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# Determination of oil in water and soil

with the oil measuring systems,  
type OMS-1 and PW-2 of the company  
dvb environmental measurement

A collection of working- and  
laboratory instructions.  
Based on existing German  
industrial standard methods  
(DIN), adapted to the conditons  
of industrial effluents.

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subject to alternations



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**ACCESSORIES:**

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**Accessories especially for the PW-2/OMS-1**

Beaker, 250 ml, low typ	1 pc.
Glass bowl, 500 ml, d. 115 m	1 pc.
Beaker, 25 ml, low type	2 pcs.
Measuring cylinder, 250 ml, high type, graduated	2 pcs.
Measuring cylinder, 50 ml, high type, graduated	2 pcs.
Measuring cylinder, 25 ml, high type, graduated	2 pcs.
Microliter syringe, 25 µl	1 pc.
Measuring flask, 100 ml with NS-PE-stopper and glass stopper NS 12/21	1 pc.
Burettes bottle, 1000 ml with glass stopper NS 29/32	1 pc.
Automatic pipettes, 25 ml	1 pc.
Steel tweezers, 18/8, curved	1 pc.

**Accessories for the determination of difficult to extract wastewater-mud-  
and soil samples**

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Separating funnel, pear-shaped with Teflon stopcock and NS-PE-stopper, nominal volume 500 or 1000 ml	1 pc.
Chromatographic column according to DIN 38409, Part 18, complete	1 pc.
Erlenmeyer flask, 250 ml with glass stopper NS 45/40	1 pc.
Glass funnel 100/5 mm	1 pc.
Glass rod 250/6 mm	1 pc.
Test tube rack (wood) for 12 test tubes	1 pc.
Test tubes, 18 x 180 mm	6 pcs.
Cork stopper, conical, 16/19/22 mm	6 pcs.
Powder funnel out of polypropylene 65/15 mm	1 pc.
Chemist spoon 150 mm	2 pcs.



Retort plate (210 x 130 mm)	1 pc.
Retort rod 600 mm	1 pc.
Retort ring with bosshead, d. 130 mm	1 pc.
Retort clamps with bosshead, d. 40 mm	2 pcs.

#### **CHEMICALS:**

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- Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) = 0.5 mol/l \*
- Sodiumsulphate anhydrous ( $\text{Na}_2\text{SO}_4$ ) for analysis
- Magnesiumsulfate Heptahydrate ( $\text{MgSO}_4 \times 7 \text{H}_2\text{O}$ ) for analysis
- Aluminiumoxide 90 active ( $\text{Al}_2\text{O}_3$ )
- 1,1,2-Trichlorotrifluoroethane ( $\text{C}_2\text{Cl}_3\text{F}_3$ ) for the spectroscopy (other solvents on request).
- Squalane ( $\text{C}_{30}\text{H}_{62}$ ) for the gaschromatographic

(Other calibration oils can also be applied !

Please consult dvb environmental measurement before use !)

#### **CONSUMABLES**

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- Teflonfilter
- Vinyl gloves
- Folded filter, d. 185 mm
- pH-indication stripes

The listed accessories and consumables can be obtained at dvb environmental measurement.

\* Is not obtainable at dvb environmental measurement !

#### **GENERALLY:**

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The measuring device, type PW-2 has the same function as the measuring device, type OMS-1 in operation mode "A". That means, that if in the further text measurements or calibrations in operation mode "A" are mentioned, these hints or prescriptions are also valid for the PW-2.



## Zero calibration

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A zero calibration is always performed after switching the device on again.  
The device requests "CAL":

It should be taken care, that the device has been warmed up for approx. 30 min. before carrying out the zero calibration.

Otherwise the device might perhaps request for a new zero calibration during the day.

### Example:

At a sample measuring "CAL" is displayed instead of a measuring value.

### Cause:

1. The zero calibration has been performed in cold state of the device (warm-up running time > 30 min.).  
The sample is to be found in the negative range (< 0) that means: the infrared spectroscopic absorption is lower than the one of the previous zero calibration --> measuring value lower than 0 = display reading: "CAL".
2. A calibration with another solvent has been made (from another bottle) and the new solvent has a higher degree of purity than the solvent which has been used before.
3. The degree of purity of the used solvent has been increased by aluminium oxide.

### Example:

The device has been zero calibrated.

Afterwards the sample (oil content: 0 mg/l) has been externally extracted and poured over aluminium oxide.

After the measurement the device requests for "CAL", since the solvent has been treated by the aluminiumoxide, that means infrared active residual concentrations have been eliminated.

4. Contrary to expectations the tap water is contaminated, which has been used for the zero calibration in order to reach the necessary hydrostatic pressure. Due to it already at the zero calibration hydrocarbons have been extracted from the tap water, which result in a contaminated solvent extract for the setting of the zero point.

