**This document supports an Energy Institute Standard. It is a record of the robustness trial study from which the precision of the test method was derived. It is available on request for study, however if the information in this document is intended to be used as part of a new document or presentation, the approval of the Standardization (ST) Committee Secretariat of the Energy Institute is required.**

# Marine Distillate Fuels

# Research Report – IP 570

Issue 2

## Determination of Hydrogen Sulfide in Fuel Oils – Rapid Liquid Phase Extraction Method

**SC-G-5**

**Author: Ian Mylrea, Chair EI SC-G-5 $H_2S$ Task Group**

**Dated 15th September 2011**

**Following feedback on the first statistical evaluation of the precision, regarding r being larger than R, the ASTM D6259 Pooled Limit of Quantitation criteria not being met for all samples, as well as discussion with colleagues at the ASTM meeting in Baltimore, June 2011, another approach has been adopted, and has been agreed by both Energy Institute and ASTM statisticians, to compensate for the loss in Hydrogen Sulfide due to the increase in headspace of the bottles during the day**

## Round Robin Study Report Summary

A round robin was held using ten $H_2S$ Analyser Instruments and eight samples in duplicate, to produce the repeatability and reproducibility of the test method. The samples used were distillate fuel oils and components. Values of measured $H_2S$ concentration varied from 0.40 to 9.70 mg/kg.

The resulting calculated expressions of repeatability and reproducibility (valid from 0.40 to 9.70 mg/kg) were as follows:

$$\text{Repeatability} = 0.2099x^{0.7} \text{ mg/kg}$$

$$\text{Reproducibility} = 0.2389x^{0.7} \text{ mg/kg}$$

The round robin results have shown that IP 570 is suitable for measuring very low levels of $H_2S$ (down to 0.4 mg/kg according to the 2R rule and the pooled limit of quantitation) in the liquid phase. It is therefore recommended that the method be balloted with the inclusion of this new precision for approval with this Research Report.

## Introduction

Energy Institute Test Method IP 570 was developed in response to demand from industry for a quick and reliable test to determine the level of hydrogen sulfide present in the liquid phase in fuel oils.

IP 570 was first published in 2009 following an Energy Institute Round Robin in March 2009. Distillate fuels were omitted from the round robin due to there not being any suitable test specimens with $H_2S$ present. Although it is unusual to get $H_2S$ in distillate fuels it is not unprecedented and occurrences have been reported.

The information contained herein represents the finding of an Energy Institute round robin held at the Nalco Laboratory, Fawley, UK, on the 20th April, 2011. The trial compared the performance of 10 instruments testing 8 samples in duplicate and in a random order. In total 10 operators took part and a number of independent observers were present.

The purpose of the round robin was to update the current test method IP 570 “Determination of hydrogen sulfide in fuel oils – Rapid liquid phase extraction method” to include precision for marine distillate fuels.

## 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 for Marine Distillate Fuels as per ISO 8217.

## Test Method

The test method used for this study was titled IP 570 “Determination of hydrogen sulfide in fuel oils – Rapid liquid phase extraction method” and is attached as Appendix B.

**List of Participating Laboratories and Operators**

Owing to the unstable nature of $H_2S$ in marine fuels, all testing was done at a single site in one day. The laboratory used in this study was at Nalco Ltd, Block 102 Cadland Road, Hardley, Southampton SO41 8FU. The contact names for the responsible person(s) were Ron Sharpe & Simon Crozier. The following people took part in the round robin.

| Name | Company |
|---|---|
| Serge Esson | Total France |
| David Browbank | Lintec |
| Sydney Crooks | SGS Belfast |
| Steve Aylieff | SGS West Thurrock |
| Kranthi Nandyala | Saybolt/ Core Labs |
| Gary Ogborn | ITS West Thurrock |
| Anna Prendergast. | ITS West Thurrock |
| Willie Schermer | Shell |
| Bert Decelle | ExxonMobil |
| Patrik Jernberg | Preem AB |

The following people were independent observers at the round robin

| Name | Company |
|---|---|
| Jim Crighton | Energy Institute |
| Alister Jackson | ExxonMobil |
| Keith Forget | Consultant to DnVPS |
| Peter Stanley | ConnocoPhillips |
| Harry Read | BP International |

**Test Specimens**

| Sample ID | Value (mg/kg) | Material | Bottle ID | | |
|---|---|---|---|---|---|
| RR014 | 0.62 | DMB (95%) | 1 | 12 | Morning |
| RR004 | 1.07 | Component Gas Oil | 13 | 7 | |
| RR001 | 2.20 | Component Gas Oil | 11 | 2 | |
| RR015 | 2.76 | F76 | 9 | 8 | |
| RR008 | 4.79 | F76 | 4 | 3 | Afternoon |
| RR012 | 5.07 | DMA | 16 | 10 | |
| RR009 | 8.62 | F76 | 15 | 6 | |
| RR013 | 9.11 | F76/DMA 50/50 Blend | 5 | 14 | |

Table 1

During the round robin the Bottle ID was used as the identifier for the sample. Each bottle was provided with a label which showed the Bottle ID only, in order that the samples were not identifiable to the round robin participants. Two bottles of each sample were provided. Participants therefore shared the same bottle.

Table 1 above describes the samples used in the round robin. The Component Gas Oil samples were samples from a refiner which contained Hydrogen Sulfide. Due to the difficulty in obtaining

samples which contain Hydrogen Sulfide, the remaining samples were purged with Hydrogen Sulfide in order to create a range of concentrations.

In order to minimise the possibility of the concentration of $H_2S$ altering significantly over the test period, the samples were divide up into two groups to ensure that the duplicate test result was obtained within a maximum of 4 hours of the first test result. One group was tested in the morning and one group was tested in the afternoon. In the morning samples RR014, RR004, RR001 and RR015 were tested in duplicate and in a random order. The duplicate was also in a random order and did not necessarily follow the first sample. In the afternoon RR008, RR012, RR009 and RR013 were tested in the same manner as the morning samples. No samples were tested on more than one day and no samples were tested in the morning and afternoon.

**Round Robin Protocol**

See Appendix A

**Apparatus**

Ten $H_2S$ Analyser Instruments were used for testing. As part of the instrument apparatus, 10ml disposable syringes were supplied and fitted with a needle with leur fitting. These were used for taking the fuel sample, the length of tubing ensuring that the sample could be taken from below the surface of the sample, and so better represent the bulk material. The size of the sample taken was 5ml. Although the sample size does depend on the $H_2S$ concentration of the sample as per the table in section 11.7 of the method, the samples were all less than 10.0 mg/kg.

**Software**

The instruments used utilised software versions 4.02/2.00

**Data**

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

| Instrument Serial Number | Repeat | RR014 | RR004 | RR001 | RR015 | RR008 | RR012 | RR009 | RR013 |
|---|---|---|---|---|---|---|---|---|---|
| 1018039 | 1 | 0.4 | 0.85 | 1.79 | 1.95 | 4.25 | 4.56 | 6.74 | 9.37 |
| | 2 | 0.39 | 0.90 | 1.42 | 1.89 | 4.32 | 4.35 | 8.2 | 8.28 |
| 1017987 | 1 | 0.41 | 0.95 | 1.65 | 1.68 | 4.3 | 5.02 | 7.62 | 6.48 |
| | 2 | 0.38 | 0.92 | 1.63 | -999.9 | 4.04 | 4.24 | 7.82 | 6.66 |
| 1018040 | 1 | 0.39 | 0.58 | 1.13 | 2.11 | 4.4 | 4.52 | 6.29 | 8.46 |
| | 2 | 0.39 | 0.91 | -999.9 | 1.19 | 4.34 | 4.87 | 7.3 | 6.16 |
| 1017988 | 1 | 0.41 | 0.85 | 1.27 | 1.99 | 4.35 | 3.76 | 6.99 | 7.29 |
| | 2 | 0.38 | 0.93 | 1.64 | 1.96 | 3.4 | 3.91 | 8.33 | 8.23 |
| 1018044 | 1 | 0.4 | 0.89 | 1.6 | 1.62 | 4.03 | 4.96 | 7.04 | 8.53 |
| | 2 | 0.37 | 0.79 | 1.72 | 2.05 | 4.05 | 3.28 | 7.53 | 7 |
| 1017990 | 1 | 0.37 | 0.73 | 1.34 | 1.86 | 3.83 | 3.67 | 7.19 | 8.14 |
| | 2 | 0.35 | 0.87 | 1.38 | 1.76 | 2.98 | 4.51 | 6.08 | 7.35 |
| 1018043 | 1 | 0.42 | 0.93 | 1.6 | 1.88 | 4.38 | 5.11 | 8.59 | 7.98 |
| | 2 | 0.41 | 0.78 | 1.79 | 1.83 | 3.68 | 3.94 | 6.19 | 9.56 |
| 1017989 | 1 | 0.38 | 0.82 | 1.57 | 1.84 | 3.49 | 4.29 | 8.38 | 7.79 |
| | 2 | 0.42 | 0.92 | 1.78 | 2.15 | 3.41 | 5.04 | 7.42 | 9.01 |
| 1018041 | 1 | 0.44 | 0.79 | 1.38 | 2.07 | 3.81 | 3.93 | 7.76 | 5.76 |
| | 2 | 0.43 | 0.76 | 1.46 | 1.84 | 4.13 | 3.9 | 8.26 | 9.16 |
| 1018042 | 1 | 0.31 | 0.87 | 1.21 | 1.77 | 4.09 | 4.7 | 5.96 | 9.02 |
| | 2 | 0.33 | 0.72 | 1.63 | 1.5 | 3.53 | 4.53 | 8.09 | 7.39 |

Table 2

Repeats 1 and 2 are the first and repeat results. All results are in mg/kg.

