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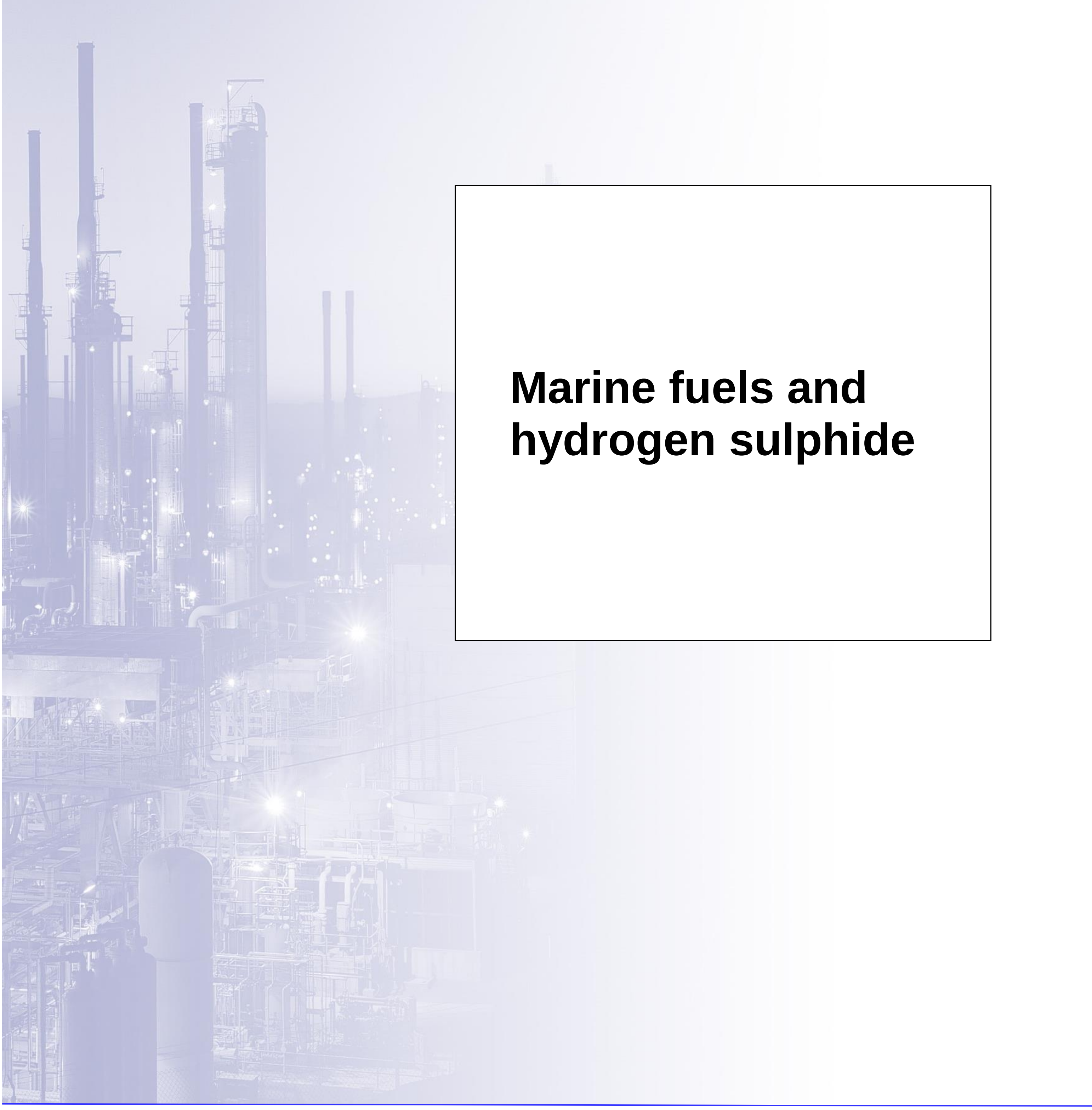

Marine fuels and hydrogen sulphide

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ABSTRACT

The safe handling of petroleum cargoes and refined products that may contain hydrogen sulphide (H_2S) is an important issue for the marine and inland fuel industries. Attention has refocused recently on H_2S due to the revision of the ISO 8217:2012 [1] specification for marine fuels which limited the maximum content of H_2S in the liquid fuel to 2.00 mg H_2S/kg fuel (2.00 ppmw).

