalco, Statoil Hydro, Kuwait Petroleum, and Shell.

Thanks to ExxonMobil, BP Marine, Total, and Shell for supplying the test samples, and particular thanks to Nalco for the very generous use of their facilities.

Thanks are also due to Lloyd's Register Group FOBAS Service for their continuous support.

Appendix A Test Method used for Round Robin

IP PM DX

09 February 2009

Determination of hydrogen sulfide in fuel oils – Rapid liquid phase extraction method

This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations.

1 Scope

This proposed standard specifies a procedure for the determination of the hydrogen sulfide (H₂S) content of fuel oils such as marine residual fuels, in the range 0 to 50 mg/kg as measured in the liquid phase.

NOTE 1 - The precision of this method is critically dependent on the sampling, thermal history, and handling of the test sample.

NOTE 2 - This standard is not suitable for materials with a viscosity of over 700 mm²s⁻¹ at 50°C. (see 7.4)

WARNING – Safety. Hydrogen sulfide (H₂S) is a very dangerous, toxic, explosive, colourless and transparent gas which can be found in marine residual fuels. Hydrogen sulfide can be formed during the manufacture of the fuel at the refinery or during handling and storage. At very low concentrations the gas has the characteristic smell of rotten eggs. However, at higher concentrations it causes a loss of smell, headaches and dizziness, and at very high concentrations instantaneous death. It is strongly recommended that personnel involved in the testing for hydrogen sulfide are aware of the hazards of vapour-phase H₂S and have in place appropriate processes and procedures to manage the risk of exposure.

2 Normative references

The following normative documents contain provisions, which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below.

IP 475 *Petroleum liquids — Manual sampling.*

3 Principle

A weighed test portion is introduced into a heated test vessel, containing a diluent base oil. Air is bubbled through the oil to extract the H₂S gas. The H₂S is passed, with the air, over a detector to enable the H₂S content of the air to be measured and amount in the liquid phase to be calculated in mg/kg.

4 Reagents and materials

4.1 Diluent oil, proprietary water white API Group 2 base oil with a typical viscosity of 100 mm²/s at 40 °C.

4.2 Verification materials, pressurized nitrogen, of at least 99.999 % (v/v) purity, containing certified levels of H₂S.

5 Apparatus

5.1 General

The apparatus, as detailed in Annex A, comprises an air pump, test vessel, heating jacket, filters, H₂S specific detector, integral computer, automatic solenoid valves, gas flow detectors, a 5ml disposable syringe, and a 1ml positive displacement pipette.

5.2 Analytical balance, single-pan or double-pan balance capable of weighing to the nearest 0.001g.

5.3 Syringe, 20 ml polypropylene disposable type, for introduction of the diluent oil (4.1), accuracy 1%

5.4 Refrigerator (optional), for storing the test sample (see 6.5).

NOTE 3 - The refrigerator should be of a type safe for storing volatile materials.

5.5 Oven/water bath (optional), for warming the sample to 40°C with an accuracy of ± 2°C (see 7.4). The oven shall be of a type suitable for use with volatile materials.

6 Sampling and sample handling

6.1 Unless otherwise agreed, samples shall be taken in accordance with IP 475.

NOTE 4 – ISO TR 13739^[1] describes the practices and procedures used for the transfer of bunker fuels from bunker tanker (barge) to ships, which also includes the procedure for obtaining a representative sample of bunkers delivered to a ship (vessel).

6.2 During sampling operations, care shall be taken to ensure that the integrity of the material is maintained and the possible loss of H₂S is kept to a minimum.

6.3 Draw the sample directly into a suitable clean H₂S inert container, of a minimum of 500ml, such as a dark brown borosilicate bottle or an epoxy lined container fitted with an impervious gas-tight closure. The closure aperture shall allow the drawing of a test portion with the pipette (A.1.1.12).

Epoxy lined containers shall be visually inspected to ensure that the lining has not been damaged and that the containers are not dented.

If a clear glass bottle is used, this shall be placed in the dark as soon as possible after filling.

To ensure sample integrity fill the sample container to approximately 95% full and cap immediately.

NOTE 5 – Lower volume containers may be used, however the precision may be affected.