The two results recorded as -999.9, 1018040, RR001, Repeat 2, and 1017987, RR015, Repeat 2, were not obtained due to the operator disturbing the test vessel during the test. The apparatus is programmed to halt the test in this case and so the test was stopped prematurely. In both cases the analyser reported “no test vessel” and did not display a test result.

The data was analysed according to ISO 4259 (IP 367) using the ASTM D2PP software package to generate values for repeatability and reproducibility. This analysis highlighted two features of the data: the calculated repeatability was higher than the reproducibility; the mean result was less than the pooled limit of quantitation for six out of eight samples. These features can be accounted for by the degradation of the samples due to the increase of headspace after each measurement. Further information can be found in the Discussion Section.

The data was compensated for degradation, by working out the average rate of loss per 5ml sample taken. The data can be found in Table 3.

| Instrument Serial Number | Repeat | RR014 | RR004 | RR001 | RR015 | RR008 | RR012 | RR009 | RR013 |
|---|---|---|---|---|---|---|---|---|---|
| 1017987 | 1 | 0.40 | 0.98 | 1.98 | 2.12 | 4.67 | 5.23 | 8.86 | 9.60 |
| 1017987 | 2 | 0.37 | 0.99 | 1.75 | -999.9 | 4.30 | 5.18 | 8.66 | 9.78 |
| 1017988 | 1 | 0.41 | 0.98 | 1.94 | 1.96 | 4.35 | 4.57 | 8.59 | 9.24 |
| 1017988 | 2 | 0.37 | 0.91 | 1.72 | 2.15 | 4.54 | 5.24 | 8.56 | 9.01 |
| 1017989 | 1 | 0.37 | 0.95 | 2.03 | 2.42 | 4.42 | 5.04 | 8.99 | 10.5 |
| 1017989 | 2 | 0.41 | 0.91 | 1.57 | 2.22 | 4.50 | 5.28 | 8.64 | 10.2 |
| 1017990 | 1 | 0.37 | 0.87 | 1.83 | 1.97 | 4.12 | 4.67 | 8.17 | 8.92 |
| 1017990 | 2 | 0.34 | 0.85 | 1.59 | 2.03 | 4.33 | 4.82 | 7.71 | 9.30 |
| 1018039 | 1 | 0.40 | 0.91 | 1.42 | 2.11 | 4.57 | 5.17 | 8.98 | 9.37 |
| 1018039 | 2 | 0.38 | 0.93 | 2.09 | 2.22 | 4.50 | 5.22 | 8.57 | 9.84 |
| 1018040 | 1 | 0.38 | 0.95 | -999.9 | 1.57 | 4.53 | 5.20 | 9.13 | 10.0 |
| 1018040 | 2 | 0.39 | 0.63 | 1.33 | 2.11 | 4.47 | 5.34 | 8.38 | 9.67 |
| 1018041 | 1 | 0.43 | 0.86 | 1.86 | 2.06 | 4.63 | 5.05 | 8.26 | 9.27 |
| 1018041 | 2 | 0.43 | 0.89 | 1.73 | 2.18 | 4.69 | 5.25 | 8.54 | 9.55 |
| 1018042 | 1 | 0.31 | 0.80 | 1.83 | 1.99 | 4.29 | 5.02 | 8.61 | 9.41 |
| 1018042 | 2 | 0.33 | 0.87 | 1.61 | 1.99 | 4.47 | 5.19 | 8.31 | 9.73 |
| 1018043 | 1 | 0.41 | 0.90 | 1.89 | 2.16 | 4.56 | 5.26 | 8.54 | 10.3 |
| 1018043 | 2 | 0.40 | 0.94 | 1.75 | 2.32 | 5.01 | 5.44 | 8.59 | 9.56 |
| 1018044 | 1 | 0.39 | 0.88 | 1.87 | 2.10 | 4.43 | 4.76 | 8.84 | 9.70 |
| 1018044 | 2 | 0.37 | 0.92 | 1.65 | 2.11 | 4.79 | 4.96 | 8.35 | 9.73 |

TABLE 3

**Statistical Evaluation on the Data**

The data in Table 3 was analysed according to ISO 4259 (IP 367) using the D2PP software package to generate values for repeatability and reproducibility. Full details of data used and the D2PP report can be found in Appendix C.

The repeatability and reproducibility were found to be:

Repeatability = $0.2099x^{0.7}$ mg/kg (DF 77)

Reproducibility = $0.2389x^{0.7}$ mg/kg (DF 136)

These relationships are summarised in

| H2S Concentration (mg/kg) | Repeatability (mg/kg) | Reproducibility (mg/kg) |
|---|---|---|
| 0.40 | 0.11 | 0.13 |
| 1.00 | 0.21 | 0.24 |
| 1.50 | 0.28 | 0.32 |
| 2.00 | 0.34 | 0.39 |
| 5.00 | 0.65 | 0.74 |
| 9.70 | 1.03 | 1.17 |

TABLE 4

and Figure 1:

| H2S Concentration (mg/kg) | Repeatability (mg/kg) | Reproducibility (mg/kg) |
|---|---|---|
| 0.40 | 0.11 | 0.13 |
| 1.00 | 0.21 | 0.24 |
| 1.50 | 0.28 | 0.32 |
| 2.00 | 0.34 | 0.39 |
| 5.00 | 0.65 | 0.74 |
| 9.70 | 1.03 | 1.17 |

TABLE 4

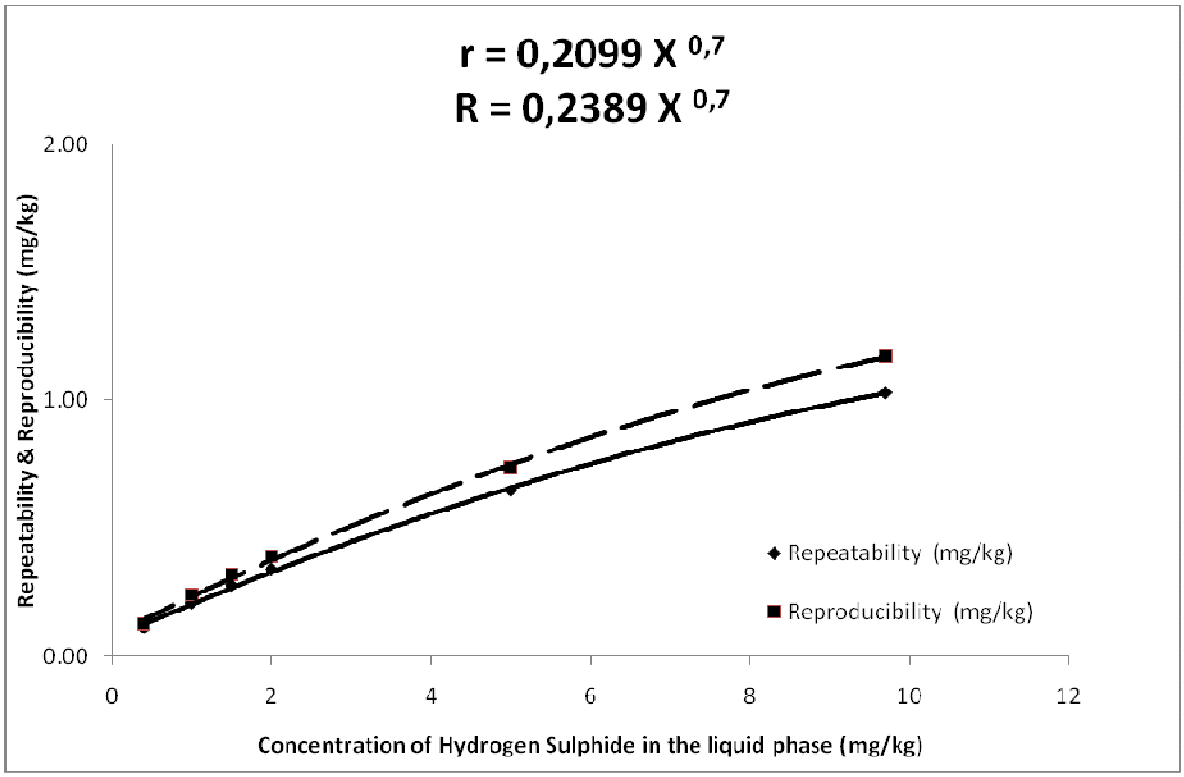


Figure 1 Repeatability and Reproducibility for distillate fuels

## Discussion

As previously found with residual fuels, excessive variability, according to the concept of Limit of Quantitation (LOQ) which compares the ratio of the mean levels with ten times the standard deviation of repeat tests, was found for six of the eight samples. There is sufficient evidence to suggest that a significant contributor to this variation was due to sample degradation due to the repeated opening and closing of the sample containers during the round robin.

In this case what is meant by sample degradation or decay is where the Hydrogen Sulfide which is normally in the liquid phase at a particular concentration is gradually lost, lowering the concentration which IP 570 measures. Data plotted for one of the round robin samples is shown below in Figure 2.