This report summarizes issues associated with the presence of H_2S in residual marine fuels including:

- Sources of H_2S in petroleum products;
- Exposure levels for H_2S in the vapour phase and the effects of exposure;
- Relationship between the H_2S concentration in liquid fuel and in the vapour phase;
- Measurement methods for H_2S in marine fuel and in the vapour phase;
- Interpretation of results and guidance on maximum H_2S levels; and
- Guidelines for the safe handling of liquid petroleum products that may contain H_2S.

Importantly, the report reinforces the need for safe handling procedures, training, and personnel protection when transferring or storing fuels that may contain H_2S, rather than relying only on a measured H_2S level in the liquid product.

KEYWORDS

Marine fuel, residual marine fuel, residual fuel oil, marine distillate fuel, hydrogen sulphide

INTERNET

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SUMMARY

The safe handling of petroleum cargoes and refined products that may contain hydrogen sulphide (H_2S) is an important issue for the marine and inland fuel industries. Attention has refocused recently on H_2S due to the revision of the ISO 8217:2012 [1] specification for marine fuels which limited the maximum content of H_2S in the liquid fuel to 2.00 mg H_2S/kg fuel (2.00 ppmw).

To raise awareness of the industry's experience with the safe handling of marine fuels, this report reviews issues associated with the presence and measurement of H_2S in liquid fuels and the importance of safe handling procedures to limit personnel exposure to H_2S.

At vapour concentrations well below 1 ppmv, H_2S has the distinctive smell of rotten eggs which provides an early warning to personnel. At moderate vapour concentrations from 50 to 100 ppmv, H_2S causes a marked sensory irritation, a temporary loss of sensitivity to H_2S smell (transitory olfactory fatigue), headaches and dizziness. Exposure to H_2S in the vapour phase may cause unconsciousness at concentrations higher than about 300 ppmv and death at concentrations higher than about 700 ppmv.

Hydrogen sulphide (H_2S) is naturally present in crude oils and can be formed during the refining process and in storage tanks downstream of the refinery. Residual marine fuels and marine distillate fuels can contain H_2S at various concentrations in the liquid phase. The H_2S concentration in the liquid phase will depend on the crude oil, the specific refining processes (such as visbreaking or thermal cracking) used to produce the residual marine fuel, and the conditions under which the fuel is stored after production. H_2S in the liquid phase of a petroleum product can evolve into the available vapour space of the product's storage tank. The relationship between liquid and vapour phase H_2S concentrations is difficult to predict, however, because the vapour phase concentration depends on a number of fuel- and storage-related factors.

Although marine distillate fuels do not typically contain enough H_2S in the liquid phase to cause safety concerns, higher liquid-phase levels of H_2S can be found which can result in higher than expected vapour phase concentrations of H_2S under some circumstances.

The oil and shipping industries routinely handle cargoes (such as sour crude oils and high-sulphur process streams) that contain much higher liquid phase H_2S levels than those that are typically found in residual marine fuels. Robust safety procedures, based on industry experience and reinforced by personnel training, have been successful in providing a high degree of protection to personnel working in the vicinity of these cargoes. Proper safety, handling, and emergency procedures are the primary control measure to prevent H_2S-related safety incidents and to ensure that personnel are not exposed to high vapour phase H_2S levels (see Section 6).

In order to provide even greater protection to personnel, a maximum liquid phase H_2S limit of 2.00 mg H_2S/kg fuel, as measured by test method IP 570 [2], was added to the ISO 8217 specification in 2010 for marine fuels, effective August 2012.

The Standard Method IP 570 is the recommended test method for measuring H_2S in the liquid phase of fuel oils. This method provides an approximation of the total H_2S which can be evolved into the vapour phase from a given sample of fuel oil. Other methods, such as IP 399[1] [3] may also be used to analyse liquid fuels as long as users

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[1] The Energy Institute's IP Test Panel is no longer technically revising IP 399.

satisfy themselves that the alternative method gives reliable results compared to IP 570. However, in cases of dispute, IP 570 is the referee test method.