### Procedure:

1. Fill the following volumes through the filling funnel into the extractor glass:
  - 25 ml pure 1,1,2-Trichlorotrifluoroethane
  - 250 ml clean, oilfree water (tap water)
2. Seal the filling funnel with the funnel lid and press the key button "Zero Cal".
3. The measuring runs automatically in the device. The display shows 0 and the Auto-Start-key flashes.



### **Generally instructions for the calibration of the device:**

- It must be taken care, that the zero calibration and the final value calibration are carried out in the same operation mode and with the same extraction time than the later sample measurings.

#### **E.g.:**

Sample on operation mode "C" and extraction time: 4 min.

Calibration: Select operation mode "C" and extraction time: 4 min..

- Also it must be taken care, that the calibration and the sample measuring is carried out with the same solvent.

### **Zero calibration (only OMS-1)**

#### **Procedure:**

Select operation mode "B"!

1. Detach side panel with the CAMLOC-screwing.
2. Set selector valve to direct injection.  
(Set selector valve to passage from syringe coupling in the front panel to measuring cell)  
Lever points to the left !
3. Fill sample syringe with 5 ml solvent free of hydrocarbons (zero solution) and rinse the measuring cell over the separation screwing by several injections and drawing ups.

#### **HINT:**

Always inject the solvent extract slowly into the measuring cell.

Take care that every time the LED for the measuring cell flashes !

4. Afterwards discard the zero solution and inject slowly new solution until the LED for the measuring cell flashes.
5. Now press the "Zero Cal"-key button.
6. The OMS-1 turns immediately to the mode "P" (sample measuring).
7. After the measurement the display shows "0", and the "Auto Start"-key flashes.



### Calculation example calibration solution

Density of Squalane: 0.81 kg/l

0.81 kg correspond to a volume of 1 Liter

810 g correspond to a volume of 1000 ml

20.25 g correspond to a volume of 25 ml

202.5 mg correspond to a volume of 250  $\mu$ l

20.25 mg correspond to a volume of 25  $\mu$ l

### That means:

25  $\mu$ l Squalane dissolved in 1 Liter liquid correspond to a concentration of 20.25 mg/l, that means that 25  $\mu$ l Squalane dissolved in 100 ml fluid correspond to a concentration of 202.5 mg/l.

### Preparation of standard solution

You need:	1 Microliter syringe	for 25 $\mu$ l
	1 Measuring flask with glass stopper	for 100 ml
	Squalane	25 $\mu$ l
	1,1,2-Trichlororifluoroethane	100 ml

1. Fill up the microliter syringe with 25  $\mu$ l Squalane, subsequently wipe of the needle of the syringe.
2. Inject the filled up Squalane into a 100 ml measuring flask. Wipe off the last drop on the needle point on the inside of the flask neck.
3. Fill up the measuring flask with solvent up to the calibration line.
4. Seal the measuring flask with a glass stopper and shake well (turn it to the top several times.)

### Calibration on mg/l

The such prepared solution corresponds to a hydrocarbon concentration of 203 mg/l taking into account the density of Squalane (density = 0.81 kg/l) (refer to calculation example calibration solution page 10).



### Calibration on ppm (parts per million)

The such prepared solution corresponds to a standard concentration of 250  $\mu\text{l/l}$  (= 250 ppm). When performing the calibration on ppm it is more sensible to prepare a standard on 200 ppm (= 20  $\mu\text{l}$  calibration oil on 100 ml solvent), since the linear relation between extinction (absorbance) and concentration at concentrations higher than 200 mg/l turns into a non-linear relation.

#### Hint for calibration:

Apart from Squalane also other single hydrocarbons or hydrocarbon mixtures can be used for the calibration (preparation of the standard solution). With reference to the measuring-, detection- and calculation principle Lambert-Beer-Law) the obtained measuring value is as much exact as the hydrocarbon to be measured (or the hydrocarbon mixture) is more similar to the calibration oil (that means as much similar as the group extinction coefficients of the hydrocarbon to be measured and the calibration hydrocarbon are to each other).

#### HINT:

It is also possible to prepare a standard of for example 100 mg/l and to calibrate the device on this standard.  
In this case series of dilutions are recommended since the preparation with the microliter syringe at smaller standards becomes too inexact.

### Final value calibration

#### How often?

- varies (daily up to monthly) depending on operation (slightly or highly contaminated samples) ↵  
Matter of experience !  
Slightly contaminated wastewater samples, **see page 16**.  
Highly contaminated wastewater samples: **see page 19**.
- when selecting a new operation mode and extraction time
- when using solvent from another charge (bottle, barrel, etc.)  
or using another solvent.





## Working instructions 1.0

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for the final value calibration at the OMS-1 in operation mode "A", "C" or "D"

OMS-1:

PW-2:

Select operation mode !

Select extraction time !

Select extraction time !

Set selector valve to  
passage from extraction to  
measuring cell.

(Cock points to the bottom.)