6.4 If a dedicated H₂S sample cannot be taken, then the H₂S measurement shall be the first test carried out on the sample as any additional handling can lead to loss of H₂S and low results.

6.5 Take the samples to the laboratory as soon as is practicable after sampling (within 24 hours maximum). Test immediately if possible. If samples are not tested immediately, store in a cool place such as a refrigerator (5.4) and analyse within 3 days.

7 Sample preparation

7.1 To minimize the loss of H₂S gas, do not homogenize and avoid shaking the sample before taking a test portion.

7.2 To minimize the loss of H₂S gas, do not transfer the sample to another container.

7.3 The sample needs to be flowing freely enough to allow it to be drawn into the syringe or pipette (5.1)

7.4 A sample that is not free flowing at ambient temperature shall be gently warmed in a water bath or oven (5.5) set at a temperature not exceeding 40 °C.

8 Apparatus preparation

8.1 General

Follow the manufacturer's instructions for the correct set up, verification, calibration and operation of the apparatus.

8.2 Location of apparatus

Use the apparatus under a suitable fume hood and vent the gas exit tube to a suitable extractor as the test will release small amounts of H₂S gas during test portion introduction and during the measurement.

8.3 Filters

8.3.1 The inlet air filter shall be replaced every 3 months, or earlier if discoloured.

8.3.2 Follow the manufacturer's instructions regarding the replacement intervals of the air pump and moisture filters.

8.3.3 Replace the moisture filter if any discolouration is visible.

9 Verification

9.1 Air flow rate

Verify that the air flow rate is $375 \text{ ml/min} \pm 55 \text{ ml/min}$, at least once a year using a suitable flow meter connected to the air input connection. If the flow rate is incorrect, recalibrate the flow (10.1).

9.2 Test vessel heater

Verify that the temperature of the heater is $60.0 \text{ }^\circ\text{C} \pm 1.0 \text{ }^\circ\text{C}$, at least every six months, by inserting a calibrated platinum resistance thermometer into the heater. If the temperature is incorrect, recalibrate the heater temperature (10.2).

9.3 Validation of H₂S detector

Follow the manufacturer's instructions to verify the performance of the detector at least every six months, or when a new detector is fitted, at two concentration levels, using pressurised nitrogen (4.2) containing certified levels of H₂S. If the measurement is not within 10 % of the certified value, replace the moisture filter and check the cleanliness of the liquid trap, test vessel and associated tubing. Purge the system with air for 30 minutes and attempt the verification again. If the measurement is still outside the allowed tolerance, the detector needs recalibration or replacing. This verification is to be undertaken at ambient temperature.

10 Calibration

10.1 Air flow rate

Follow the manufacturer's instructions to calibrate the air flow rate.

10.2 Test vessel heater

Follow the manufacturer's instructions to calibrate the heater temperature.

10.3 H₂S detector Calibration

The detector is factory calibrated to allow for both the static and dynamic response to H₂S. This calibration information is held digitally on the detector assembly and is read directly by the computer in the apparatus. The calibration enables results in mg/kg to be calculated from the test results.

Follow the manufacturer's instructions for installing a new detector and verify the performance immediately afterwards (9.3).

11 Procedure

11.1 On switch on, the H₂S apparatus shall control the test vessel heater to $60.0 \text{ }^\circ\text{C} \pm 1.0 \text{ }^\circ\text{C}$ and purge by pumping air directly to the detector.

11.2 Clean the test vessel and screw cap before each test. The test vessel shall be clean and dry before use. Fit the screw cap tightly.

11.3 Empty and clean the liquid trap if any liquid or discolouration is visible.

NOTE 6 – Toluene, followed by petroleum spirit (60/80), and acetone, and an ultrasonic bath have been shown to be effective in cleaning the test vessel, cap, and liquid trap.

11.4 Remove the screw cap from the test vessel and introduce 20.0 ml ± 0.5 ml of diluent oil (4.1) using the syringe (5.3) and replace the screw cap. Place the test vessel in the temperature controlled heating jacket and fit the input/output tubing.

11.5 Air is pumped through the diluent in the test vessel and to the detector for 5 minutes. This allows the diluent oil to warm up, and the system to be purged.