For measuring H_2S in field applications, some methods can be used to estimate vapour phase H_2S concentration, such as the use of stain detector tubes or electronic monitors. Although these methods are reliable and suited for monitoring H_2S concentrations in the workplace, the conditions under which the vapour phase sample is taken can introduce variability in the measured H_2S levels in the vapour phase, resulting in abnormally low results and a false sense of security that the fuel contains a low level of liquid phase H_2S.

This new liquid phase H_2S limit in ISO 8217 is intended to provide an additional margin of safety by reducing the risk that personnel are exposed to levels of H_2S vapour that can cause sudden and severe health effects. This limit alone, however, should not be considered a completely safe level and does not eliminate the risk that H_2S vapour will evolve to very high concentrations in enclosed spaces. It also does not replace the need for proper procedures, control measures, and appropriate personal protection for all operations in which personnel could be exposed to H_2S in the vapour phase.

A risk assessment of vapour phase H_2S inhalation risks should be conducted in order to anticipate the most appropriate safety procedures, training, and personal protective equipment for situations that could involve storage tank headspaces, confined spaces, areas in the vicinity of tank venting pipes, storage containers for product residue, waste and waste water, as well as areas surrounding unintentional spills and releases.

For protecting personnel working in the vicinity of fuel storage tanks or vents, electronic alarms should be used that continuously monitor vapour phase H_2S concentrations. When high vapour phase H_2S concentrations are suspected or measured around a spilled product, additional or specialized personnel protection may be warranted, including restricting access to the spill area, using personal protective equipment, and ensuring the use of proper safety procedures.

Importantly, this report reinforces the need for safe handling procedures and appropriate personal protection when transferring or storing fuels that may contain H_2S, rather than relying only on a measured H_2S level in the liquid product.

1. BACKGROUND

The safe handling of petroleum cargoes and refined products that contain hydrogen sulphide (H_2S) in the liquid phase is an important issue for the marine and inland fuel industries. Attention has refocused recently on H_2S due to revision of ISO 8217:2012 ‘Petroleum products — Fuels (class F) — Specifications of marine fuels' [1]. This specification for marine fuels limited the maximum content of H_2S in the liquid fuel to 2.00 mg H_2S/kg fuel (2.00 ppmw).

This report reviews issues associated with the presence of H_2S in residual marine fuels including:

- Sources of H_2S in petroleum products [4];
- Exposure levels to H_2S in the vapour phase and the effects of exposure [5,6];
- Relationship between H_2S in the liquid and vapour phases;
- Measurement methods for H_2S in the liquid and vapour phases;
- Interpretation of results and guidance on maximum H_2S levels; and
- General guidelines for the safe handling of liquid petroleum products that may contain H_2S [5].

Unlike residual marine fuels, marine distillate fuels do not normally contain H_2S at concentrations in the liquid phase that would result in safety concerns for fuel storage and handling. Under certain circumstances, however, higher H_2S levels can be present in the liquid phase of marine distillate fuels (e.g. when produced from sour crude oils without extensive hydroprocessing). The revised ISO 8217 marine fuel specification states that the liquid phase H_2S limit shall be measured by IP 570 [2] and the scope of this method now includes marine distillate fuels.

2. SOURCES OF HYDROGEN SULPHIDE

Hydrogen sulphide (H_2S) occurs naturally in crude oils and the H_2S concentration in the liquid phase can vary depending upon the origin of the crude. H_2S can also be formed during the refining process from the conversion of sulphur-containing compounds in the crude oil by thermal processing or by catalytic cracking in the presence of hydrogen. Higher liquid phase H_2S levels are typically found in fuel products produced by thermal or catalytic processes, such as hydrodesulphurisation, hydrocracking, and visbreaking.

Thus, the concentration of liquid-phase H_2S that can be found in fuel products will depend upon the sulphur levels in the crude oil before processing and the type and severity of refinery processes used to produce the fuel product. In addition, hydrogen sulphide can be produced from sulphur-containing fuel products in storage by the action of anaerobic bacteria that can sometimes be found in the fuel supply and distribution system. Good housekeeping practices [7,8] can avoid these problems.