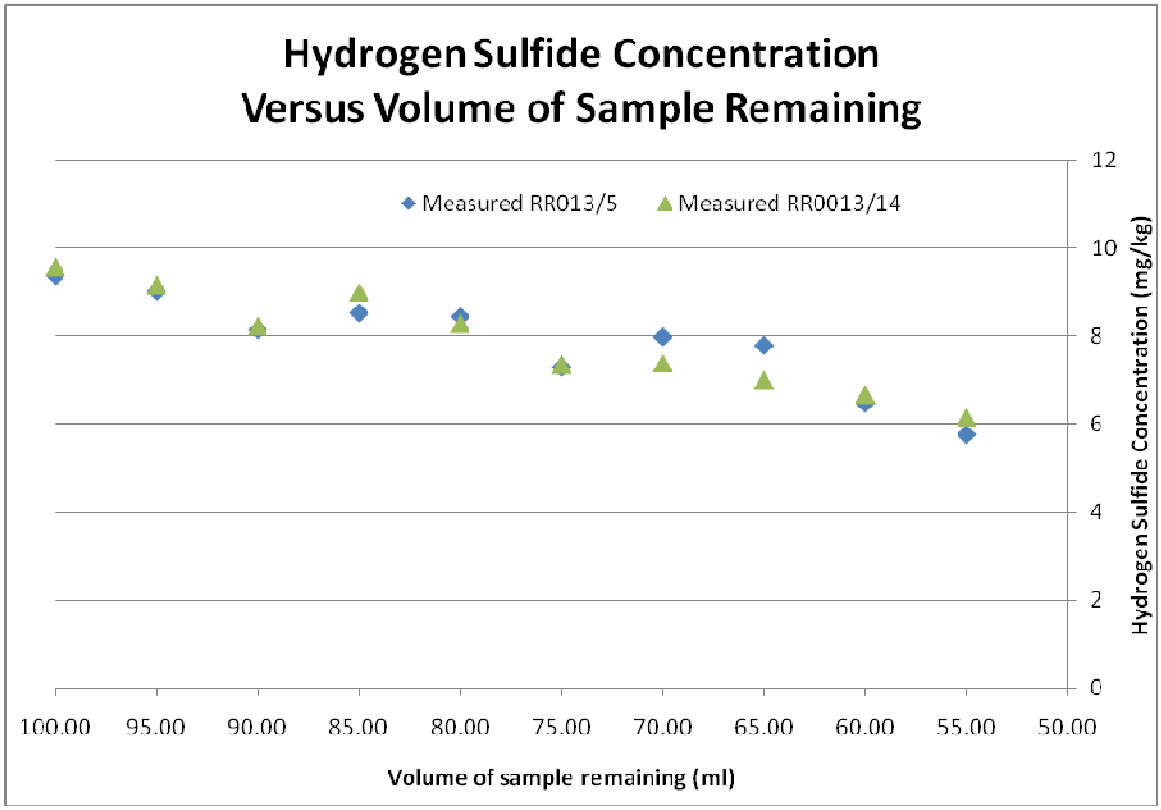


FIGURE 2

Extensive research into this area was carried out prior to the round robin. Tests were run to determine the rate of loss of Hydrogen Sulfide in different situations. Prior to the round robin, the sample RR001 was bottled into several bottles at the same time. Two bottles were tested in the round robin. Three other bottles were tested on different dates. Another bottle was tested several times in one day.

**Loss of $H_2S$ over time when bottles are unopened**

Measurements were made on three bottles which were not opened until tested (Figure 3). The sample maintained its concentration within the requirements for LOQ over a period of a few weeks.

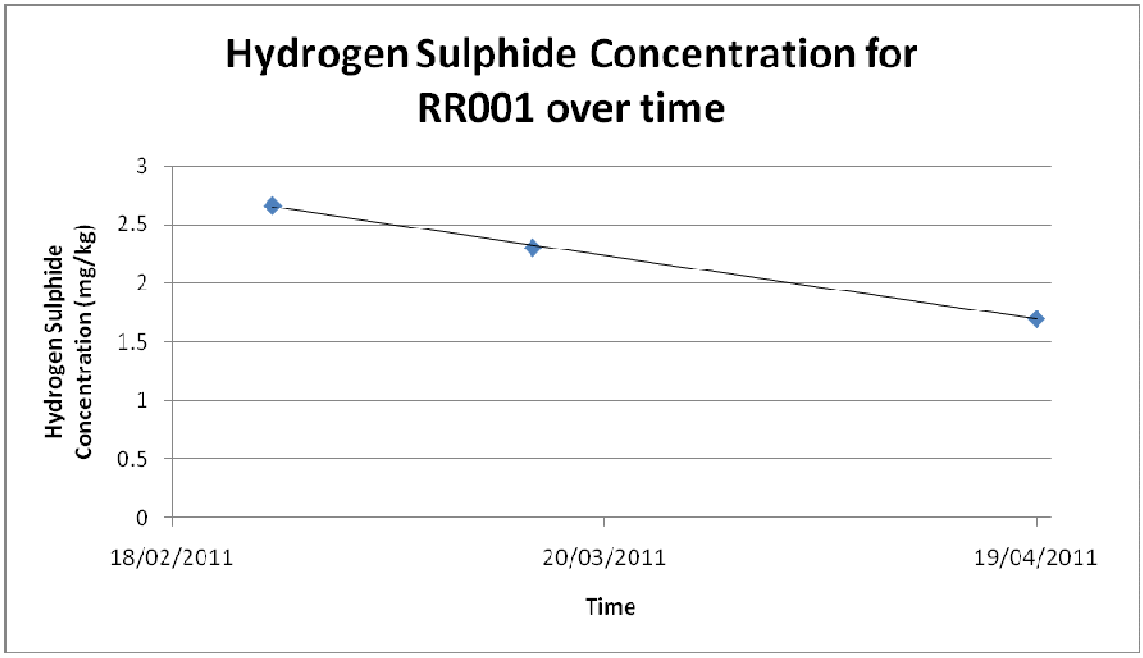


Figure 3

The rate of decay is 0.13 mg/kg per week. It is estimated that if measurements were made once per week on a fresh bottle then it would take six weeks before the LOQ test would fail as Table 5 demonstrates (LOQ reaches 2.4 by Week 6). The source of this 'ageing' degradation in this example is not known. Possible mechanisms include oxidation, permeation through the bottle enclosure or reaction with another component in the sample.

| Week | mg/kg |
|---|---|
| 1 | 2.60 |
| 2 | 2.47 |
| 3 | 2.35 |
| 4 | 2.22 |
| 5 | 2.09 |
| 6 | 1.97 |
| | |
| SD | 0.24 |
| Average | 2.3 |
| 10 x SD | 2.4 |

TABLE 5

It is worth noting that the rate of decay shown is far slower than experienced during the round robin in a single day.

**Loss of $H_2S$ when bottles are opened multiple times**

Another test was run on a single bottle (Figure 4), to mimic the conditions of the round robin. In this case a single instrument was used to measure the same bottle multiple times. That is the cap of the bottle was opened several times to take a sample.

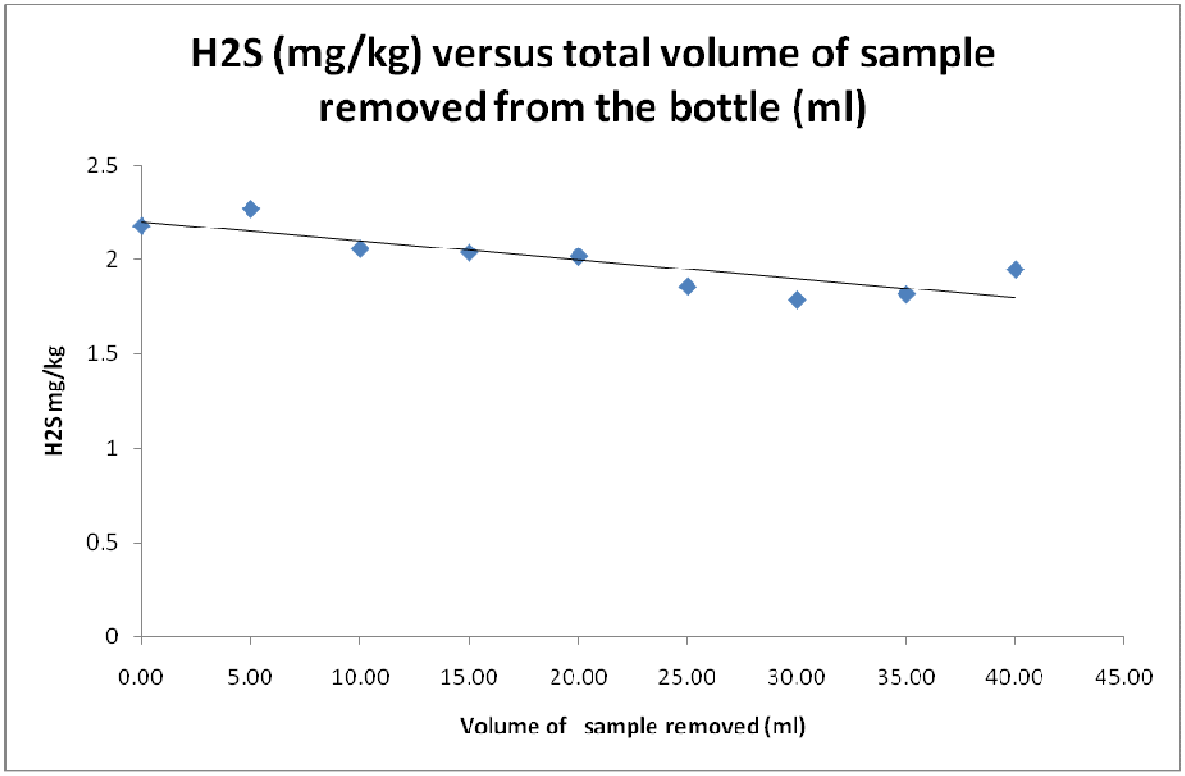


Figure 4

The rate of decay is 0.03 mg/kg per 5ml sample removed. After 4 x 5ml aliquots have been removed the amount of decay is similar to one week of degradation due to ageing.