1. Fill the following fluid volumes over the filling funnel into the extractor glass:

25 ml standard solution

250 ml clean, oilfree water (tap water)

2. Seal filling funnel with funnel lid and press the "Auto-Start"-key button.

3. The measuring in the device runs fully automatic. After 3 rinsings the measuring value is displayed in mg/l.

### HINT:

At the OMS-1 it must be taken care, that at calibration in operation mode "D", the rinsings and the measuring after the extraction and the settling time must be started again by pressing the "Auto-Start"-key button.

4. The display indicates a 3-digit value.

5. If the displayed value does not correspond to the nominal value of the standard solution adjust it by a screw driver on the transconductance potentiometer (beneath the display on the front panel).

6. Perform a control measuring (refer to point 1-5).

7. If the displayed value corresponds to the prepared standard solution the final value has been calibrated.



### **Working instructions 1.1 (only OMS-1)**

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#### **for the final value calibration in operation mode "B"**

Select operation mode "B" !

1. Detach the side panel with the CAMLOC-screwing.
2. Switch selector valve to direct injection.  
(Set selector valve to passage from syringe coupling in the front panel to measuring cell)  
Lever points to the left!
3. Fill sample syringe with 5 ml standard solution and rinse the measuring cell over the separation screwing by several slowly injections and drawing ups.  
Take care that every time the LED for the measuring cell on the flow chart of the front panel flashes !
4. Afterwards discard the standard solution and inject slowly new solution until the LED for the measuring cell flashes.
5. Now press the key button "Auto-Start".
6. The OMS-1 turns immediately to the mode "P" like sample measuring.
7. After the measurement a 3-digit-value is displayed.
8. If the displayed value does not correspond to the nominal value of the standard solution, adjust the value with a screw driver on the transconductance potentiometer (beneath the display of the front panel).
9. Perform a control measuring.
10. If the displayed value corresponds to the prepared standard solution, the final value is calibrated.

#### **HINT:**

Always rinse the measuring cell before each measurement by several slowly injections of the extract to be measured !

#### **Selection of the measuring range**

1. Large measuring range: 0 - 200 mg/l
2. Small measuring range: 0 - 20 mg/l



## 1. Large measuring range

In case of the proportion of solvent/sample 1:1 the large measuring range is to be selected:

Solvent: 25 ml  
Sample: 25 ml  
Water: 225 ml

**Result:**      **mg/l**

**Example:** A wastewater sample contaminated with 10 mg/l hydrocarbon is extracted in the proportion 1:1.  
Result: 10 mg/l

## 2. Larger or smaller measuring range

In case of the proportion solvent/sample 1:10 it can be selected between the measuring ranges:

Solvent: 25 ml  
Sample: 250 ml

Result: mg/l x 0.1 (in larger measuring range)  
mg/l x 1 (in smaller measuring range)

### Example:

A wastewater sample contaminated with 10 mg/l hydrocarbons is extracted in the proportion 1:10.

Result in larger measuring range:      100 mg/l    : 10    =      10 mg/l  
Result in smaller measuring range:    10.0 mg/l

### HINT:

The smaller measuring range is also calibrated with the standard 203 mg/l.  
The smaller measuring range has the function of a :10-key.

### Series of preliminary analysis for the classification of the samples

For a direct measuring (filling from the top) of the samples in operation mode "A", "C" or "D" several limiting conditions must be observed:

- The content of solid- or suspended matters should not exceed 20 mg/l.
- No visible oil- and grease substances may be contained.
- The sample may not foam when shaking.

**By a series of preliminary tests in boundary cases uncertainties can be eliminated.**

### HINT:





**REMARK:**

- The less sample or/and the more solvent is taken, the more inexact are the measuring results. If the measuring accuracy should not be sufficient anymore, please refer to the working instructions "Measuring of difficult to extract water samples after corresponding pretreatment", perhaps in accordance with the working instructions for the "Measuring of residual hydrocarbons after separation of the polar substances (refer also to DIN 38409 Part 18).
- In case no good phase separation has been observed: Proceed according to working instructions "Measuring of difficult to extract water samples with corresponding pre-treatment".

**NOTE (only OMS-1):**

If the series of preliminary tests has shown that a phase separation happened first after 1.5 min.:

Select operation mode "C".

At operation mode "D":  
(only OMS-1)

- If the preliminary tests have shown that e.g. first after 10 min. a perfect phase separation happens, it can be measured in operation mode "D" (filling from the top).
- At operation mode "D" the "Auto-Start"-key must be pressed after the extraction to interrupt the settling time and to continue the measuring process (rinsings and measuring).
- For this the zero- and final value calibration can be carried out in operation mode "A" or "C" and with extraction time 4 min..



**At operation mode "D" the OMS-1 can also be used as extraction appliance.**

**Example:**

A sample shall externally be extracted and be measured in operation mode "B".