H_2S will partition into the vapour phase from liquid fuel products that contain H_2S, for example, from liquid fuels in storage tanks, product barges and customer tanks. H_2S will also dissolve in water layers in tanks and barges that are in contact with the liquid fuel product. Heated surfaces (e.g., in-tank electrical heaters, steam coils, etc.) that are in direct contact with the liquid can also generate H_2S from the conversion of sulphur-containing molecules in the liquid product by localised overheating. Importantly, this could happen after the fuel product has left the refinery, for example, in storage tanks at distribution terminals or at the customer's facility.

Hence, it is important that all parties involved in the manufacture, supply, distribution and use of residual fuels fully understand these effects and follow appropriate storage and handling procedures. It is also important that ship owners, operators and other parties maintain appropriate safety procedures, practices, and personnel training that are designed to protect the crew and others who could be exposed to H_2S. Most importantly, a maximum liquid phase H_2S specification in ISO 8217 [1] does not replace these safety requirements even though it is intended to limit the maximum H_2S that can evolve from the liquid fuel into the vapour phase.

H_2S, if present in the fuel product, will be present in the liquid and vapour phases, as well as in a water phase if one is present. In a closed storage vessel, H_2S will partition from the liquid phase into the vapour phase until an equilibrium has been reached between the two phases. The equilibration time and the concentrations in each phase will depend upon a number of factors including:

- temperature of the liquid fuel;
- the fuel's chemical composition, including other contaminants and additives;
- the fuel's physical properties, particularly its viscosity;
- volume of fuel in the storage vessel (which governs the fuel volume relative to the head space volume);
- amount of applied heating to surfaces in contact with the liquid fuel;
- degree of liquid agitation;
- configuration of the tank, and, in particular, how the tank is vented;
- length of time the liquid fuel has been in storage;

- presence of water and a separate water phase; and
- ambient conditions (governing the amount of headspace purging/breathing).

In principle, H_2S concentrations at equilibrium can be estimated from Raoult's Law for vapour pressures of multicomponent solutions. In practice, the confounding factors mentioned above make such estimates very difficult to do except in the simplest circumstances.

The H_2S liquid to vapour ratio is therefore very difficult to predict. Available information suggests that this ratio for residual fuel oil can be in the range 1:50 to 1:100 in some instances, that is, 1 ppmw H_2S in the liquid phase could produce between 50 to 100 ppmv H_2S in the vapour phase. This is an approximation only and should be used with care as specific circumstances may produce H_2S levels in the vapour phase that could be much higher. These estimates are based on published data [6,8] and on unpublished studies carried out by oil companies.

A 2010 study [10] by DNV Petroleum Services (DNVPS) compared the liquid phase H_2S levels in 75 heavy fuel oil samples stored in bunker barge tanks against the vapour phase H_2S levels in the tank's headspace. These samples represented 25 bunkerings and were analysed using the IP 570 test method recommended in ISO 8217.

The H_2S concentration in the liquid fuels averaged 0.94 mg H_2S /kg fuel (ppmw) with a range of 0.3 to 4 mg/kg (ppmw). Measurements showed that different fuel samples having the same liquid phase H_2S level could result in vapour phase H_2S levels that ranged from negligible amounts to more than 5 ppmv. The H_2S levels in liquid samples from the tank were also consistently higher than those found in liquid samples taken at the ship's manifold and returned to an on-shore laboratory for analysis. The study showed that the vapour phase H_2S concentration does not depend solely on the H_2S concentration in the liquid fuel.

Although the H_2S vapour/liquid/ ratios were lower than have been reported in previous studies [6,8], the authors of the DNVPS study concluded that the 2.00 mg H_2S/kg fuel limit in ISO 8217 did not provide an adequate level of protection on its own against H_2S in the vapour phase, even though the measured values were within occupational short-term exposure limits (see Section 3).

3. EFFECTS AND PROPERTIES OF H_2S

At ambient temperatures, H_2S is a highly toxic gas and the effects on exposed personnel depend on the H_2S concentration and the duration of exposure. At very low concentrations, the gas has the characteristic smell of rotten eggs. However, at moderate concentrations, H_2S causes sensory irritation, a temporary loss of sensitivity to H_2S smell (transitory olfactory fatigue), headaches and dizziness. At high concentrations above 300 ppmv, H_2S may cause unconsciousness and death. Exposure to H_2S concentrations above 700 ppmv is immediately fatal.