During the round robin the rate of decay was higher for more concentrated samples, for example see Figure 2, where the average rate of decay was 0.40 mg/kg per 5ml sample removed.

The action of opening the bottle and removing some sample accelerates the loss of hydrogen sulfide.

Hydrogen Sulfide is a volatile gas at room temperature with an extremely high vapor pressure. Opening of the lid of the sample container and releasing the pressure in the bottle disturbs the equilibrium between the liquid and vapour phases and allows more Hydrogen Sulfide to emanate from the liquid.

**Determination of LOQ by ASTM D6259**

As further evidence to this theory and following the round robin, ASTM D6259 was carried out on three samples using a single analyser to determine the limit of quantitation (LOQ). See Figure 5.

To avoid the decay of Hydrogen Sulfide due to the opening and closing of the bottle when the sample bottle was opened for the first time a number of syringes were filled, enough for 7 or 8 tests. For each test only part of the syringe was used. The remaining sample in the syringe was not exposed to the air and did not have a headspace or ullage above the sample. Using this procedure the loss of Hydrogen Sulfide was not noticeable, as shown in Figure 5.

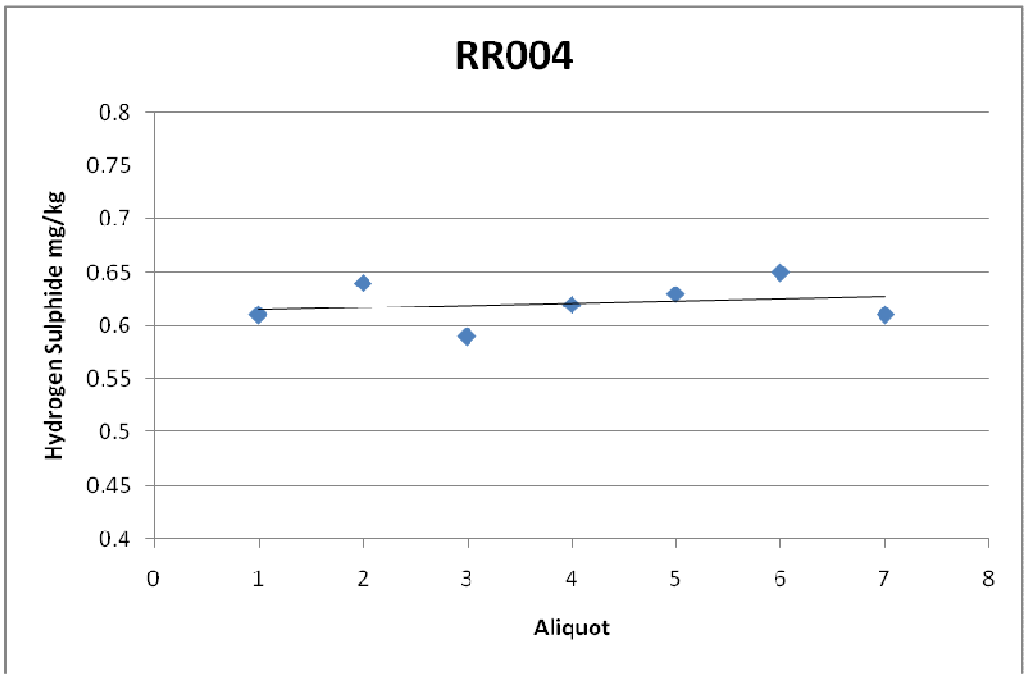


Figure 5

A summary of the results from the LOQ study are shown in Table 6. Values stated are in mg/kg.

| SAMPLE | MEAN | STANDARD DEVIATION | RATIO MEAN/ STANDARD DEVIATION |
|---|---|---|---|
| DILUENT | 0.02 | 0.02 | 1 |
| RR014 | 0.22 | 0.016 | 13 |
| RR004 | 0.62 | 0.020 | 31 |

TABLE 6

According to the principle outlined in ASTM D6259, Standard Practice for a Pooled Limit of Quantitation, the LOQ (Limit of Quantitation) for distillate fuels is 0.22 mg/kg.

Another approach used is to apply the so called 2R rule. That is as long as the value being measured is more than 2R then the methodology is applicable at that value. At 0.4 mg/kg, 2R is 0.26 mg/kg and so the rule applies and the methodology is suitable at that value.

The specification limit for Hydrogen Sulfide set by ISO 8217 is 2 mg/kg. The reproducibility at 2 mg/kg is 0.39 mg/kg, and 2R is 0.78 mg/kg and so the rule applies and the methodology is suitable at that value.

Thanks and acknowledgements

Members of the Working Group and to the participants of the round robin

Royal Navy, ExxonMobil, Qinetiq, Total and Shell for supplying the test samples

Particular thanks to Nalco for the very generous use of their facilities

Nigel Elliot (ExxonMobil), Harry Read (BP International), Simon Crozier (Nalco) and Ron Sharpe (Nalco) for the assistance in planning and executing the round robin on schedule

Appendix A

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ROUND ROBIN STUDY – IP 570

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

**SC-G-5 Task Group on Measurement of $H_2S$ in the Liquid Phase**

**Ian Mylrea**

**Task Group Chair**

**Stanhope-Seta**

**ISSUE 1.0**

Dear EI TMS G-5 Panel H2S Task Group member,

As I am sure you aware that all our EI Panel activity in the EI TMS committees and panels is carried out on the understanding that the meetings discussions and shared documents are for Panel use only and are not to be shared outside that EI Panel membership, with the exception that within your organisation technical additional input can be shared/ supplied to enhance the method development.

Please observe this protocol of maintaining the activity/discussions involving EI Interlaboratory Studies (i.e. Robustness Studies & Round Robins), any data/observations derived from these studies are also deemed to be only for discussion within the EI Panel group activity (our Task Group), until the final agreement and release of any Official EI TMS Panel reports that have been approved by the EI Panel Membership, EI Subcommittee Chair and EI TMS for public release and discussion.

## 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 test method IP 570 “Determination of hydrogen sulfide in fuel oils – Rapid liquid phase extraction method” being balloted to add precision for marine distillate fuels.

The study will be carried out at Nalco’s laboratory in Fawley, on the 20th April 2011 using 10 production instruments and 10 operators plus observers nominated by the Task Group members. 8 samples will be tested in duplicate and the EI statistician will determine the repeatability and reproducibility.

## 2 INTRODUCTION

The test apparatus is already used by industry to measure residual marine fuels, for which precision data was obtained in 2009. This round robin is required to add precision data for distillate fuels.

ISO 8217:2010 requires the liquid phase Hydrogen Sulfide level to be determined according to this method. There is a phased entry for this part of the specification to enable industry to prepare itself for the limit of 2 mg/kg. The limit comes into force in July 2012.

10 production instruments are being used for this round robin study.

The test requires a weighed 1 ml to 5 ml sample, depending on $H_2S$ concentration, and tests are completed in 15 minutes.

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

The SC-G-5 Task Group on Measurement of $H_2S$ 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

| Value (mg/kg) | Fuel Grade Types |
|---|---|
| 0 to 1.00 | DMB (95%) |
| 0 to 1.00 | Component Gas Oil |
| 1.00 to 5.00 | Component Gas Oil |
| 1.00 to 5.00 | F76 |
| 1.00 to 5.00 | F76 |
| 5.00 to 10.00 | DMA |
| 5.00 to 10.00 | F76 |
| 5.00 to 10.00 | F76/DMA 50/50 Blend |

The above table outlines the desired range of $H_2S$ levels for this round robin. This is for information only, as the actual $H_2S$ concentrations will depend on the samples available for the testing on the day of the study.

## 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 $H_2S$ and the need to test the potential of the apparatus and not the sampling, samples are provided in 100ml containers. For each sample there are 4 containers. 2 containers are provided as spares and 2 containers, numbered randomly, provide the first and duplicate tests. The four containers were bottled, with minimum headspace, simultaneously to ensure homogeneity. Tests were run in order to validate this.

**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 $H_2S$, 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 $H_2S$.

**5.6.3** The correct size of sample is 5ml FOR ALL SAMPLES and can be determined by reference to table 1 below:

**Table 1: Appropriate Test Volume for Expected $H_2S$ Concentration**

| Expected $H_2S$ 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 sample 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 equipment or vessel glassware, immediately refit the glassware screw cap tightly to prevent leakage.