11.6 Air is then pumped directly to the detector, bypassing the test vessel, to allow the test portion to be introduced without purge air affecting the concentration of the H₂S. Ensure that the instrument is operating in bypass mode before entering sample. Entering sample before this condition is met will likely result in premature loss of H₂S and an erroneously low result. If this is suspected the test must be abandoned and repeated.

11.7 Depending on the expected H₂S concentration, draw the appropriate volume of the sample from at least 3 cm below the sample surface into the 1 ml positive displacement pipette or disposable syringe (A.1.1.12 and A.1.1.13) and weigh to the nearest 0.001 g (5.2). Using the keypad, enter the total test portion mass, which includes the pipette and sample, into the apparatus. The appropriate volume may be determined by reference to table 1 below.

Table 1: Appropriate Test Volume for Expected H₂S Concentration

Expected H ₂ S Concentration	Required Test Volume
0 - 10 mg/kg	5 ml
10 - 20 mg/kg	2 ml
20 mg/kg +	1 ml

NOTE 7 – Estimating the mass of the test portion, using volume and density, could affect the precision and accuracy of the results.

NOTE 8 – By using a smaller volume of sample taken by a suitable positive displacement pipette, it is possible to extend the range of the instrument over 200 mg/kg.

11.8 Introduce the test portion into the test vessel, ensuring that the pipette or syringe is held vertically to avoid sample adhering to the test vessel walls. Ensure that the pipette or syringe does not touch the surface of the diluent liquid. Any pickup of diluent oil onto or into the pipette or syringe will result in the mass of the oil being included in the mass of the empty pipette or syringe (11.7) leading to an erroneously high result. If this is suspected the test must be abandoned and repeated.

11.9 Fit the screw cap tightly.

11.10 Weigh the empty pipette to the nearest 0.001 g (5.2) and using the keypad enter the mass into the apparatus.

11.11 Start the test.

11.12 The detector reading is normalized to zero.

11.13 Air is pumped through the test portion and diluent in the test vessel and to the detector.

11.14 The millivolt readings (mV) from the detector are recorded every second throughout the test until 15 minutes have elapsed. The result is automatically calculated and displayed in mg/kg.

11.15 Air is pumped to purge the detector.

11.16 Remove and clean the test vessel (11.2 and 11.3).

11.17 When the test vessel is removed for cleaning, check that the sample and diluent oil have properly mixed. If two distinct phases exist, check the gas connections and repeat the test.

12 Calculation

$$H_2S = (A \times M)/m \text{ mg/kg} \quad (1)$$

Where:

A = Integrated area of cell output over the test time (mV.s)

M = Calibration constant of the detector (μg)/(mV.s)

m = mass of the sample to be tested (g)

13 Expression of results

Report the H₂S content to the nearest 0.1 mg/kg

14 Precision

14.1 General

The precision, as obtained by statistical examination of laboratory test results according to IP 367^[2] is given in 14.2 and 14.3.

14.2 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on nominally identical test material would, in the normal and correct operation of the test method, exceed the value below only in one case in 20:

To be determined.

14.3 Reproducibility

The difference between two test results independently obtained by different operators using different apparatus on nominally identical test material would, in the normal and correct operation of the test method, exceed the value below only in one case in 20:

To be determined.

15 Test report

The test report shall contain at least the following information:

- a) a reference to this standard;
- b) all details necessary for complete identification of the product tested;
- c) the result of the test (see clause 14);

- d) any deviations, by agreement or otherwise, from the procedures specified;
- e) the time and date of the test.

Annex A
(normative)
H₂S Apparatus

A.1 Apparatus

A.1.1 General

The apparatus, as shown diagrammatically in Figure A.1, is self contained and operates automatically to measure the amount of H₂S in liquid samples of fuel oils.

A.1.1.1 Air pump filter, 5 micron nylon encapsulated, to remove dust from the air.

A.1.1.2 Air pump, capable of supplying air at 375 ml/min ± 55 ml/min. The air is used :

- a) To purge the detector, glassware and tubing
- b) To agitate the test portion and diluent mixture
- c) As a carrier for the extracted H₂S gas

A.1.1.3 Inlet air filter, carbon type to remove moisture and contaminants from the air supply.

A.1.1.4 Solenoid valves, to divert the air supply from the test vessel as required during the normal test sequence and to divert the H₂S gas away from the detector, if high levels of H₂S are measured that could saturate the detector.