The following table summarises the effects of exposure at different concentrations.

Table 1 Effects of exposure to different vapour phase concentrations of H_2S [11,12,13]

H_2S concentration (ppmv)	Physiological Effects
0.0005 - 0.5	First detectable by smell (disagreeable odour of rotten eggs)
1 - 5	Limit for 8 hours working May cause some nausea
5 - 10	Short-term exposure limit (STEL) May cause nausea and eye lacrimation after prolonged exposure in sensitive individuals
50 – 100	Respiratory tract and eye irritation after 1 hour Headaches and dizziness. Longer exposures to concentrations up to 100 ppmv result in a gradual increase in the severity of these symptoms. Unconsciousness leading to death may occur after 4 – 48 hours of exposure
100	Loss of sense of smell. Olfactory paralysis occurs after 3 to 15 minutes exposure to 100 ppmv
200	Exposures of over 30 minutes may cause delayed chemical pneumonitis (lung oedema)
350	Unconsciousness leading to death may occur after 30 minutes exposure
>500	Rapid (‘knock down’) unconsciousness and death. Causes seizures, loss of control of bladder and bowels. Breathing will stop and death will result if victim is not rescued and resuscitated promptly.
700+	Immediately fatal

Long-term Occupational Exposure Limits (OELs) typically represent the time-weighted average (TWA) exposure concentration of a toxic substance permitted over an 8-hour working day and a 40-hour working week. They represent a concentration to which most workers may be repeatedly exposed, day after day, without significant adverse health effects. In the case of hydrogen sulphide, the limit is primarily based on avoiding transient sensory irritation in the eyes, nose, and throat.

Such limits are based on professional assessments of the best available information at a particular point in time and are regularly updated by health regulatory authorities. OELs are intended to protect most of the working population from adverse health effects but some exceptions may occur with unusually sensitive individuals. For some substances, as is the case for H_2S, brief exposures to high vapour concentrations may cause localised irritation that require establishing short-term exposure limits (STELs). STELs typically represent a 15-minute TWA concentration that should not be exceeded.

3.1. OCCUPATIONAL EXPOSURE LIMITS FOR H_2S IN THE VAPOUR PHASE

Occupational limits for vapour phase H_2S have been revised and lowered in many different countries and regions:

- The European Commission's Scientific Committee on Occupational Exposure Limits (SCOEL) recommends a 5 ppmv (7 mg/m^3) TWA (8-hour), with a 10 ppmv (14 mg/m^3) STEL (15 minutes) [14];
- In the Netherlands, the current Maximally Allowed Concentration (MAC) is 1.6 ppmv (or 2.3 mg/m^3) [13];
- In the United Kingdom, 5 ppmv (7 mg/m^3) is recommended for the derived and OEL limits (8 hours TWA) with a 10 ppmv (14 mg/m^3) STEL [11];
- In Germany, 5 ppmv (7.1 mg/m^3) is recommended by the MAK Commission [21];
- ACGIH® has recommended 1 ppmv as the Threshold Limit Value (TLV) with a 5 ppmv (or 7 mg/m^3) STEL [12]. This TLV has also been legally adopted in several European countries.

The prevailing limit values should be carefully reviewed to ensure compliance before storing or handling products containing liquid or vapour phase H_2S or that have the potential to evolve H_2S under storage conditions.

4. MEASUREMENTS OF H_2S

Test methods have been developed by the Energy Institute (EI), ASTM, and others to measure H_2S in the liquid or vapour phase. In-house methods have also been developed by some oil companies, inspection services, and other companies.

4.1. MEASUREMENTS OF H_2S IN THE LIQUID PHASE

Measurements of H_2S in the liquid phase report the amount of H_2S dissolved in the liquid fuel. These liquid phase values indicate the potential levels of H_2S that could be generated in the vapour phase if all of the liquid phase H_2S were to be released to the vapour phase. As indicated above, however, the liquid/vapour ratio can be very variable and liquid phase measurements provide only an approximate indication of potential vapour phase H_2S levels.