## Summary Guide to follow and run samples

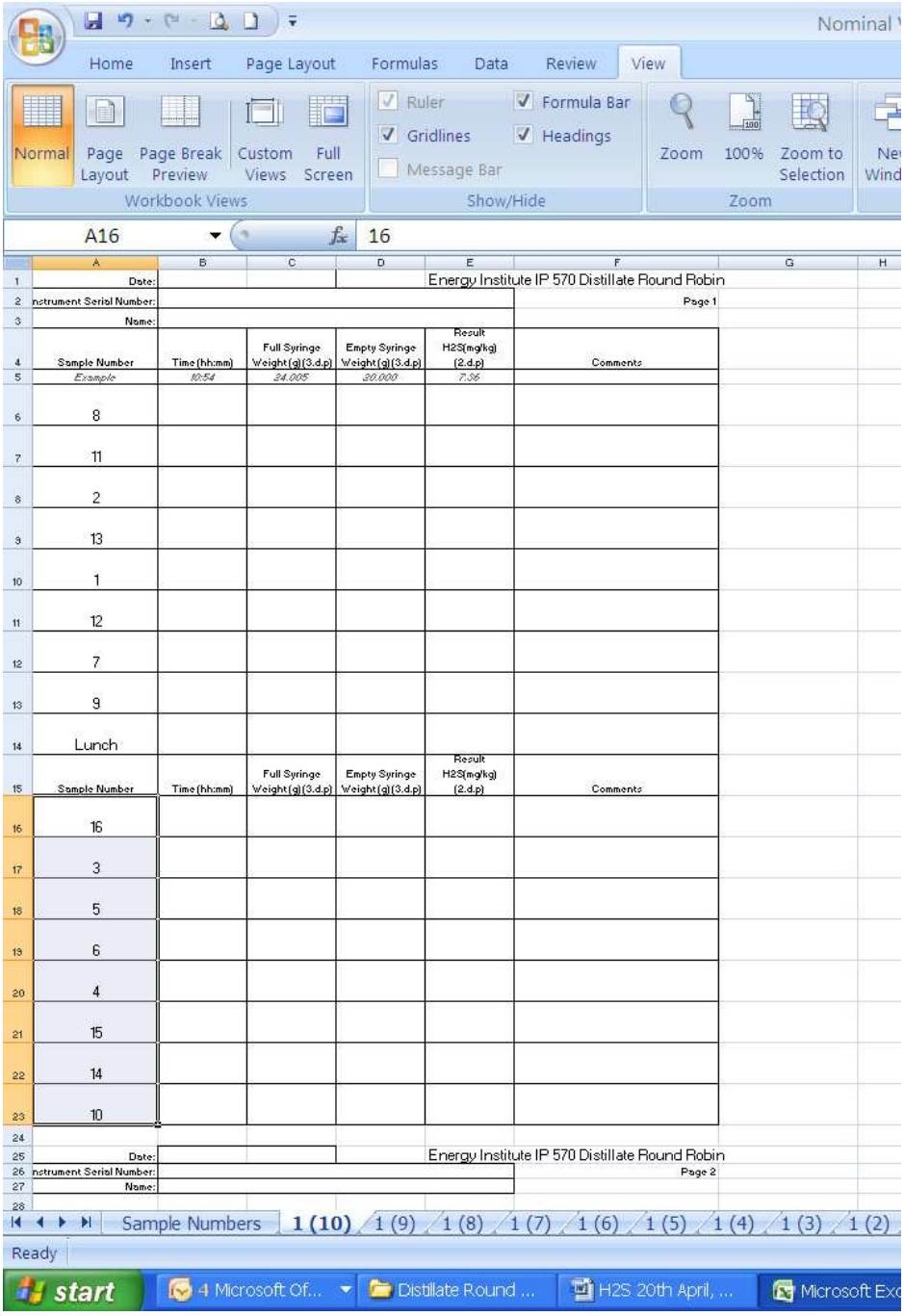
1. Using a 20ml syringe put 20ml diluent oil into a clean test vessel
2. Place the vessel in the apparatus
3. Set the mode of the apparatus to enable bubbling
4. Wait for 5 minutes to allow diluent to warm up before obtaining the sample
5. Type in the Sample ID
6. Type in the Operator ID
7. Go to the Samples….
    a. choose the correct bottle number.
    b. Obtain the **5ml sample** using a clean 10ml syringe fitted with a Leur type needle.
    c. Draw the sample into the syringe slowly and carfeully to avoid exposing the sample to a strong vacuum.
    d. Take 10 to 20 seconds to draw the sample in for example. Draw the sample to the 5ml mark and no higher.
    e. Make sure the sample needle is at least 3cm below the liquid surface of the sample container (i.e. sample from the bottom).
    f. Avoid drawing air through the sample during sampling.
8. Go to the weighing balance…
    a. weigh the syringe and write down the Time in the Time column and the weight in the "Full Syringe Weight" column
9. Go to the apparatus….
    a. select the mode of the apparatus to enter the weight
    b. enter the weight of the sample syringe.
    c. check the weight is correct.
    d. press the enter button.
    e. open the red cap of the sample vessel and inject the sample
    f. replace the cap immediately
10. Go to the SAME weighing balance…
    a. weigh the syringe and write down the weight in the "Empty Syringe Weight" column
11. Go to the apparatus…
    a. Enter the empty syringe weight, press return/enter and once the apparatus is ready press Start
12. The test is now under way
13. DO NOT TOUCH the apparatus/ test vessel etc while a test is running
14. Get the next sample test vessel ready by putting diluent in – go to step 1
15. When the result appears write it down in the column for H2S

## 6 APPARATUS

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

| No | Instrument | Serial No | Software Issue |
|---|---|---|---|
| 1 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1017990 | 4.02/2.00 |
| 2 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1017988 | 4.02/2.00 |
| 3 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1017989 | 4.02/2.00 |
| 4 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1018040 | 4.02/2.00 |
| 5 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1018039 | 4.02/2.00 |
| 6 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1018042 | 4.02/2.00 |
| 7 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1018044 | 4.02/2.00 |
| 8 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1017987 | 4.02/2.00 |
| 9 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1018043 | 4.02/2.00 |
| 10 | STANHOPE-SETA $H_2S$ Analyser SA 4000-0 | 1018041 | 4.02/2.00 |
| | | | |

## 7 EXAMPLE RESULTS PROFORMA



Energy Institute IP 570 Distillate Round Robin

Page 1

Date:

Instrument Serial Number:

Name:

| Sample Number | Time (hh:mm) | Full Syringe Weight (g) (3.d.p) | Empty Syringe Weight (g) (3.d.p) | Result H2S(mg/kg) (2.d.p) | Comments |
|---|---|---|---|---|---|
| *Example* | *10:54* | *24.005* | *20.000* | *7.56* | |
| 8 | | | | | |
| 11 | | | | | |
| 2 | | | | | |
| 13 | | | | | |
| 1 | | | | | |
| 12 | | | | | |
| 7 | | | | | |
| 9 | | | | | |
| Lunch | | | | | |
| Sample Number | Time (hh:mm) | Full Syringe Weight (g) (3.d.p) | Empty Syringe Weight (g) (3.d.p) | Result H2S(mg/kg) (2.d.p) | Comments |
| 16 | | | | | |
| 3 | | | | | |
| 5 | | | | | |
| 6 | | | | | |
| 4 | | | | | |
| 15 | | | | | |
| 14 | | | | | |
| 10 | | | | | |

Energy Institute IP 570 Distillate Round Robin

Page 2

Date:

Instrument Serial Number:

Name:

**Appendix B**

**IP 570/11**

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

## 1 Scope

This document specifies a procedure for the determination of the hydrogen sulfide ($H_2S$) content of fuel oils such as marine residual fuels and blend stocks, in the range 0,40 to 15,0 mg/kg as measured in the liquid phase with viscosities up to 3 000 $mm^2s^{!1}$ at 50EC.

NOTE 1 - By using a smaller volume of sample taken by a suitable positive displacement pipette, it is possible to extend the range of the instrument to over 200 mg/kg.

NOTE 2 - The precision of this method is critically dependent on the sampling, thermal history and handling of the test sample.

NOTE 3 - This standard is suitable for materials with a viscosity of over 3 000 $mm^2s^{!1}$ at 50EC, (see 7.3.1), but the precision could be affected.

NOTE 4 - For the purposes of this standard, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent respectively the mass fraction and the volume fraction.

NOTE 5 - Some samples can give elevated Hydrogen Sulphide readings if they contain thiols or alkyl sulphides above a liquid phase concentration of approximately 5 mg/kg.

**WARNING 1 – $H_2S$ is a very dangerous, toxic, explosive, colourless and transparent gas which can be found in crude oil. It can be formed during the manufacture of the fuel at the refinery and can be released during handling, storage and distribution. 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 can be fatal. It is strongly recommended that personnel involved in the testing for H2S are aware of the hazards of vapour-phase H2S and have in place appropriate processes and procedures to manage the risk of exposure.**

**WARNING 2 – The use of this standard may involve hazardous materials, operations and equipment. 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**

**determine the applicability of regulatory limitations prior to use.**

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IP 475, *Petroleum liquids — Manual sampling (EN ISO 3170)*

ISO TR 13739, *Petroleum Products – Procedures for the transfer of bunker fuel(s) to ships*

## 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 $H_2S$ gas. The $H_2S$ is passed, with the air, over a detector to enable the $H_2S$ content of the air to be measured and the amount of $H_2S$ in the liquid phase to be calculated.

## 4 Reagents and materials

Use only reagents of recognised analytical grade.

**4.1 Diluent oil**[1]**,** proprietary water white API Group 2 base oil with a typical viscosity of 100 $mm^2/s$ at 40EC.

**4.2 Verification materials**[1]**,** pressurized nitrogen, of at least 99,999 % (*V/V*) purity, containing certified levels of $H_2S$.

**4.3 Toluene,** technical grade.

**4.4 Petroleum ether (60/80),** technical grade.

**4.5 Acetone,** technical grade.

---

[1] A list of suppliers is available from the Energy Institute.

## 5 Apparatus

### 5.1 General

The apparatus, as detailed in Annex A, comprises an air pump, test vessel, heating jacket, filters, $H_2S$ specific detector, integral computer, automatic solenoid valves, gas flow detectors, a disposable syringe and a 1 ml positive displacement pipette.

**5.2** **Analytical balance,** single pan or double pan balance capable of weighing to the nearest 0,001 g.

**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 6.4). The refrigerator shall be of a type suitable for storing volatile materials.

**5.5** **Oven/water bath (optional),** for warming the sample to 40EC with an accuracy of ∀ 2EC (see 7.3.1). The oven shall be of a type suitable for use with volatile materials.