A.1.1.5 Flow sensors, electronic sensors incorporated to ensure that the air / H₂S gas mixture reaches the detector, to enable the air flow to be controlled and that any flow problems are detected.

A.1.1.6 Liquid trap, 25 ml borosilicate glass tube with an internal input tube, to trap any liquid or heavy vapours. The top half of the tube shall be loosely filled with glass fibre.

A.1.1.7 Moisture filter, 5 micron nylon encapsulated, to remove moisture from the air / H₂S mixture.

A.1.1.8 Heater jacket, 50 Watt, aluminium block, controlled to 60.0° C ± 1.0° C, with an over temperature cutout.

A.1.1.9 Temperature probe, platinum resistance thermometer to measure and control the heating jacket temperature.

A.1.1.10 Test vessel, 50 ml borosilicate glass tube with an internal input tube for the air supply. This test vessel is heated by the heater jacket. See Figure A.2

A.1.1.11 H₂S detector, electrochemical type specifically for H₂S measurement, range (gas) 0-50 ppm (V/V), repeatability 1%, response time T₉₀ < 30 seconds.

A.1.1.12 Pipette, 1 ml positive displacement pipette, for the introduction of the test portion. The accuracy as stated by the manufacturer should be typically ±0.25 % at 1.000 ml, with a

coefficient of variation of 0.04%. It is recommended that the syringe be of the same type as specified by the equipment manufacturer for optimum system performance.

A.1.1.13 Disposable syringe, typically 5ml, though 10ml is acceptable, for the introduction of the test portion. Typical accuracy 1%. This may be fitted with a needle or extra tube to allow sample to be taken from 3cm below the surface, if appropriate.