1. Carry out zero- and final value calibration in operation mode "B".
2. Switch device to operation mode "D" and set extraction time to 4 min..
3. Fill the solvent (e.g. 50 ml) and the sample (e.g. 100 ml) directly into the extractor glass.
4. Press the "Auto Start"-key button. The device extracts for 4 min.. Afterwards the "Zero-Cal- and the Auto-Start-key flash.
5. It follows a free-selectable settling time, which is only interrupted by pressing the "Zero Cal" or the "Auto-Start"-key button again.
6. The solvent can now be discharged by the solenoid valves SV 1 and SV 2 by pressing the "Zero Cal." - key button. It is collected in a glass receptacle beneath the solvent outlet. Discard the first 1 - 2 ml.
7. After the solvent phase has been almost completely discharged, press the "Stop"-key-button, to interrupt the procedure and to drain the extraction unit.  
The receptacle (e.g. beaker), in which the solvent is collected, must remain beneath the solvent outlet until the extraction unit has been completely drained.

**HINT:**

By the TEFLON filter it is secured that even when not pressing the "Stop"-key water cannot enter the discharged solvent. But since due to this the TEFLON filter is highly contaminated with water and thus no solvent can pass it anymore, the filter must be exchanged.

8. Now the extract can be measured in the device directly in operation mode "B".
9. If the polar substances shall be separated this extract can be filled directly into the chromatographic column.  
You do not need sodiumsulphate anhydrous for drying since the solvent has already passed the TEFLON filter in the device, which separates residual water traces.

**Easy to extract water samples**

The series of preliminary tests has shown that a phase separation happens. That means, solvent and water separate rather well or clearly.

The wastewater can be measured directly in the device without further sample pretreatment.



## Working instructions 2.0 "low contaminated water"

### Prerequisite:

Sample does not foam when shaking and  
the content of solid substances is < 20 mg/l and  
no visible oil- and fat particles are contained and  
no solid substances sink into the solvent phase and  
no non-hydrocarbons are contained in the wastewater sample.

## Working instructions 2.0

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### Measuring of low contaminated wastewater samples

#### Prerequisite:

The device is ready for measuring, that means the start of operation, the zero calibration and the final value setting have been carried out correctly. The key "Auto-Start" flashes.

1. Adjust measuring range: (top key button)

0 - 20 mg/l key button pressed.  
0 - 200 mg/l key button in normal position.

2. Set extraction time: (switch at the bottom on the left side)

4 min. when using 1,1,2-trichlorotrifluoroethane

3. At the OMS-1 select the operation mode according to the wished settling time: "A", "C" or "D" or the operation mode, in which the calibration was carried out.

4. Take off the lid from the filling funnel.

5. Pour into the extractor glass over the filling funnel:

At proportion:

Solvent/water 1:10  
Measuring range 0 - 20 mg/l

25 ml solvent  
250 ml sample water

At proportion:

Solvent/water 1:1  
Measuring range: 0 - 200 mg/l

25 ml solvent  
25 ml sample water  
225 ml tap water



**HINT:**

For the correctly carrying out of 3 rinsings and one measurement at measuring procedures in operation mode "A", "C" or "D" every time a total fluid volume of 275 ml must be contained in the extractor glass (for generation of the necessary hydrostatic pressure).

**Take care that always first the solvent and then the water is filled in.**

6. Place lid on the filling funnel.
7. Press the key button "Auto-Start". The measuring program runs now automatically:
  - Extraction
  - Settling process
  - 3 rinsings
  - Measuring
8. The display indicates the measuring value in mg/l.
9. Extractor and measuring cell are automatically drained off separately to make a separate collection of oil contaminated solvent and extracted sample water possible.
10. Flashing of the key "Auto-Start" again: The device is ready for the next measuring.

**Difficult to extract water samples**

The preliminary test has shown that no phase separation happens. That means, solvent and water do not separate clearly enough or not at all, an emulsion exists.

The wastewater must be pretreated:

**Working instructions 2.1: "Contaminated water"**

**Expected:**

Sample foams when shaking or / and

the solid matter content is > 20 mg/ or / and

it exists a visible oil film or / and

solid matters sink into the solvent phase  
or / and

non-hydrocarbons are contained in the sample.





## Working instructions 2.1

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### Measuring of contaminated wastewater samples

1. Select measuring range.
2. At the OMS-1 select operation mode "B".  
At the PW-2 set the extraction time to 0 min..
3. The sample is externally extracted in a separating funnel. Fill 50 - 1000 ml wastewater sample into a separating funnel. It should be taken care that the sample is homogeneous, otherwise it is recommended to extract the wastewater sample directly in the sample bottle (point 4 - 7). Afterwards transfer the mixture into a separating funnel and wait for the phase separation. Now proceed according to point 8.

homogeneous: evenly distributed dirt particles.

e.g. oils are evenly distributed in the sample.

