IMPCA
INTERNATIONAL METHANOL PRODUCERS & CONSUMERS ASSOCIATION

IMPCA

"METHANOL SAMPLING METHODS"

"Procedures for Methanol Cargo Handling on Shore and Ship"

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Introduction

A subcommittee, chaired by Mr. Peter Meeusen of Inspectorate Bureau Veritas, Rotterdam has prepared a proposal for specifications for "Standardisation of Methanol Sampling Methods", i.e. an "IMPCA Inspection Manual" for use during surveying operations, , Members of the committee are presented at the end of this document.
It is the intention that these sampling specifications shall contribute to more efficient logistical operations in the movement of methanol from the producer to the end user.
Members of IMPCA may notify on documents that "Methanol sampling has been taken in accordance with the procedures as laid down in the latest version of IMPCA Methanol Sampling Methodes, f.i. by use of the IMPCA approval sign as shown below. Membership in IMPCA is open to all companies having paid the annual fee for membership and whose activities involve production of methanol, marketing or distribution or the use of methanol as feedstock in further chemical process or for fuel purposes.

REFERENCES:

- IMO – ICS -Tanker Safety Guide
- ISGOTT – International Safety Guide for Oil Tankers and Terminals
- ISGINTT – International Safety Guide for Inland Tank-Barges and Terminals
- API MPMS – Chapter 17.12 / EI HM 51 – Procedure for bulk liquid chemical cargo inspection by cargo surveyors
- API MPMS - Chapter 17.8 – Guidelines for pre-loading Inspection of Marine Vessel Cargo Tanks
- ASTM E 300 – Standard Practice for Sampling of Industrial Chemicals
- API Recommended Practice 1141 – Guidelines for Confined Spaces Entry on Board Tank Ships in the Petroleum Industry.
- IBC code – International Code for the Construction and Equipment of Ships carrying Dangerous Chemicals in Bulk.

All of the guidance and procedures described in this document are based on these references documents, which still fully apply. The mentioned instructions in these documents are an uncomplicated excerption but not a replacement of the international standards and norms. Furthermore local regulations and legislation are applicable, and cannot be superseded by anything described here below.

Brussels October 2014

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CONTENT

"METHANOL SAMPLING METHODS"

I. PROCEDURES related to cargo handling / product movements:

1. **Loading**
2. **Discharge**
3. **Transhipment**

II. SAMPLE BOTTLES:

A. Bottle:

- Colourless glass bottles have to be used
- Bottle cap has to be UV resistant and should have no influence on quality of methanol.

B. Labels:

- Correct date & time of sampling has to be placed on label.
- Place – exact location point of sampling will be written
- Sampling type has to be correct described, including stipulating open or closed sampling.

C. Samples:

All samples will be retained for a period of 3 months.

D. Sealed samples:

Every seal has to be a unique number.

E. Sampling:

- Tap sample is not representative
- Open sampling is preferable.
- Please follow safety guidelines conform to the latest instructions, related to industry standards.

III. SAFETY DURING INSPECTION:

Tanks can only be entered, if appropriate tank entry permit is in place.

IV. VISUAL TANK INSPECTION:

- Check for moisture, wet surfaces and odourless. Be aware of deviating odour.
- Extra attention has to be given to problem areas:
  a) Visible residues
  b) Shadow areas of butterworth cleaning machine
  c) Heating coils and esp. underneath heatingcoils

d) Deepwell pump and dry sump at deepwell pump
e) Loadingline / dropline inside
f) Ladder, level indicators, thermocouples
g) UTI pipeline

- Check all cargo lines:
  a) Cross over at manifolds with blind flanges removed and open valves
  b) All taps has to be drained and liquid free
- Visual inspection can be followed by wall wash procedure

V. CHOICE OF CORRECT SOLVENT for wall wash procedure:

- Most of the time methanol is a good solvent for majority of previous cargoes.
- Methanol is a poor solvent for animal and vegetable oils & fats, heavy petroleum products and lubricants. MEK and hexane are a good solvent.
- Demi-water is a better solvent compared to methanol for acids & caustics and salt.