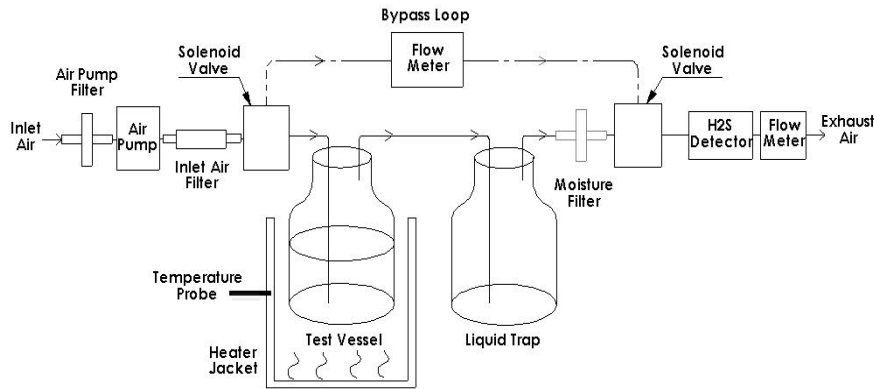


Figure A.1 H₂S apparatus

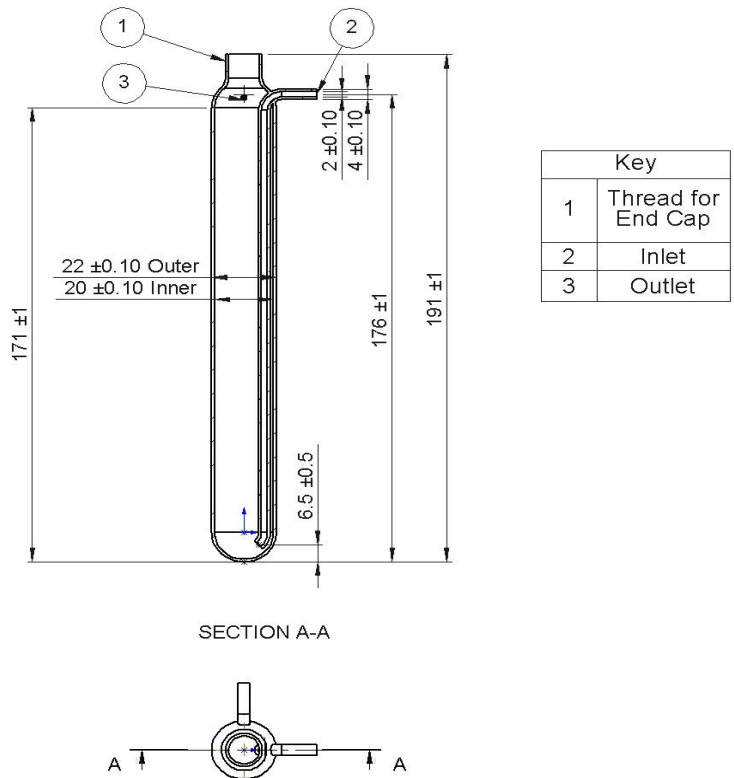


Figure A.2 Test vessel

BIBLIOGRAPHY

[1] ISO TR 13739 Petroleum Products – Procedures for the transfer of bunker fuel(s) to ships

(Currently being revised and converted to a full ISO standard)

[2] IP 367 Petroleum Products – Determination and application of precision data in relation to methods of test.

Annex C
(Informative)
Preliminary Precision

An ST-G-5 robustness trial comprising 3 instruments, 6 operators, and 8 samples in duplicate covering the range 0 – 15 mg/kg was conducted in a single location. The number of laboratories involved in this trial did not meet the minimum requirement of ISO 4259, however the following preliminary estimate of precision was made:

$$\begin{aligned}\text{Repeatability} &= 0.32 (X + 0.43) \text{ mg/kg} \\ \text{Reproducibility} &= 0.34 (X + 0.43) \text{ mg/kg}\end{aligned}$$

where X is the average of the H₂S results

Limit of quantification

Using the above preliminary precision the expected limit of quantitation is approximately 0.9 mg/kg.

Appendix B

Round Robin Protocol

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Round Robin Study – IP PM-DX 08

Determination of hydrogen sulfide in fuel oils – Rapid liquid phase extraction method

TMS SC-G-5 Task Group on Measurement of H₂S in the Liquid Phase

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1 SUMMARY

The objective of this round robin study is to determine the precision of the test method in accordance with ISO4259.

The successful outcome will result in the current draft test method “Determination of hydrogen sulfide in fuel oils – Rapid liquid phase extraction method IP PM DX 08” being balloted to become an IP method.

The study will be carried out at Nalco’s laboratory in Fawley, on the 5th and 6th March 2009 using 7 production instruments and 7 operators plus observers nominated by the Task Group members. 15 samples will be tested in duplicate and the EI statistician will determine the repeatability and reproducibility. The samples will be retained for further analysis by IP 399 which will be undertaken as soon as is practicable after the round robin.

2 INTRODUCTION

The test apparatus has been developed over the last two years and 7 production instruments are being used for this round robin study.

The test requires a weighed 1 ml to 5 ml sample, depending on H₂S concentration, and tests are completed in 15 minutes.

Over 800 tests have been carried out on a wide range of samples from sites around the globe. These include marine fuel and crude oils with H₂S concentrations from 0.1 to 200 mg/kg.

The development would not have been possible without the encouragement and support of Lloyd's Register Group FOBAS Service, Intertek OCA and major refiners.

A new ST-G-5 Task Group on Measurement of H₂S in the Liquid Phase met at the EI and agreed on the draft test method being used for this study.

3 TEST METHOD (attached)

“Determination of hydrogen sulfide in fuel oils– Rapid liquid phase extraction method”

4 SAMPLES

Sample Number	Sample reference	Target H ₂ S value	Notes
1		0	
2		0 to 5	
3		0 to 5	
4		0 to 5	
5		0 to 5	
6		5 to 10	
7		5 to 10	
8		5 to 10	
9		5 to 10	
10		10 to 15	
11		10 to 15	
12		10 to 15	
13		15 to 20	
14		15 to 20	
15		15 to 20	
Practice			

The above table outlines the desired range of H₂S levels for this round robin. This is for information only, as the actual H₂S concentrations will depend on the samples available for the testing.

5 PROTOCOLS – INSTRUCTIONS FOR PARTICIPANTS

5.1 Each operator will be designated an individual apparatus and printer, and be given a copy of the test method and this protocol.

5.2 Operators will be given training before the tests commence.

5.3 Due to the volatility of the H₂S and the need to test the potential of the apparatus and not the sampling, each 1 litre sample will be retained in a single container and will be used by each operator for first and duplicate tests. This will help ensure that each test sample is as identical as possible.