4. For emulsion splitting magnesiumsulfate heptahydrate is added to the wastewater sample. (On approx. 500 ml sample approx. 100 g magnesiumsulfate heptahydrate are poured).
5. Acidify the mixture with sulphuric acid to a pH-value of 2 to 1.
6. Add 50 - 100 ml 1,1,2-trichlorotrifluoroethane to the mixture in the separating funnel.

**The sample- and the solvent volume can be changed depending on demand (write down volumes).**

7. Shake sample by machine or by hand for 4 min..

### HINT:

Due to the solvent a vapor pressure builds up in the separating funnel. That's why it must be taken care that the separating funnel is regularly ventilated. At the same time it should be paid attention to the vaporization ↗ can result in measuring inaccuracies. Measuring inaccuracies can be prevented by selection of a separating funnel corresponding to the volumes of sample water and solvent, in which as little as possible gas volume remains after filling in the fluids. Another measure is the treatment of the used standard solution at the final value calibration before, following the same procedure.

8. Place the separating funnel in a retort ring, wait for the phase separation.

Meanwhile the chromatographic column can be prepared:

- Fix the chromatographic column on the support.
- Place a 50 ml or 100 ml measuring flask beneath the chromatographic column.
- By means of a powder funnel 8 g aluminium oxide 90 active (6 heaped chemist spoons) are given on the frit of the chromatographic column.



9. The solvent phase is drained over sodiumsulphate anhydrous. For this place a glass funnel into an Erlenmeyer flask and cover the funnel with a folded filter, pour approx. 10 g sodiumsulphate anhydrous on the filter. Drain off solvent out of the separating funnel over sodiumsulphate anhydrous into the Erlenmeyer flask.
10. Then fill the dried extract by means of a glass funnel into the prepared chromatographic column and seal the column with bow piece and clamp. The extract passes the chromatographic column and is collected in the measuring flask.

#### **EVALUATION:**

##### **OMS-1:**

Fill up the sample syringe with the so gained extract and rinse the measuring cell by repeated injecting and drawing up of the extract.

Then discard the solution, fill up new solution and inject into the measuring cell, until the LED for the measuring cell flashes in the flow chart on the front panel.

Then press the key button "Auto-Start".

The OMS-1 turns immediately to the mode "P", like sample measuring.

After the measurement the measuring value is displayed.

##### **PW-2:**

Fill 25 ml from the obtained extract into the filling funnel of the measuring device.

Add 250 ml tap water to the solvent to obtain the total needed fluid volume of 275 ml (necessary for the hydrostatic pressure).

Seal funnel with lid. Press the key button "Auto-Start". The measuring runs automatically in the device. After 3 rinsings the measuring value is indicated in mg/l in the display. The measuring result is correspondingly put in the same formula as for the calculation of the hydrocarbon content for mud samples (working instructions 3.0).

The displayed measuring value can be taken on if it has been extracted in the large measuring range 0 - 200 mg/l in the volume proportion 1:1 (solvent to sample water).

In the small measuring range 0 - 20 mg/l it must have been extracted in the proportion 1:10.

#### **Remark:**

In case of highly contaminated wastewater samples earlier a dilution can be obtained by selecting a higher solvent volume and less wastewater volume at the sample preparation.

#### **Measuring of mud samples**

##### **HINT:**

The composition of mud samples can vary from very watery (similar to wastewater samples) up to very firm (similar to soil samples) consistency.

Depending on the consistency of the sample it should be followed either the working instructions for difficult to extract wastewater samples or to the instructions for soil samples.



### Working instructions 3.0

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#### Preparation of mud samples (consistency like difficult to extract wastewater samples)

Setting of the measuring devices:

PW-2 : Set extraction time to 0 min..

Measuring range: 0 - 200 mg/l

OMS-1: Select operation mode "B".

Measuring range: 0 - 200 mg/l

Switch selector valve to direct injection.

1. Measure out a defined quantity of mud sample into a measuring cylinder and fill into a separating funnel or an Erlenmeyer flask. Write down the quantities. (Volume of the mud sample = VS)
2. Add a defined volume of solvent to the mud sample (but at least 50 ml). Write down the volume = V1.

#### HINT:

If the mud sample had been measured out in the measuring cylinder it is recommended to measure out the solvent, which shall be added, in the same measuring cylinder to rinse also possible residues of the mud sample.

3. Shake the mud sample with the solvent by machine or by hand for 4 min..
4. Fix the separating funnel on the support and watch the phase separation. In case the sample had been extracted in an Erlenmeyer flask transfer the mixture into a separating funnel and watch the phase separation.
  - 4.1 If the solvent phase should not separate clearly the same will be poured together with the solid particles over a folded filter in a hydroextractor glass and will be centrifugalized. This so gained extract which might be still very watery must be dried by adding of sodium-sulphate anhydrous. For this add some chemist spoons of sodiumsulphate anhydrous to the extract, swing the sample slightly. Then filter off the sodiumsulphate anhydrous from the solvent phase with a folded filter.