There are a number of different methods for measuring the concentration of H_2S in the liquid phase. A comprehensive study was undertaken by the EI in the late 1980’s, which concluded that many methods could give inaccurate results. To overcome problems with mostly in-house laboratory methods, the EI developed and published method IP 399 [3], titled ‘Determination of hydrogen sulphide in fuel oils’.

IP 399 is a “wet” chemical procedure requiring the use of hazardous chemicals and well-trained and competent laboratory technicians. The procedure is time-consuming and too complex to be used routinely. Changes to the test method have taken place over time, primarily a change of one of the key chemical reagents (cadmium sulphate was replaced by zinc acetate). It is believed that the published precision from the most recent round robin exercise for IP 399 is no longer valid when the zinc acetate reagent is used.

To overcome perceived weaknesses in the IP 399 method, the EI developed IP 570, ‘Determination of Hydrogen Sulphide in Fuel Oils - Rapid liquid phase extraction method’. In this method, a weighed liquid sample is placed in a heated test vessel, containing a base oil diluent. Air is bubbled through the heated liquid to extract the H_2S gas which is then passed over a selective detector to measure the H_2S content in the air. The amount of H_2S in the liquid phase is then calculated in mg H_2S/kg fuel.

The IP 570 test was originally only applicable to marine residual fuels, however, additional testing coordinated by the EI has seen the scope of the test method extended to include marine distillate fuels.

Interference problems with the IP 570 measurement have been noted by some users when low boiling point materials, such as ethyl and methyl mercaptans and alkyl sulphides, are also present in the fuel. To address this problem, the equipment manufacturer has developed a cold trap called a Vapour Phase Processor (VPP). The VPP traps the interfering molecules in a cold trap at -20°C, separating the H_2S measured by the detector from the other contaminants. Interfering molecules are likely to lead to higher measured values of H_2S in the liquid phase.

The EI recently completed an inter-laboratory study to establish the precision of the IP 570 test method using the VPP. The 2012 version of IP 570 now includes Procedure A (with the VPP) and Procedure B (without the VPP). Since many marine fuels will not contain interfering molecules, it is not always necessary to follow Procedure A when testing samples and Procedure B will be sufficient. However, if it is suspected that interfering molecules may be present, then it is recommended that

Procedure A is used. The newest edition of ISO 8217 includes Procedure A as the reference test method.

CONCAWE recommends that IP 570 is used both as the definitive referee method (Procedure A) and for routine sample testing (Procedure A or B).

4.2. SAMPLING AND HANDLING CONSIDERATIONS

To ensure reliable and consistent liquid phase H_2S measurements, great care must be taken during sampling and subsequent handling and in the selection of sample containers. The following sampling and handling requirements for residual fuel oil samples are included in IP 570 [2]:

- It is recommended that only epoxy-lined cans or dark brown borosilicate glass bottles with impervious gas-tight closures of a minimum volume of 500 ml should be used for collecting liquid fuel samples for testing;
- These cans or bottles should be completely filled to approximately 95% volume capacity and should then be immediately sealed;
- Sample containers should be taken to the test laboratory as soon as possible after sampling and should be immediately tested if possible. If samples are not tested immediately, they should be stored in a cool place such as a refrigerator and analysed within no more than 3 days.
- IP 570 shall be the first test performed on the sample as any additional handling can lead to loss of H_2S and low results.

IP 570 further specifies that samples must be drawn in accordance with IP 475 (ISO 3170) [15]. This standard describes various sampling methods either for taking “grab” samples from various positions within a tank’s fuel volume (usually top, middle and bottom) or from a pipeline, or for taking “running” samples from a vertical column through the liquid. These methods are very different from the continuous drip sampling method [16] that is generally used for drawing a representative sample during a marine bunker delivery.

Most samples of marine fuels are drawn in accordance with sampling procedures developed by the International Maritime Organisation (IMO, [16]) for the purpose of determining the sulphur content in the fuel. These guidelines specify that the fuel sample should be obtained at the receiving ship’s inlet bunker manifold and drawn continuously throughout the bunker delivery period. This is done using a drip sampler where the sample literally drips into a closed sample container throughout the bunkering operation. The drip sample is subsequently split into a number of smaller samples, some of which are retained by the fuel supplier while others are taken by the ship operator. In order to ensure that the fuel sample is homogenous before it is split into smaller samples, the IMO guideline specifies that the sample should be thoroughly agitated before splitting.