5.4 The sequence of testing will be in a random order and different for each operator.

5.5 Each operator will be given a results sheet that gives the required sequence of testing.

5.6 Testing should be in accordance with the test method, with these following points being of particular importance:

5.6.1 In order to minimise loss of H₂S, do not homogenize and avoid shaking the sample before taking a test portion.

5.6.2 Once a sample has been taken, immediately tightly replace the container seal to prevent the release of further H₂S.

5.6.3 The correct size of sample can be determined by reference to table 1 below:

Table 1: Appropriate Test Volume for Expected H₂S Concentration

Expected H₂S Concentration	Required Test Volume
0 - 10 mg/kg	5 ml
10 - 20 mg/kg	2 ml
20 mg/kg +	1 ml

5.6.4 Ensure that the “Input sample weight in grams” screen is displayed before removing the bubbler vessel cap and introducing the test portion.

5.6.5 When introducing the sample into the test vessel, it is recommended that the operator lift the test vessel proud of the surface. This enables the level of the liquid to be seen which helps prevent the tip of the pipette or syringe touching the diluent oil.

5.6.6 Pipette or syringe the test portion into the test vessel ensuring that the pipette or syringe is held vertically to avoid sample adhering to the test vessel walls.

5.6.7 Once the sample has been entered into the glassware, immediately refit the glassware screw cap tightly to prevent leakage.

6 APPARATUS

The apparatus to be used for the robustness study will be:

No	Instrument	Serial No	Software Issue
L1	STANHOPE-SETA H ₂ S Analyser SA 4000-0	1009083	3.01/2.00
L2	STANHOPE-SETA H ₂ S Analyser SA 4000-0	1009084	3.01/2.00
L3	STANHOPE-SETA H ₂ S Analyser SA 4000-0	1009085	3.01/2.00
L4	STANHOPE-SETA H ₂ S Analyser SA 4000-0	1009086	3.01/2.00
L5	STANHOPE-SETA H ₂ S Analyser SA 4000-0	1009087	3.01/2.00
L6	STANHOPE-SETA H ₂ S Analyser SA 4000-0	1009088	3.01/2.00
L7	STANHOPE-SETA H ₂ S Analyser SA 4000-0	1009092	3.01/2.00

7 RESULTS PROFORMA

IP PM H2S Day 1
Determination of total hydrogen sulfide in fuel oils
Rapid liquid phase extraction method
ST-G-5 Robustness Study

Instrument: Stanhope Seta SA4000-0
Serial Number: 1009083
Software Issue: 3.01/2.00

Instrument number: L1
Operator:
Date:

Sample Numbers	Result mg/kg	Test duration minutes	Area mV.min	Comments
3				
11				
10				
14				
7				
19				
5				
12				
2				
20				
4				
13				
6				
15				
8				
17				
1				
16				
9				
18				

IP PM H2S Day 2
Determination of total hydrogen sulfide in fuel oils
Rapid liquid phase extraction method
ST-G-5 Robustness Study

Instrument: Stanhope Seta SA4000-0 U
Serial Number: 1009083
Software Issue: 3.01/2.00

Instrument number: L1
Operator:
Date:

Sample Numbers	Result mg/kg	Test duration minutes	Area mV.min	Comments
3				
11				
10				
14				
7				
19				
5				
12				
2				
20				

Appendix C
Data analysis

Energy Institute Precision Study

10:35, 12 Mar 2009

PM-DX Determination of H2S in Fuel Oils

Repeatability = $0.2970 * (X + 1.000E-04) ^ 0.6000$ mg/kg
 Reproducibility = $0.5232 * (X + 1.000E-04) ^ 0.6000$ mg/kg

	Initial	Final
Number of laboratories	7	7
Number of samples	15	15
Number of repeats	2	

REGRESSIONS (AFTER OUTLIER TESTS)