Meanwhile the chromatographic column can be prepared:

- Fix chromatographic column on the support
  - Place a 50 ml or 100 ml measuring flask beneath the column.
  - By means of a powder funnel 8 g aluminium oxide 90 active (6 heaped chemist spoons) are given on the frit of the chromatographic column.
5. The solvent phase is drained over sodiumsulphate anhydrous. For this place a glass funnel into an Erlenmeyer flask and cover the funnel with a folded filter, pour approx. 10 g sodiumsulphate anhydrous on the filter. Drain off solvent out of the separating funnel over sodiumsulphate anhydrous into the Erlenmeyer flask.



6. Then fill the dried extract by means of a glass funnel into the prepared chromatographic column and seal the column with bow piece and clamp. The solvent passes the chromatographic column and is collected in the measuring flask.
7. If the separation of the polar substances (chromatographic column) shall be dropped, the sample can be measured after drying with sodiumsulphate anhydrous.
8. Now the extract can be measured with the OMS-1, PW-2 undiluted or diluted (with solvent).

#### **EVALUATION:**

##### **OMS-1:**

Fill in the such gained extract into a sample syringe and rinse the cell by repeated injecting and extracting the solution. Then discard the solution and fill in new solution and inject into cell until the LED of the measuring cell in the flow chart on the front panel flashes. Then press the "Auto-Start" - key button.

The OMS-1 turns immediately to the mode "P" (sample measuring).

After the measurement the measuring value is indicated on the display.

##### **PW-2:**

Fill in 25 ml of the gained extract into the filling funnel of the measuring device. Fill 250 ml tap water on solvent for the totally needed fluid volume of 275 ml (for the necessary hydrostatic pressure). Close funnel with lid. Press the "Auto-Start"-key button.

The measuring in the device runs automatically. After 3 rinsings the display indicates the measuring value in mg/l.

##### **HINT:**

At a dilution it must be taken care that the solvent extract is sufficiently intermixed.

9. Write down the volumes which are used for obtaining the wished dilution on the report sheet.
10. The display indicates the measuring result in mg/l which has to be put in the following formula.



**FORMULA 1:**

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**Formula for mud samples**

$$\frac{A \times V1 \times V3}{VS \times V2} = \text{mg Hydrocarbons/l mud sample}$$

A = Displayed value

V1 = Volume of the solvent, which is used for extraction, in ml.

V2 = Volume of the solvent, which has been taken for dilution from V1, in ml.

V3 = Volume of the solvent on which V2 has been filled up, in ml.

VS = Volume of the mud sample

**Calculation examples for mud samples**

**1st Example: Diluted solvent**

500 ml mud sample had been extracted with 50 ml solvent. From this solvent extract 1 ml had been diluted in a 100 ml measuring flask and measured in the OMS-1 /PW-2. The display showed 125 mg/l.

A = 125

V1 = 50

V2 = 1

V3 = 100

VS = 500

$$\frac{125 \times 50 \times 100}{500 \times 1} = 1250 \text{ mg/l}$$

**2nd Example: Undiluted solvent**

5 ml mud sample had been extracted with 200 ml solvent and this extract had been measured undiluted in the OMS-1/PW-2. The display showed 23 mg/l.

A = 23

V1 = 200

V2 = 1

V3 = 1

VS = 5

$$\frac{23 \times 200 \times 1}{5 \times 1} = 920 \text{ mg/l}$$



### 3rd Example: Low contaminated samples

500 ml mud sample had been extracted with 100 ml solvent and this extract had been measured undiluted in the OMS-1/PW-2. The display showed 9 mg/l.

A = 9

V1 = 100

V2 = 1

V3 = 1

VS = 500

$$\frac{9 \times 100 \times 1}{500 \times 1} = 1.8 \text{ mg/l}$$

### Working instructions 3.1

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#### Preparation of mud samples (consistency like soil samples)

Setting of the measuring devices:

PW-2 : Set extraction time to 0.  
Measuring range: 0 - 200 mg/l

OMS-1: Select operation mode "B".  
Measuring range: 0 - 200 mg/l  
Switch selector valve to direct injection.

1. Weigh 5 - 50 g mud sample into a 250 ml Erlenmeyerflask (with ground stopper).  
E = Weight of mud sample in mg.
2. Add sodiumsulphate anhydrous to the sample and mix (pound possible nodules with a glass rod) until it seems powdery-dry (i.e. no sample sticks to the wall of the flask and no nodules are build up when shaking).
3. Add 50 - 100 ml solvent to the dry mud sample.
4. Shake sample by machine or by hand for 4 min..

Meanwhile the chromatographic column can be prepared.

- Fix the chromatographic column on the support.
- Place a 50 or 100 ml measuring flask beneath the column.
- By means of a powder funnel 8 g aluminium oxide 90 active (6 heaped chemist spoons) are given on the frit of the chromatographic column.