SOLVENT	**Previous Cargo:**
Demi-water	Inorganic Acids: e.g. hydrochloric acid – nitric acid – sulphuric acid – phosphoric acid
Demi-water	Organic acids: e.g. formic acid – acetic acid – propionic acid
Demi-water	Inorganic caustics: caustic potash – caustic soda
Demi-water	Salt from seawater, sodiumchloride
Hexane and MEK	Animal & vegetable oils & fats – biodiesel – FAME – heavy petroleum products and lubricants MEK = Methyl Ethyl Ketone
Methanol	for most other products and organic caustics

VI. MINIMUM QUALITY of standard methanol for use as wall wash solvent for :

- Chlorides, as Cl-, ppm — max. 1.0
- Colour ,Pt/ Co — max. 5
- Watermiscibility — passes
- Permanganate Time Test, minutes — min. 60
- Water, % m/m — max. 0.10
- Nonvolatile Matter, mg/ 100 ml — max. 2
- Odour — nonresidual

MINIMUM QUALITY of methanol UV-grade for use as wall wash solvent for UV methanol cargo to load:

- See minimum quality as above
- UV Absorbance at 220 nm, 10 mm — max. 0.30
  UV Absorbance at 275 nm, 10 mm — max. 0.15
  and a smooth UV curve

VII. TANK INSPECTION BY MEANS OF WALL WASHING:

1. Equipment:

- We use PVC or nitriles gloves for skin protection and in order to prevent for chlorides contamination from hands.
- Laboratory wash bottle
- Selected solvent: methanol – demi-water - hexane – MEK methylethylketone
- Wall wash funnel, by preference from stainless steel

2. Procedure:

- Rinse the wash bottle and funnel (and sample bottle) with a small proportion of solvent
- Make a selection of minimum 5 spots and maximum 9 spots, pending on tankcapacity, divided over the tankwalls, basis visual inspection.
  Spot are 1.0 meter high – wide 10 centimeter, equals to 1000 sq. cm or 10 sq. dm
  Five spots equals to 50 sq. dm or ½ square meter for ½ liter solvent.
- Spray tank wall with a steady stream of solvent, ca. 1 meter above the funnel.
  The wash liquid runs down the wall and has to be collected with funnel in the sample bottle. Check visual for appearance of collected wash sample.
- Repeat for other spots and collect in same sample bottle, per shipstank.
- Inspect visual spots, after drying.
- Original wash solvent has to be kept as reference:
  a) In order to allow additional testing
  b) In order to verify wall wash solvent as used
  c) In order to use as blanco, esp. for Permanganate Time Test and UV testing.

VIII. PROCEDURE A: LOADING

1. Shoretank sampling, prior loading.

- A minimum of 2 x 1 litres has to be taken for each shoretank, excluding samples for distribution.
- At the time of sampling, our report will be guided with a print out from actual quantity, for verification of measurements.
- One time 1 litre per shoretank should be delivered against Receipt of Samples to C/O, destined for cargo receivers.
- In case a shoretank is not allowed to be taken, a shoreline sample at start of loading, after emptying shoreline quantity, can be used as shore reference.

2. End of shoreline, prior arrival of vessel:

- 1 x 1 litre will be taken for keypoints testing and retain

3. **Inspection of ships' cargo tanks:**
   - A visual inspection of each of the ships tanks is the minimum requirement, preferable, if allowed by physical entrance of each tank.
   - Visual inspection can be followed by wall sampling and testing, basis previous cargoes.
   - Wall wash procedure acc. section VII – item 2 can be followed.
   - Limitations related to adjacent tank temperatures are not stated.
   - All inspections has to be done on a safe and professional way.

4. **Manifold sampling:**
   A quantity of 1 x 1 litre has to be taken at start of loading.

5. **Pumpstack sampling:**
   We recommend that samples will be taken at pumpstack:
   - In order to verify cleanliness of shipslines, which were impossible to inspect as inaccessible.
   - When previous cargoes are high boilers – vegetable & animal oils & fats – coloured. A pumpstack sampling can be examined visual and tested for keypoints, upon choice of cargo inspector.
   - Based on visual inspection and /or keypoints testing, a pumpstack drain can be followed.