**5.6** **Ultrasonic bath (optional),** general purpose for cleaning the test vessel (note under clause 11.3).

## 6 Sampling and sample handling

**6.1** Unless otherwise specified, samples shall be taken as described in IP 475.

During sampling operations, care shall be taken to ensure that the integrity of the material is maintained and the possible loss of $H_2S$ is kept to a minimum.

**6.2** Draw the sample directly into a suitable clean $H_2S$ inert container, of a minimum volume of 500 ml. It is recommended that containers such as dark brown borosilicate bottles or epoxy lined containers fitted with impervious gas-tight closures are used. The closure aperture shall allow the drawing of a test portion with the pipette (A.1.1.12) or syringe (A1.1.13).

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

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

NOTE - Lower volume containers may be used, however the precision could be affected.

**6.3** If a dedicated $H_2S$ sample cannot be taken, then the $H_2S$ measurement shall be the first test carried out on the sample as any additional handling can lead to loss of $H_2S$ and low results.

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

## 7 Sample preparation

**7.1** To minimize the loss of $H_2S$ gas, do not homogenize and avoid shaking the sample before taking a test portion.

**7.2** To minimize the loss of $H_2S$ 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 pipette (A.1.1.12) or syringe (A.1.1.13).

**7.3.1** 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 40ºC.

NOTE – It has been found that samples over 500 $mm^2/s$ at 50EC usually require warming.

## 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 $H_2S$ 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 if any discolouration is visible.

**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 ml/min ∀ 55 ml/min at least once a year using a calibrated flow meter connected to the air output 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 60,0EC ∀ 1,0EC at least every 6 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 $H_2S$ detector

Follow the manufacturer's instructions to verify the performance of the detector at least every 6 months or when a new detector is fitted at two concentration levels using pressurised nitrogen (4.2) containing certified levels of $H_2S$. 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 min 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 $H_2S$ detector calibration

The detector is factory calibrated to allow for both the static and dynamic response to $H_2S$. 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 $H_2S$ apparatus shall control the test vessel heater to 60,0EC ∀ 1,0EC 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 - Toluene (4.3) followed by petroleum ether (60/80) (4.4) and acetone (4.5), in conjunction with an ultrasonic bath (5.6) 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 min. 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 $H_2S$. Ensure that the instrument is operating in bypass mode before introducing sample. Introducing the sample before this condition is met will likely result in premature loss of $H_2S$ and an erroneously low result. If this is suspected the test must be abandoned and repeated. The instrument will warn the user if they attempt to introduce the test portion before it is operating in bypass mode.

**11.7** Depending on the expected $H_2S$ concentration, draw the appropriate volume of sample from at least 3 cm below the sample surface into the 1 ml positive displacement pipette (A.1.1.12) or disposable syringe (A.1.1.13) and weigh to the nearest 0,001 g (5.2). Using the keypad, enter the total mass, which includes the pipette and sample, into the apparatus. The appropriate volume shall be determined by reference to table 1.

**Table 1: Appropriate test volume for expected $H_2S$ concentration**

| **Expected $H_2S$ concentration** (mg/kg) | **Required test volume** (ml) | **Sample introduction** |
|---|---|---|
| 0 -10 | 5 | Disposable syringe |
| 10 - 20 | 2 | Disposable syringe |
| 20+ | 1 | Pipette |

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

**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 syringe or pipette to the nearest 0,001 g (5.2) and using the keypad enter the mass

into the apparatus.

**11.11** Start the test. The following actions take place automatically:

**11.11.1** The detector reading is normalized to zero.

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

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

**11.11.4** Air is pumped to purge the detector.

**11.12** Remove and clean the test vessel (11.2 – 11.3).

**11.13** 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

Calculate the $H_2S$ content of the sample, expressed in mg/kg, using the equation:

$$H_2S = \frac{A \times M}{m}$$

where:

A is the integrated area of cell output over the test time (mV.s).

M is the calibration constant of the detector (:g)/(mV.s).

m is the mass of the sample (g).

## 13 Expression of results

Report the $H_2S$ content to the nearest 0,01 mg/kg for < 10 mg/kg, and to the nearest 0,1 mg/kg for ∃ 10 mg/kg.

## 14 Precision[2]

### 14.1 General

The precision values given in 14.2 and 14.3 were derived from a 2009 laboratory study which used 7 instruments operators at a single location, to test 15 samples in duplicate and in random order. The sample types covered the $H_2S$ levels of 0,01 to 15,3 mg/kg and viscosities up to 3 000 $mm^2s^{!1}$ at 50EC.

As the precision was determined from results obtained at a single location the reproducibility may not be comparable when results obtained at different times and locations are compared, due to sampling, shipping, storage and environmental factors. In practice two results obtained from different locations would be acceptable if their difference did not exceed the published reproducibility.

### 14.2 Repeatability, r

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following value in absolute value in only one case in twenty.

$$r = 0{,}2970\ X^{0{,}6}$$

where X is the average of the results being compared, in mg/kg.

See Table 2 for a tabular illustration and Annex B for a graphical illustration of this relationship.

### 14.3 Reproducibility, R

---

[2] The round robin research report is available from the Energy Institute.

The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty.

$$R = 0{,}5232\ X^{0{,}6}$$

where X is the average of the results being compared, in mg/kg.

See Table 2 for a tabular illustration and Annex B for a graphical illustration of this relationship.

**Table 2: Calculated values of repeatability and reproducibility for typical $H_2S$ concentrations**

| **$H_2S$ concentration** (mg/kg) | **r** | **R** |
|---|---|---|
| 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 |

## 15 Test report

The test report shall contain at least the following information:

a) a reference to this standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 13);

d) any deviations, by agreement or otherwise, from the procedures specified;

e) the time and date of the test.

# Annex A

(normative)

# $H_2S$ Apparatus

## A.1 Apparatus

### A.1.1 General

The apparatus[1], as shown diagrammatically in Figure A.1, is self contained and operates automatically to measure the amount of $H_2S$ 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 $H_2S$ 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 $H_2S$ gas away from the detector, if high levels of $H_2S$ are measured that could saturate the detector.

**A.1.1.5 Flow sensors,** electronic sensors incorporated to ensure that the air/$H_2S$ 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/$H_2S$ mixture.

**A.1.1.8 Heater jacket,** 50 Watt, aluminium block, controlled to 60,0EC ∀ 1,0EC, 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 $H_2S$ detector,** electrochemical type specifically for $H_2S$ 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,** 5 ml, or 10 ml, 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 3 cm below the surface, if appropriate.

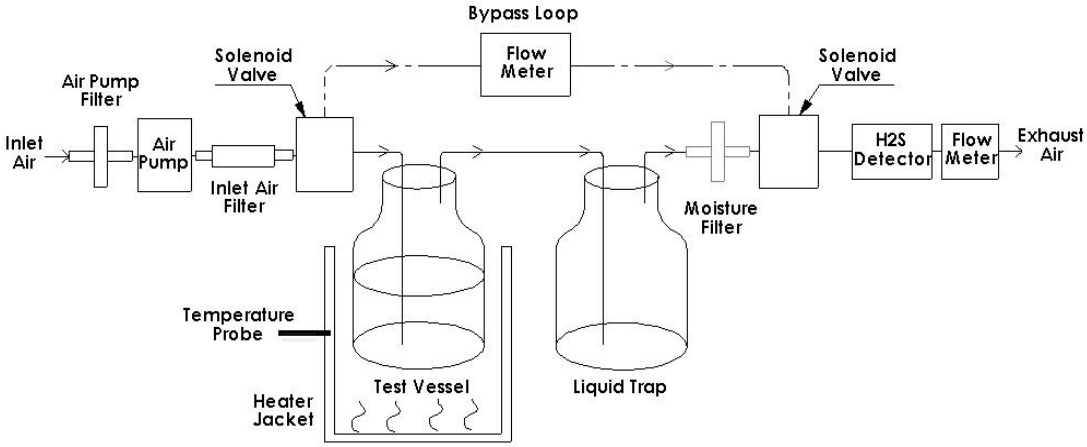



**Figure A.1: $H_2S$ apparatus**

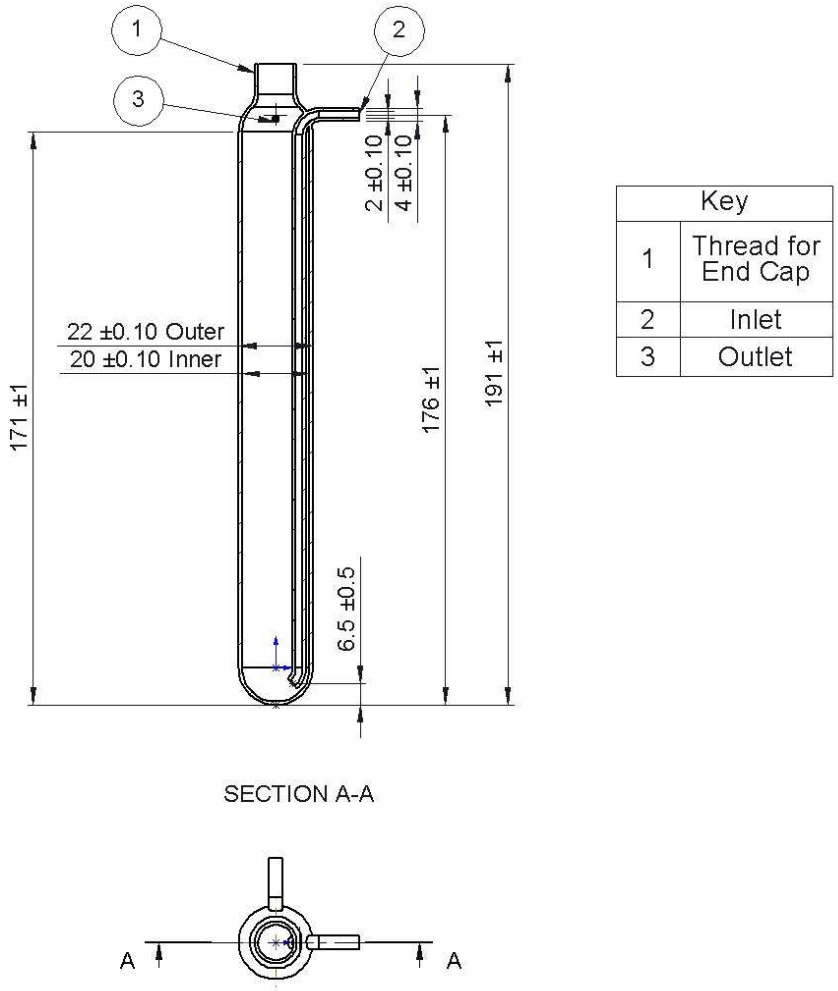



**Figure A.2: Test vessel**

# Annex B

(informative)