5. Put a glass funnel in a dry, fat free receptacle and cover it with a dry, fat free folded filter. Then pour the sample over the filter. Fill the solvent extract into the chromatographic column and seal the column with the bow piece and clamp

**or**

cover a glass funnel with a dry, fat free folded filter and filter the sample directly into the chromatographic column. Then seal the column with bow piece and clamp.

6. If the separation of the polar substances (chromatographic column) shall be dropped, the sample can be measured after filtration of the solvent extract.
7. Now the extract can be measured with the OMS-1, PW-2 undiluted or diluted (with solvent).

### **EVALUATION:**

#### **OMS-1:**

Fill in the such gained extract into a sample syringe and rinse the cell by repeated injecting and extracting the solution. Then discard the solution and fill in new extract and inject into cell until the LED of the measuring cell in the flow chart on the front panel flashes. Then press the "Auto-Start" - key button.

The OMS-1 turns immediately to the mode "P" (sample measuring). After the measurement the measuring value is indicated on the display.

#### **PW-2:**

Fill in 25 ml of the gained extract into the filling funnel of the measuring device. Fill 250 ml tap water on solvent for the totally needed fluid volume of 275 ml (for the necessary hydrostatic pressure). Close funnel with lid. Press the "Auto-Start"-key button.

The measuring in the device runs automatically. After 3 rinsings the display indicates the measuring value in mg/l.

#### **HINT:**

In case of dilution take care, that the solvent extract is sufficiently intermixed.

8. Write down the volumes used for obtaining the wished dilution on the report sheet.
9. The measuring result is correspondingly put in the same formula as for the calculation of the hydrocarbon content of soil samples (working instructions 4.0, **refer to page 26**).



## Working instructions 4.0

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### Measuring of soil samples

Setting of the measuring devices:

PW-2 : Set extraction time to 0 min..

OMS-1: Select operation mode "B".

1. Pour 5 - 50 g soil sample into a 250 ml Erlenmeyerflask (with ground stopper).  
E = weight of soil sample in mg/l.
2. Add sodiumsulphate anhydrous to the sample and mix (pound possible nodules with a glass rod) until it seems powdery-dry (i.e. no sample sticks to the wall of the flask and no nodules are build up when shaking).
3. Add 50 - 100 ml solvent to the dry soil sample.
4. Shake sample by machine or by hand for 4 min..

Meanwhile the chromatographic column can be prepared.

- Fix the chromatographic column on the support
  - Place a 50 or 100 ml measuring flask beneath the column.
  - By means of a powder funnel 8 g aluminium oxide 90 active (6 heaped chemist spoons) are given on the frit of the chromatographic column.
5. Put a glass funnel in a dry, fat free receptacle and cover it with a dry, fat free folded filter. Then pour the sample over the filter. Fill the solvent extract into the chromatographic column and seal the column with the bow piece and clamp

**or**

cover a glass funnel with a dry, fat free folded filter and filter the sample directly into the chromatographic column. Then seal the column with bow piece and clamp.

6. If the separation of the polar substances (chromatographic column) shall be dropped, the sample can be measured after filtration of the solvent extract.
7. Select measuring range 0 - 200 mg/l.
8. The extract can be measured diluted or undiluted in the OMS-1/PW-2.

#### **At the PW-2:**

Pour 25 ml of the diluted or undiluted extract into the device.  
Add 250 ml tap water and press the key button "Auto-Start".





**At the OMS-1:**

Fill the sample syringe with 5 ml of the extract and rinse the measuring cell with the solution. Then discard the solution and inject new solution in the cell until the LED of the measuring cell flashes. Now press the key button "Auto-Start".

**HINT:**

In case of a dilution it must be taken care that the solvent extract is intermixed sufficiently.

9. Write down the used volumes for obtaining the wished dilution on the report sheet.
10. The display indicates the measuring result in mg/l, which has to be put in the formula for soil samples.
11. Additionally the concentration of dry solid matter (TS-content) of the soil sample will be determined and indicated together with the final result.

**FORMULA 2:**

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**Formula for soil samples:**

If the sample had been diluted or a different proportion sample to solvent had been selected, the following calculation formula is to be applied:

Calculation a)

$$\frac{A \text{ (mg/1000 ml)} \times V1 \text{ (ml)} \times V3 \text{ (ml)}}{V2 \text{ (ml)} \times E \text{ (mg)}} = X$$

Calculation b)

$$\begin{aligned} X \times 100 &= X \text{ weight \% hydrocarbons in the soil sample} \\ X \times 100 \times 10 &= X \text{ g hydrocarbons/kg} \end{aligned}$$

***For explanations to the used variables, please refer to the calculation of mud samples.***

E = Weight of soil sample in mg/l



**Formula for concentration of dry solid matter (TS-content)**

$$TS = \frac{\text{Weight (dry)}}{\text{Weight (moist)}} \times 100 \%$$

$$TS = X \%$$

**Formula for hydrocarbon content related to TS:**

$$\text{Hydrocarbons (TS)} = \frac{100 \%}{TS \%} \times \text{Hydrocarbon-content (moist)}$$

Hydrocarbon-content (related to TS) = X (weight % hydrocarbons) or (g hydrocarbons/kg)

**Calculation examples for soil samples**

**1 st Example:**

5105 mg soil sample had been shaken out with 25 ml solvent. 1 ml of this extract had been filled up to 100 ml and this dilution had been measured in the OMS-1/PW-2.