TRANSFORMATION TYPE: NONE

Regression	Fitted Variable	Coefficient B	Test B=0	t- Ratio	% Sig.
Unweighted d v. (m+B0)	m + 5.2851E-01	4.3817E-02	B=0	7.40	0.0
Unweighted D v. (m+B0)	m + 1.2131E+00	6.8755E-02	B=0	11.66	0.0
Weighted ln(d,D) v. ln(m+B0) (for Log Transform)	Intercept ln(m + 0.9849) Dummy Dummy * Ln(m+B0)	-3.32883E+00 1.27172E+00 3.16253E-01 -1.34751E-02	 B=1 B=0	 2.26 0.17	 3.3 86.7
Weighted ln(d,D) v. ln(m+B0) (for Power Transform)	Intercept ln(m + 0.0001) Dummy Dummy * Ln(m+B0)	-2.10049E+00 6.02003E-01 3.41708E-01 1.59111E-02	 *B=0 B=0	 10.22 0.40	 0.0 69.2
	Critical t (5%, 26) =			1.96	5.0

* Coefficient used = 0.6000

Transformation: $(X + 0.0001) ^ 0.4000$

COMMENTS:

This report was prepared using D2PP, Version 5.1.13
 from data file PM-DX.xls, D2PP.

DATA MISSING OR REJECTED (Data rejection limit 20%):

LABORATORY	SAMPLE	DUP	TEST
(L2	,S2	,)	Hawkins-cells
(L2	,S4	, 2)	Missing, <, or 0.0
(L3	,S2	, 1)	Missing, <, or 0.0
(L4	,S12	, 2)	Cochran-variances
(L6	,S12	, 2)	Cochran-variances

SAMPLE MEANS AND STANDARD DEVIATIONS
After any outlier rejections

Transform Type: NONE

Sample	No. of Results	Mean	Between Labs			Between Repeats		
			S.D.	DF	R	S.D.	DF	r
*S12	12	.11667E-01	.1483E-01	10	.47E-01	.1483E-01	5	.54E-01
*S10	14	.12143	.6279E-01	7	.21	.2138E-01	7	.71E-01
*S8	14	.29714	.9355E-01	9	.30	.6211E-01	7	.21
*S3	14	.32000	.5100E-01	10	.16	.3723E-01	7	.12
*S5	14	.33071	.7539E-01	12	.23	.6398E-01	7	.21
S13	14	.41071	.1080	6	.37	.1753E-01	7	.59E-01
S11	14	.43500	.1095	7	.37	.3674E-01	7	.12
S7	14	.45429	.7035E-01	6	.24	.1890E-01	7	.63E-01
S14	14	.63429	.1255	6	.43	.1927E-01	7	.64E-01
S4	13	.74000	.1014	7	.34	.3189E-01	6	.11
S15	14	.79929	.1264	6	.44	.2375E-01	7	.79E-01
S9	14	.88643	.1842	6	.64	.4217E-01	7	.14
S6	14	4.4407	.5744	6	2.0	.1410	7	.47
S2	11	6.0627	.6942	9	2.2	.5793	5	2.1
S1	14	15.250	1.005	9	3.2	.6042	7	2.0

* Mean < 10*Between Repeats SD

SAMPLE MEANS AND STANDARD DEVIATIONS
After any outlier rejections

Transform Type: Power

Sample	No. of Results	Mean	Between Labs			Between Repeats		
			S.D.	DF	R	S.D.	DF	r
S12	12	.12345	.1234	10	.39	.1234	5	.45
S10	14	.41957	.8354E-01	7	.28	.3471E-01	7	.12
S8	14	.61058	.6653E-01	9	.21	.3953E-01	7	.13
S3	14	.63238	.3943E-01	10	.12	.2874E-01	7	.96E-01
S5	14	.63883	.5834E-01	11	.18	.4825E-01	7	.16
S13	14	.69567	.7296E-01	6	.25	.1137E-01	7	.38E-01
S11	14	.71226	.7106E-01	7	.24	.2420E-01	7	.81E-01
S7	14	.72757	.4552E-01	6	.16	.1196E-01	7	.40E-01
S14	14	.83004	.6778E-01	6	.23	.1004E-01	7	.34E-01
S4	13	.88483	.4906E-01	7	.16	.1489E-01	6	.52E-01
S15	14	.91192	.5849E-01	6	.20	.1077E-01	7	.36E-01
S9	14	.94849	.8142E-01	6	.28	.1993E-01	7	.67E-01
S6	14	1.8123	.9491E-01	6	.33	.2292E-01	7	.77E-01
S2	11	2.0534	.9311E-01	9	.30	.7797E-01	5	.28
S1	14	2.9724	.7861E-01	9	.25	.4781E-01	7	.16