## Repeatability and reproducibility illustration

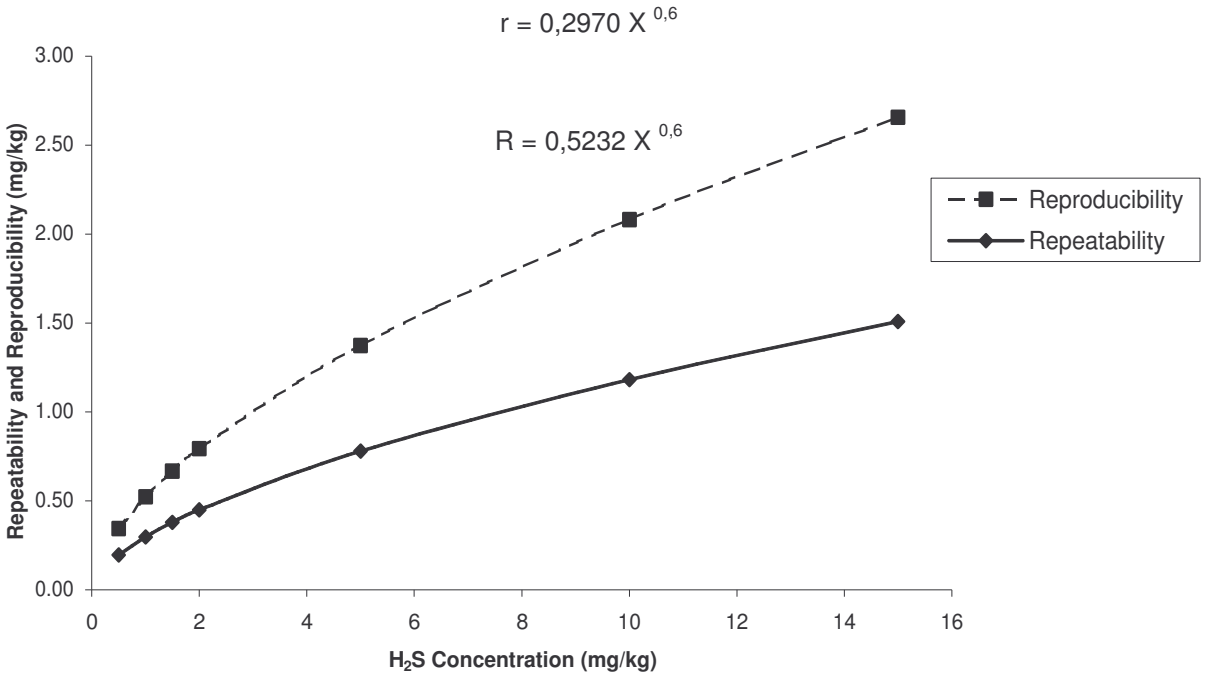



**Figure B1: Repeatability (r) and reproducibility (R) for a range of $H_2S$ values**

**Summary of changes**

The location of selected changes made to this standard since the last version, that may impact the use of this standard, are:

1) Note 5 added.

## Appendix C

### H2S IP570 Round Robin Compensated Results

Mr I Mylrea
Stanhope-Seta
London Street
Chertsey
Surrey
KT16 8AP

**JFC Consultants**
**IT Telecomms Statistics**
Telephone +44 (0) 1244 300362
Email JFChurch97@aol.com

6 July 2011

Dear Ian

**EI Precision Study**

**IP570 $H_2S$ in Distillate Fuel Oils – Corrected Results**

I have now re-evaluated precision for the method, according to the procedures of ISO4259 as implemented in ASTM computer program D2PP. Results have been corrected to take into account how much sample had previously been removed from the container, and are included in the attached file IP570-Distillates-Compensated.xls. These relate to duplicate tests made by ten different instruments on eight different samples.

The D2PP summary report is attached in file IP570-Distillates-Compensated.doc. Precision data is given below, with associated degrees of freedom in parentheses.

| Range of Results | Repeatability | Reproducibility |
|---|---|---|
| 0.4 – 9.7 | $0.2099\ x^{0.7}$ (77) | $0.2389\ x^{0.7}$ (80) |

In the above formulae, x is the average of results being compared. Please note that, contrary to the previous analysis on uncorrected results, there is now no evidence of excessive variability according to the concept of Limit of Quantitation. Neither is reproducibility less than repeatability as was previously determined. However there is still evidence of excessive laboratory differences according to the variance ratio F-test.

Please get in touch with me if any queries arise.

Yours sincerely

John Church

cc Jim Crighton, Energy Institute

The Hollows, Church Lane, Guilden Sutton, Chester CH3 7EW, UK

EI Precision Evaluation 21:14, 6 Jul 2011

H2S IP570 Round Robin Compensated Results

Repeatability = 0.2099 * X ^ 0.7 mg/kg

Reproducibility = 0.2389 * X ^ 0.7 mg/kg

| | Initial | Final |
|---|---|---|
| Number of laboratories | 10 | 10 |
| Number of samples | 8 | 8 |
| Number of repeats | 2 | |

REGRESSIONS (AFTER OUTLIER TESTS) TRANSFORMATION TYPE: NONE

| Regression | Fitted Variable | Coefficient B | Test | t-Ratio | % Sig. |
|---|---|---|---|---|---|
| Unweighted d v. (m+B0) | m + 3.2286E+00 | 2.2559E-02 | B=0 | 5.08 | 0.2 |
| Unweighted D v. (m+B0) | m + 1.6490E+00 | 3.4912E-02 | B=0 | 9.91 | 0.0 |
| Weighted | Intercept | -4.10555E+00 | | | |
| ln(d,D) v. ln(m+B0) | ln(m + 2.1755) | 1.29703E+00 | B=1 | 1.43 | 18.0 |
| (for Log Transform) | Dummy | 1.15728E-01 | | | |

| | | | | |
|---|---|---|---|---|
| | Dummy * Ln(m+B0) | -1.97263E-02 B=0 | 0.14 | 89.1 |
| Weighted | Intercept | -2.59634E+00 | | |
| ln(d,D) v. ln(m+B0) | ln(m) | 7.08489E-01*B=0 | 10.12 | 0.0 |
| (for Power Transform) | Dummy | 9.24794E-02 | | |
| | Dummy * Ln(m+B0) | -1.76573E-02 B=0 | 0.38 | 71.3 |
| | | Critical t (5%, 12) = | 2.18 | 5.0 |

* Coefficient used = 0.7000

Transformation used: X^0.3000

COMMENTS:

This report was prepared using D2PP, Version 5.3.32
from data file IP570-Distillates-Compensated.xls, SUMMARY, .

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

| LABORATORY | SAMPLE | DUP | TEST |
|---|---|---|---|

```
(1017987   ,RR015     , 2)  Missing, <, or 0.0
(1018039   ,RR001     , 1)  Cochran-variances
(1018040   ,RR001     ,  )  Hawkins-cells
```

SAMPLE MEANS AND STANDARD DEVIATIONS  Transform Type: NONE

After any outlier rejections

| | No. of | | Between Labs | | | Between Repeats | | |
|---|---|---|---|---|---|---|---|---|
| Sample | Results | Mean | S.D. | DF | R | S.D. | DF | r |
| RR014 | 20 | .38150 | .3204E-01 | 12 | .99E-01 | .1708E-01 | 10 | .54E-01 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| RR004 | 20 | .89550 | .7907E-01 | 19 | .23 | .7654E-01 | 10 | .24 |
| RR001 | 17 | 1.8034 | .1520 | 15 | .46 | .1770 | 8 | .58 |
| RR015 | 19 | 2.0963 | .1741 | 17 | .52 | .1528 | 9 | .49 |
| RR008 | 20 | 4.5080 | .1978 | 18 | .59 | .1732 | 10 | .55 |
| RR012 | 20 | 5.0945 | .2339 | 16 | .70 | .1863 | 10 | .59 |
| RR009 | 20 | 8.5640 | .3251 | 17 | .97 | .2754 | 10 | .87 |
| RR013 | 20 | 9.6335 | .4179 | 13 | 1.3 | .2683 | 10 | .85 |