The display showed 83 mg/l. The concentration of dry solid matters is 67 %.

$$A = 83$$

$$V1 = 25$$

$$V2 = 1 \quad \frac{83 \times 25 \times 100}{1000 \times 1 \times 5105} = 0.0406$$

$$V3 = 100$$

$$E = 5105 \quad 0.0406 \times 100 = 4.06 \text{ weight \% hydrocarbons in the soil sample}$$

$$TS = 67 \quad \times 10 = 40.6 \text{ g Hydrocarbons/kg}$$

$$\text{Hydrocarbons(TS)} = \frac{100}{67} \times 40.6 \text{ g Hydrocarbons/kg}$$

$$\text{Hydrocarbons(TS)} = 60.59 \text{ g Hydrocarbons/kg}$$

**2nd Example:**

Due to high inhomogeneity of the soil sample 101.37 g sample had been weighed in and shaken out with 250 ml solvent. 1 ml of this extract had been filled up to 250 ml and this dilution had been measured in the OMS-1 / PW-2.

The display showed 57 mg/l.

The concentration of dry solid matters (TS-content) of the soil sample is 73.6 %.

$$A = 57$$

$$V1 = 250$$

$$V2 = 1$$

$$V3 = 250$$

$$E = 101370$$

$$TS = 73.6$$

$$\frac{57 \times 250 \times 250}{1000 \times 1 \times 101370} = 0.035$$

$$0.035 \times 100 = 3.5 \text{ weight \% hydrocarbons in the soil sample}$$

$$\times 10 = 35 \text{ g Hydrocarbons/kg}$$

$$\text{Hydrocarbons (TS)} = \frac{100}{73.6} \times 35 \text{ g Hydrocarbons/kg}$$

$$\text{Hydrocarbons (TS)} = 47.55 \text{ g Hydrocarbons/kg}$$

**HINT:**

If no dilution is present, 0 may not be used for V2 and V3. In this case the numerical value 1 at V2 and V3 is used for the calculation of the equation in order to obtain the correct result.

**Use of the chromatographic column**

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The bottom two-neck part (2) is attached on the retort stand and the glass pipe with frit is fastened with a clamp.

The measuring flask (1) is placed on the plate of the support and stuck into the bottom two-neck part.

The clamp (5) and the bow piece (4) are put next to the support. The filling of the chromatographic column with aluminium oxide is done with a powder funnel which is put on the glass pipe (3).

Then rinse the column with a little volume of sample (solvent). Fill an approx. 3 cm high solvent column on the aluminium oxide. When the solvent has passed the aluminium oxide discard the solvent.

Now fill up the column with the sample.



When the solvent has been filled in, seal the column with the bow piece and fix with the clamp (5).

When the solvent-extract has passed the aluminium oxide completely the measuring flask can be taken from beneath the column.

In order to clean the column take off the clamp (5) and the bow piece (4).

Take the glass pipe with frit from the support and tap slightly with the palm of your hand against the pipe that way that the aluminium oxide will drop out.

Now the chromatographic column is prepared for the next filling.

## **RECOVERY OF USED SOLVENT AND EXTRACTED SAMPLE WATER**

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### **1. Solvent - oil mixture**

For recovery of the solvent 1,1,2-trichlorotrifluoroethane contaminated with hydrocarbons the following procedures are available.

#### **A) Recycling plant for 1,1,2-trichlorotrifluoroethane.**

**Type: LRE-T from Dvb environmental measurement GmbH**

#### **Procedure:**

The solvent, contaminated with hydrocarbons, is pumped to an activated charcoal filter unit. The activated carbon adsorbs the contaminants and the recovered solvent passes a hose which is connected to the filter unit and runs in a clean supply bottle.

### **2. Solvent - water mixture**

For the treatment of the solvent - water mixture the following procedure is offered.

- A) Separation of the phases by a decanting bottle. After the separation from water the 1,1,2-trichlorotrifluoroethane can be feed to the 1,1,2-trichlorotrifluoroethane contaminated with hydrocarbons and correspondingly be treated further (see 1.A or 1.B).

### **3. Extracted sample water, contaminated with traces of 1,1,2-trichlorotrifluoroethane**

- A) The separated waterphase (see point 2) which still contains residual traces of 1,1,2-trichlorotrifluoroethane, can be refined by a stripping plant with activated carbon.

The complete decanter- and stripping unit is available at dvb environmental measurement.