Samples obtained by the continuous-drip method could lead to an under estimation of the amount of H_2S in the delivered fuel for two reasons: (1) loss of H_2S from the liquid fuel due to the high surface area liquid/gas interface that is associated with the continuous-drip sampling method and the subsequent sample agitation/splitting process and (2) loss of H_2S due to the materials that are typically used when collecting such samples. Care should be taken to ensure that the integrity of the sample is maintained and that the possible loss of H_2S is kept to a minimum. At present, no data are available to quantify typical levels for these losses. Where samples are drawn in a manner that does not minimise vapour loss (e.g. continuous drip sampling), separate samples should be drawn for H_2S determination.

Therefore, H_2S results obtained on a liquid bunker sample collected by the continuous drip method could lead to measured H_2S concentrations that are too low due to vapour loss, which could lead to a false sense of security. Liquid fuel samples must be specifically taken for the determination of liquid phase H_2S in accordance with the guidance provided above.

4.3. MEASUREMENTS OF H_2S IN THE VAPOUR PHASE

Vapour phase H_2S measurements indicate the H_2S level at a particular location and at a particular point in time. Such measurements do not determine the potential levels of H_2S that could be generated if most of the H_2S in the liquid phase evolved into the vapour phase.

ASTM D5705 [17] ('Standard test method for measurement of hydrogen sulphide in the vapour phase above residual fuel oils') measures the levels of vapour phase H_2S under prescribed test conditions. Vapour phase measurements are reported as parts per million on a volume basis (denoted "ppmv"). Although ASTM D5705 is described as a field test method, most field measurements use a simplified version of this method in which a fixed volume of vapour is drawn through a stain-detector tube. A stain-detector tube is one that contains a material that changes colour upon exposure to H_2S vapour. Simplified methods such as this are prone to errors and are very dependent upon the location of the sampling point, in particular on its proximity to the source of H_2S.

Electronic monitoring devices are also available as an alternative to stain-detector tubes but the results from these devices are very dependent upon the location of the point of measurement. However, these devices can and should be used to alert personnel to H_2S vapours that may be emanating from open tank hatches and outlets of tank vents.

As stated earlier, the concentration of H_2S in the headspace of a tank will depend on many factors and not just the total amount of H_2S in the liquid phase and on the partitioning between the liquid and vapour phases (see Section 2). Importantly, a measurement that indicates a low concentration of H_2S does not necessarily mean that this will be the case in the future. Depending upon changing conditions in the tank, H_2S vapour could evolve from the liquid into the vapour space at a later time, especially if the amount of product in the tank has changed. Therefore, opening a tank and taking a headspace tank measurement can provide misleading results. In some circumstances, the headspace may indicate that there is no H_2S in the vapour space while the liquid fuel may contain a significant concentration of H_2S.

5. ISO 8217 GUIDANCE ON H_2S LEVELS IN THE LIQUID PHASE

The marine fuel specification (ISO 8217) now includes a maximum H_2S limit in the liquid fuel, as measured by IP 570. It should be noted that inland fuel oil and commercial blend component specifications do not typically stipulate a maximum H_2S limit in the liquid phase but it is recommended that similar safety precautions should be observed.

The inclusion of this H_2S limit in ISO 8217 can be expected to reduce the potential maximum H_2S vapour that can volatilise from the fuel. However, as described earlier, low H_2S results in the vapour phase can be obtained if the sampling requirements specified in IP 570 are not rigorously followed. Similarly, low H_2S results can also be obtained on tank headspace samples if the liquid in the tank is of high viscosity and has not been agitated. In both of these cases, a false sense of personnel safety can occur.

To ensure greater safety to personnel, it is therefore critical that ship owners, operators and other parties who may be exposed to H_2S (e.g. those involved in sampling or gauging tanks via open hatches) are properly trained on H_2S hazards and that they routinely operate within the established safe procedures. These procedures should include the use of personal H_2S alarms and, if necessary, other appropriate personal protective equipment (PPE). Many good videos and on-line training modules are now available (see [18] as an example). Local health and safety specialists who are knowledgeable in H_2S hazards should also be consulted.