6. **First foot sampling:**
   - Sampling has to be done with a minimum quantity.
     The liquid level will not exceed 35 cm.
   - Half litre bottles will be used. In case of extra sampling, we recommend the use of more ½ litre bottles.
   - Samples should be taken from shipstank:
     a) Most deviating from previous cargoes
     b) Highest potential risk on contamination
     c) Most far away from ships manifold, in order to have view on longest shipslines.
   - In case of more high boilers as previous cargoes or on judgement of cargo inspector, we recommend a second first foot sample in other cargo tank.
   - Quality testing is to the experience of the cargo inspector.
   - In case of quality failure on first foot material, it is up to the judgement of the inspection company, to place a second foot in same tank or other cargotank.

7. **Ships tanks after loading:**
   - Preferred open sampling.

- A minimum of 1 x 1 litre per shipstank for cargo inspector.
- A minimum of 2 x 1 litres for the whole cargo (one shipstank).

IX. PROCEDURE B: DISCHARGE

1. Shoretank inspection:

- Dedicated methanol shoretank can be inspected from roof level.
- In case different previous cargo, a visual inspection, can be followed by wall wash sampling.

2. Shoretank sampling, prior discharge:

- Minimum 1 x 1 litre will be taken for reference
- A measurement of quantity at time of sampling is advised.

3. Sampling of shipstanks, prior discharge:

- Samples are taken at first call in port, in order to avoid delay by analysis time.
- A quantity of 1 x 1 litre per shipstank will be taken.
  A quantity of 2 x 1 litre is a minimum per cargo.
- Method of sampling: preferable open sampling.

4. Collect samples related to loadport:

- Request for samples to Chief Officer.
- Sign document related to cargo for receipt of samples.
- Collect as most as possible number of samples.

5. Sampling at the end of shoreline, prior arrival of vessel:

We recommend that in case of quantity on shore, shoreline will be filled to end at jetty, in order to take samples and to verify quality prior arrival of the vessel.
A specific request has to be done to the terminal.

6. Measurement of shipstanks, prior discharge:

- The actual volume has to be given to the Loadingmaster of the terminal, in order to be sure, that quantity at actual temperature fits in the shoretank(s).
- A copy of ships measurements/ ullage reports from loadport (after loading) and disport (before discharge) has to be handed over to the Loadingmaster.

7. Manifold sampling:

Extra sampling from manifold has to be drawn, even when end of shoreline was taken for judgement.

8. Shoreline sampling:

a) Empty shoretank:
   Shoreline samples will be taken to the nearest point, most close to the shoretank.
b) Shoretank has pre-contents:
   Tankpipeline is most likely full to the pumproom.
   Shoreline samples are taken, where lines leaves at pumproom.

9. Shoretank first foot sampling:
First foot has always to be taken, in case of other previous cargo.

10. Check emptiness:
- Verify emptiness of all ships tanks at end of discharge prior disconnect hoses.
- Control provisional outturn in order to establish that assumed quantity of cargo is pumped to shore.

11. Shoretank sampling, after discharge:
- If shoreline has to be emptied, acc. terminal regulations, contents has to be blown in shoretank prior sampling.
- A minimum of 2 x 1 litres has to be taken from each shoretank.
- Final outturn will be taken by preference 24 hours after final discharge.

X. PROCEDURE C: TRANSHIPMENT

C1: Direct transhipment:
- See also Loading & discharge procedures
- Manifold samples has to be taken at both end of the hose(s).
- The cargo inspector has to verify cleanliness of the hoses.

C2: Indirect transhipment – from supplying vessel over shoreline to receiving vessel:
- See also Discharge Procedure B for supplying vessel.
- See also Loading Procedure A for receiving vessel.
- Sample from shoreline has to be taken at start of transhipment

XI. PROCEDURES A+B+C2 : Prepumping
- In case of quality failure at start of operation, a prepumpcontainer should be available for separating a smaller amount of deviating quality.
- At loading and esp. transhipment, the prepumpcontainer quantity is part of the cargo and all possible efforts has to be taken to add the quantity to the cargo after safe judgement.

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