SAMPLE MEANS AND STANDARD DEVIATIONS Transform Type: Power

After any outlier rejections

| | No. of | | Between Labs | | | Between Repeats | | |
|---|---|---|---|---|---|---|---|---|
| Sample | Results | Mean | S.D. | DF | R | S.D. | DF | r |
| RR014 | 20 | .74842 | .1922E-01 | 12 | .59E-01 | .1014E-01 | 10 | .32E-01 |
| RR004 | 20 | .96659 | .2744E-01 | 19 | .81E-01 | .2698E-01 | 10 | .85E-01 |
| RR001 | 17 | 1.1927 | .3014E-01 | 15 | .91E-01 | .3545E-01 | 8 | .12 |
| RR015 | 19 | 1.2477 | .3234E-01 | 17 | .96E-01 | .2896E-01 | 9 | .93E-01 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| RR008 | 20 | 1.5708 | .2057E-01 | 17 | .61E-01 | .1792E-01 | 10 | .56E-01 |
| RR012 | 20 | 1.6294 | .2277E-01 | 16 | .68E-01 | .1821E-01 | 10 | .57E-01 |
| RR009 | 20 | 1.9043 | .2189E-01 | 17 | .65E-01 | .1836E-01 | 10 | .58E-01 |
| RR013 | 20 | 1.9727 | .2557E-01 | 13 | .78E-01 | .1638E-01 | 10 | .52E-01 |

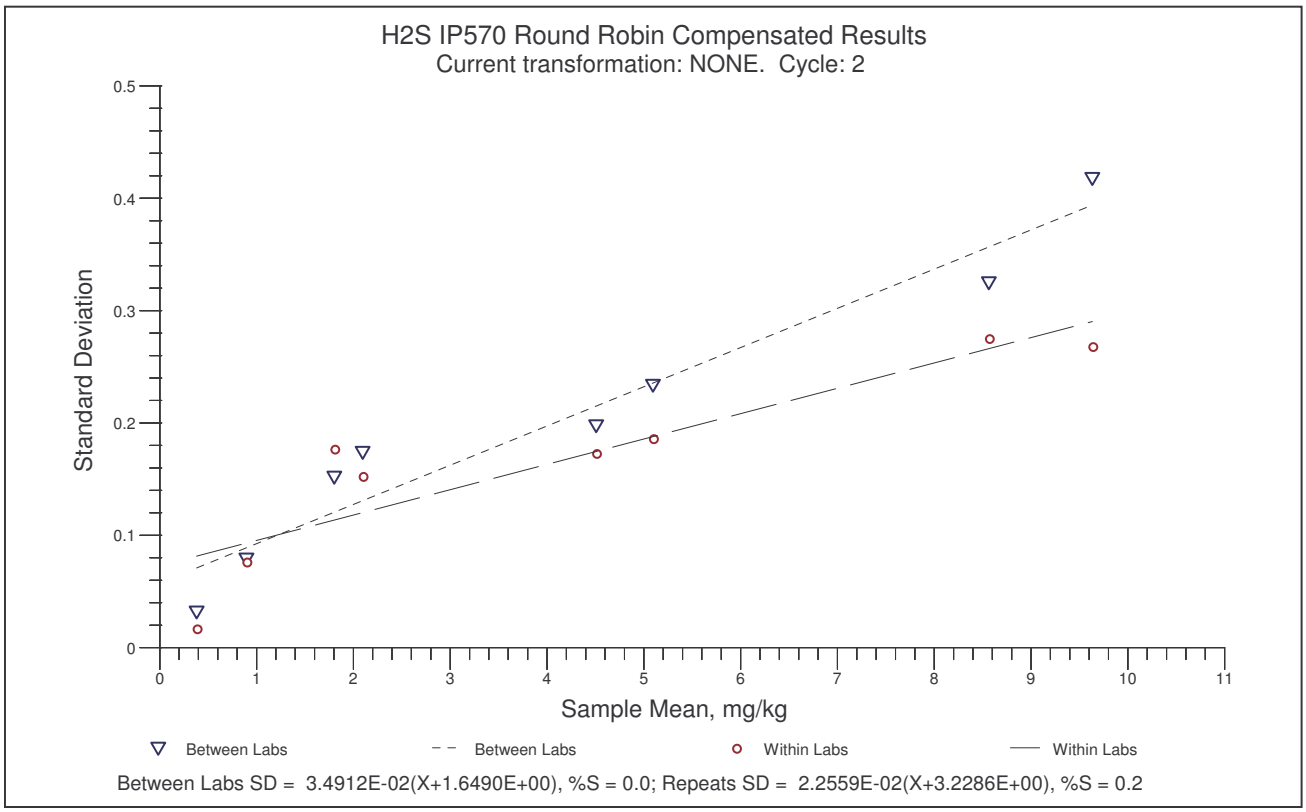
VARIANCE ANALYSIS Transform Type: Power

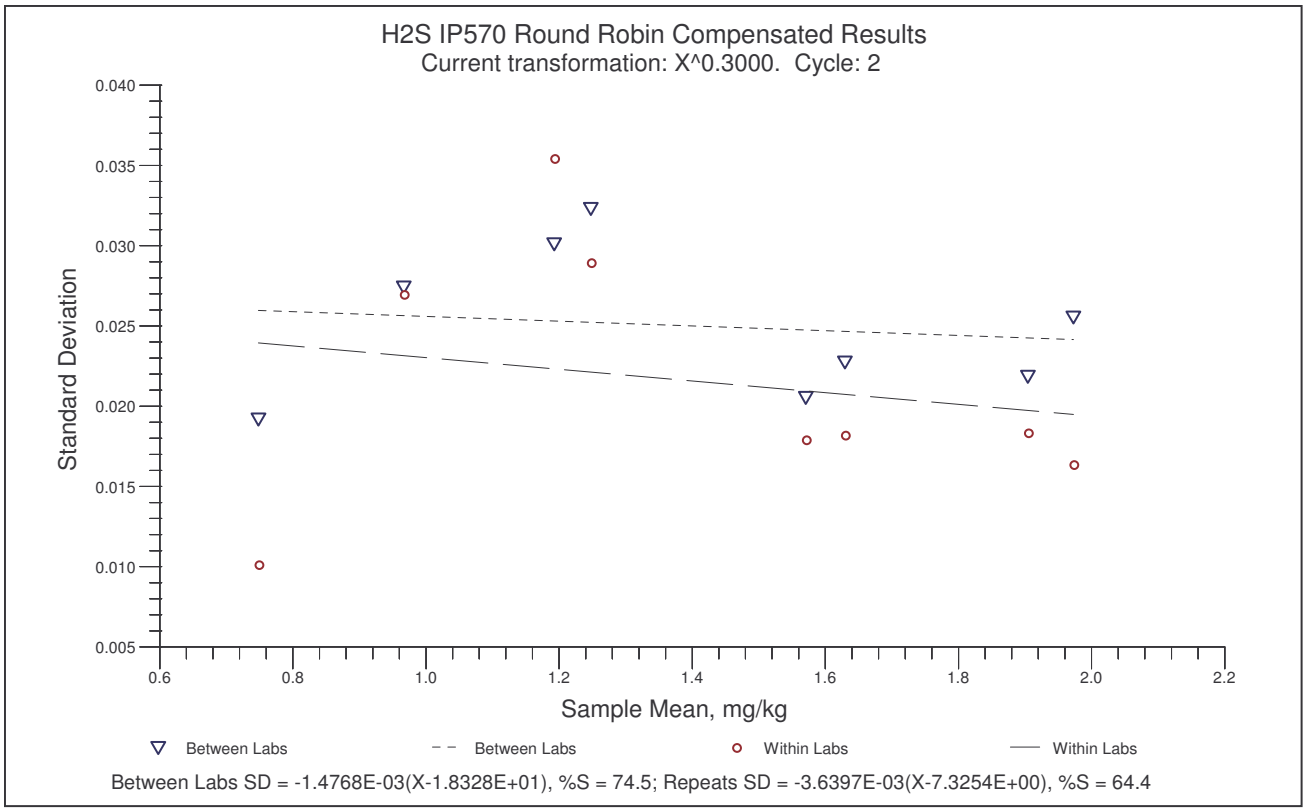
| | Sum of squares | | | | |
|---|---|---|---|---|---|
| | Estimated | Exact | DF | Mean square | F |
| Sample Means | 2.683042E+01 | 2.673583E+01 | | | |
| Lab Means | 2.600746E-02 | 2.590565E-02 | 9 | 2.87841E-03 | 5.657 |
| Interaction | 3.154831E-02 | | 62 | 5.08844E-04 | |
| Pairs | 2.688798E+01 | 2.679328E+01 | | | |
| Repeats | 3.849624E-02 | | 77 | 4.99951E-04 | |
| Total | 2.692647E+01 | | | | |
| Critical F (5%, 9, 62) = | | | | | 2.035 |

Expectation of Mean Squares

| | |
|---|---|
| Lab means | 1.0250 V(r) + 2 V(I) + 15.7778 V(L) |
| Interaction | 1.0252 V(r) + 2 V(I) |
| Repeats | 1.0000 V(r) |

| | DF | Variance | Precision |
|---|---|---|---|
| Transformed data | | | |
| Repeatability | 77 | 9.999022E-04 | 6.297E-02 |
| Reproducibility | 80 | 1.296565E-03 | 7.166E-02 |




H2S IP570 Round Robin Compensated Results
Current transformation: X^0.3000. Cycle: 2
Standard Deviation
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
Sample Mean, mg/kg
Between Labs
Between Labs
Within Labs
Within Labs
Between Labs SD = -1.4768E-03(X-1.8328E+01), %S = 74.5; Repeats SD = -3.6397E-03(X-7.3254E+00), %S = 64.4