The oil industry regularly handles cargoes (e.g. some crude oils and high-sulphur process streams) containing much higher H_2S levels than are typically found in marine fuels. These cargoes are carried by specialized ship operators who ensure that their crews through regular training are fully aware of the potential risks and the importance of prescribed handling procedures. These procedures have proven to be sufficient to provide a very high degree of personnel protection without the need for additional controls on the H_2S concentration in the cargo itself.

6. PRODUCT HANDLING AND SAFETY PRECAUTIONS

Since residual fuel oils may contain H_2S, normal operations of loading/unloading and tank sampling and gauging should take the potential presence of H_2S into account. It is therefore recommended that all facilities dealing with residual fuel oil have an H_2S safety awareness programme in place and that all employees dealing with product handling are well-trained. Details of such a programme will be location specific, but the following elements should at least be considered:

- H_2S awareness and training plan;
- Permit to work system and 'toolbox' meeting prior to starting work;
- Confined space entry procedures and training;
- H_2S detection systems, including personal alarms;
- Emergency evacuation and operational procedures;
- Personal protective equipment including supplied air respirators, eyewear, and flame-retardant clothing;
- Specific operating instructions for cargos with high liquid phase H_2S concentrations; and
- Near miss and incident reporting, with follow-up plans [19].

Routine operations in open or well-ventilated spaces are unlikely to present serious hazards when H_2S concentrations in the liquid fuel are low (that is, up to 2.00 mg H_2S/kg fuel). However, inside tanks and in the immediate proximity of open tank hatches and tank vents, H_2S levels could exceed both short-term and long-term OELs although vapour-phase H_2S levels in these locations are not likely to approach the levels at which sudden and serious health effects will occur. Nonetheless, personnel precautions and training should always be enforced even when the liquid-phase H_2S concentrations are known to be low.

Because H_2S is denser than air, it should also be recognised that higher concentrations of H_2S may be found in low points, such as in confined spaces including sumps and pits that are not well ventilated. It is therefore important that proper procedures and training are in place for all personnel who are required to work near open tank hatches (e.g. when gauging tanks) or when working for prolonged periods close to tank vent outlets [20]. This includes the use of personal H_2S alarms, supplied air respirators, and other PPE (where required), when other safety management options cannot guarantee personnel safety.

During some occasional or non-routine operations, such as during inspections and maintenance, personnel entry into tanks (even when the tanks are nominally empty) presents many very serious hazards in addition to those due to H_2S. Rigorous safety procedures are required for any occasions when personnel must enter enclosed work spaces, such as storage tanks.

When dangerously high amounts of H_2S are suspected or measured around a spilled product, additional or special actions may be warranted, including restricting access to the spill area, using special PPE, such as a self-contained breathing apparatus, and the use of proper evacuation procedures. A specific assessment of inhalation risks due to the presence of H_2S in the vapour phase of storage tank headspaces, confined spaces, and product residue, waste and waste water containers and in the area surrounding unintentional releases should be made in order to determine the most appropriate personnel protection and control measures for the given circumstances. Proper procedures and personnel training based on facility assessments are also important and should be regularly reinforced.

It is beyond the scope of this document to cover these considerations in detail, however, and specialist advice should be sought before encountering these situations.

7. ACRONYMS

ACGIH®	American Conference of Governmental Industrial Hygienists®
ASTM (International)	American Society for Testing Materials (original name)
DNVPS	DNV Petroleum Services
EI	Energy Institute (formerly called the Institute of Petroleum)
H_2S	Hydrogen Sulphide
IMO	International Maritime Organisation
IP	Institute of Petroleum
ISO	International Standards Organisation
MAC	Maximally Allowed Concentration
OEL	Occupational Exposure Level
PPE	Personal Protective Equipment
ppmw	parts per million (weight basis)
ppmv	parts per million (volume basis)
SCOEL	Scientific Committee on Occupational Exposure Limits (of the European Commission)
STEL	Short-term Exposure Limit
TLV	Threshold Limit Value
TWA	Time Weighted Average
VPP	Vapour Phase Processor

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- Harry Read, Energy Institute, United Kingdom
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- Klaas den Haan, Safety Science Executive, CONCAWE
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