VARIANCE ANALYSIS

Transform Type: Power

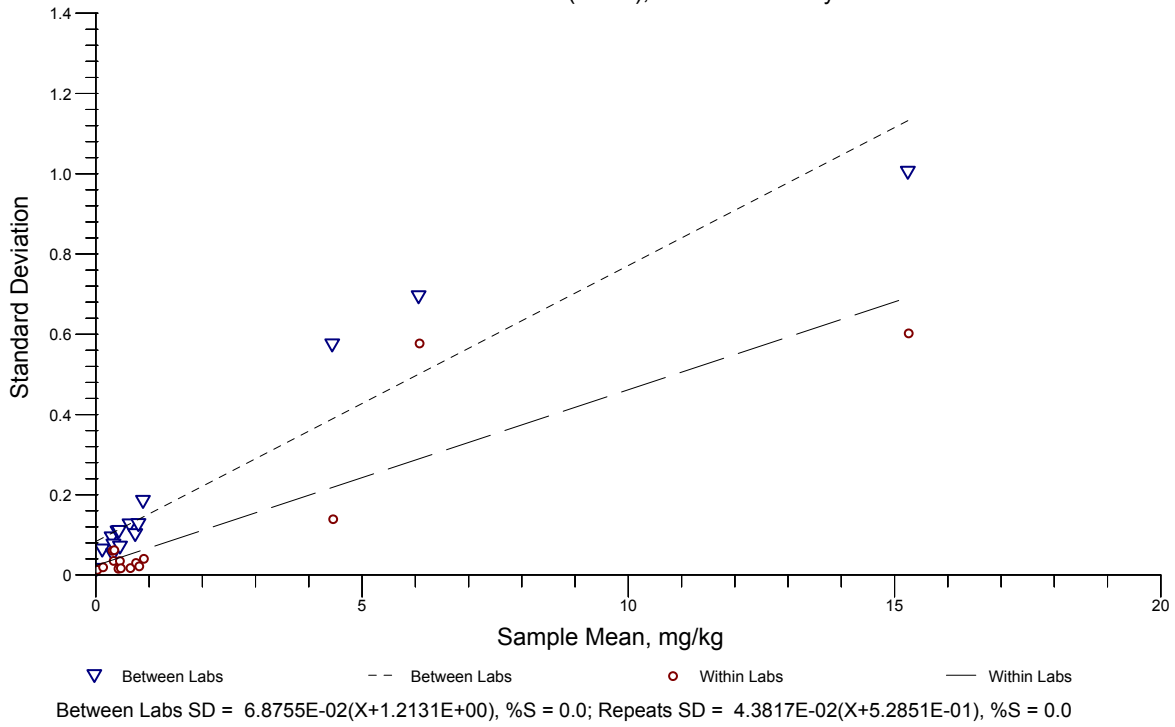
	Sum of squares		DF	Mean square	F
	Estimated	Exact			
Sample Means	1.053052E+02	1.031473E+02			
Lab Means	3.593822E-01	3.576425E-01	6	5.96071E-02	11.241
Interaction Pairs	4.401384E-01	1.039451E+02	83	5.30287E-03	
Repeats	1.793162E-01		100	1.79316E-03	
Total	1.062840E+02				
Critical F (5%, 6, 83) =					2.210

Expectation of Mean Squares

Lab means	1.0388 V(r) + 2 V(I) + 29.6667 V(L)
Interaction	1.0382 V(r) + 2 V(I)
Repeats	1.0000 V(r)

	DF	Variance	Precision
Transformed data			
Repeatability	100	3.586324E-03	1.188E-01
Reproducibility	38	1.068839E-02	2.093E-01

PM-DX Determination of H2S in Fuel Oils
 Current transformation: $Y=(X+B_0)$, $B_0 = 0.0000$. Cycle: 2



PM-DX Determination of H2S in Fuel Oils
 Current transformation: $Y=(X+B_0)^B$, $B_0 = 0.0001$, $1-B = 0.4000$. Cycle: 2

