CHARACTERISTIC, ANALYTIC AND SAMPLING OF WASTEWATER

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Domestic wastewater sources

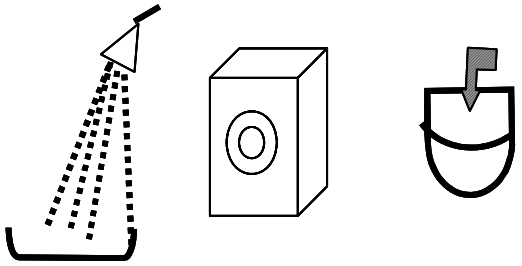
Urine

Faeces

Toilet paper (if used)

Flush water

black water (from toilets)

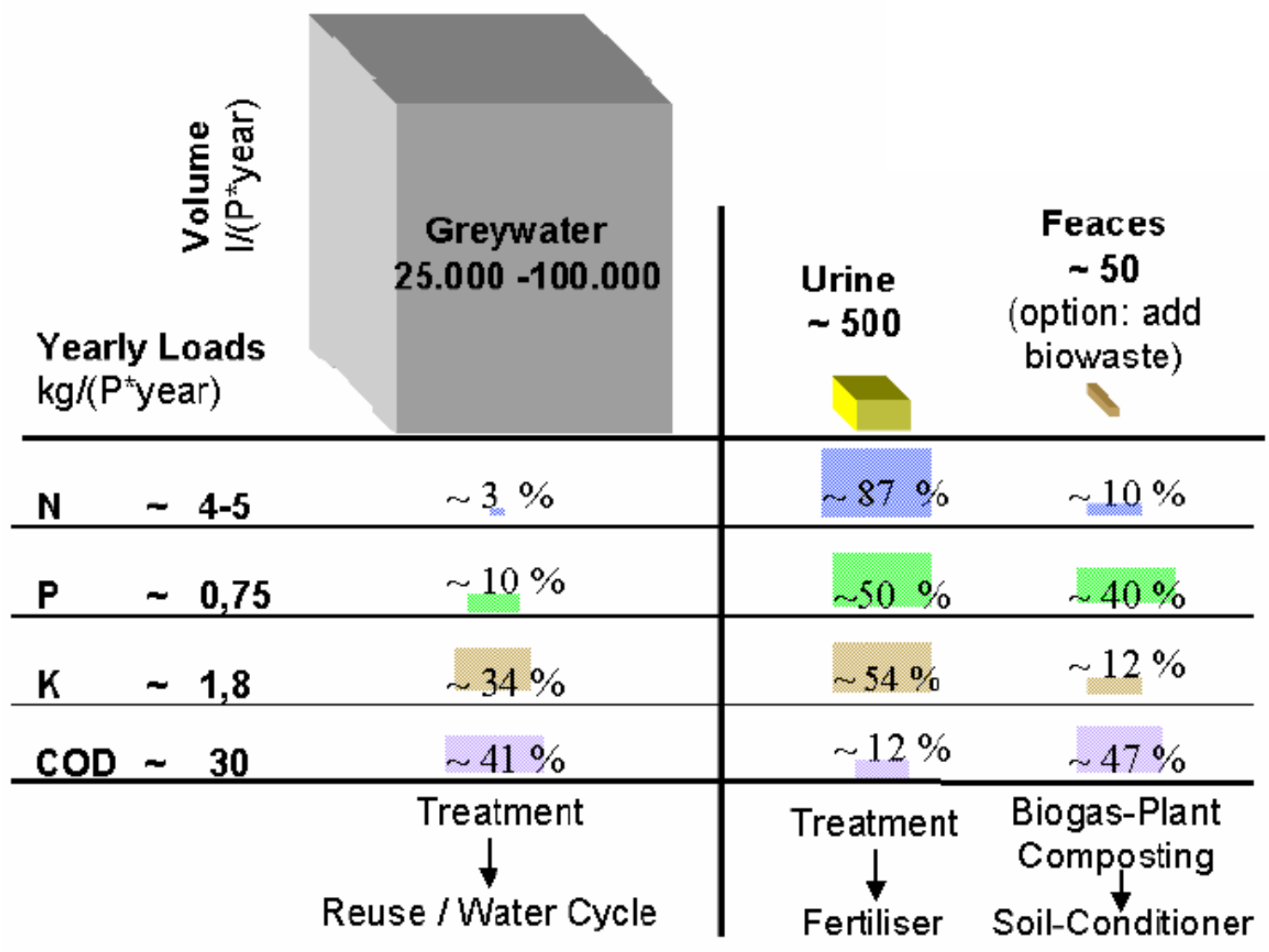


greywater

kitchen, shower, wash basin and laundry

domestic wastewater

Domestic wastewater sources



Domestic wastewater characteristics

From Henze 1982, 2001

Analysis parameters		Wastewater type			
	Unit	Concentrated*	Moderate	Diluted	Very diluted
BOD5	mg O_2/l	350	250	150	100
COD	mg O_2/l	740	530	320	210
TOC	g C/m^3	250	180	110	70
Suspended Solid	g SS/ m^3	450	300	190	120
Volatile Suspended Solid	g VSS/ m^3	320	210	140	80
Alkalinity	eqv/ m^3 *	37	37	37	37
Conductivity	mS/m **	120	100	80	70
Total Nitrogen	g N/ m^3	80	50	30	20
Total Phosphorous	g P/ m^3	23	16	10	6
Fecal coliforms (E.coli)	CFU/100ml	$5*10^8$			10^6
Fecal streptococci	CFU/100ml	10^8			10^6

* COD of Jordanian Wastewater = 1600-1930 mg/l (Halalsheh 2002)

Greywater characteristic

	Germany [Nolde 1996]		Sweden [Fittschen 1997]	USA [Brandes 1978]
	using water saving devices	using water saving devices, without kitchen greywater		
BOD_5 (mg/l)	280-360	150-250	164,6*	162
COD (mg/l)	500-600	250-430	361	366
TOC (mg/l)	-	-	-	-
N_{total} (mg/l)	8-18	-	18,1	-
P_{total} (mg/l)	2,5-4,5	-	3,9	-
Fecal coliforms (E.coli) (CFU/ml)	10^2-10^6	10^4-10^6	-	-
Fecal streptococci (CFU/ml)	-	-	-	$1,4*10^6$

Blackwater characteristic

Parameter	Vacuum toilet 0.7-1.0 l/flush [Wendland et al 2003]	Flushing toilet 4-6 l/flush [Otterpohl 2003]
COD (mg/l)	10.760	1.827
TOC (mg/l)	3.300	
N_{total} (mg/l)	1.540	274
P_{total} (mg/l)	254	46
K (K_2O) (mg/l)		85
Fecal coliforms (E.coli) (CFU/100ml)	$2*10^8$	

Preservation techniques of wastewater samples

Parameter	Preservation Method	Period of stability of parameter [d]
Oxidation with $KMnO_4$	no preservation -18 to -22°C acidified (pH 2) alkaline (pH 12) $HgCl_2$	0 32 16 8 8
COD	no preservation -18 to -22°C acidified alkaline	0 32 0 0
TOC	no preservation -18 to -22°C acidified alkaline	0 32 2 8
BOD	no preservation -18 to -22°C acidified alkaline	0 32 4 8

Parameter	Preservation Method	Period of stability of parameter [d]
ammonia	no preservation -18 to -22°C acidified alkaline $HgCl_2$	0 0 16 32 32
nitrate	no preservation -18 to -22°C acidified alkaline $HgCl_2$	0 8 1 4 0
sulfate	no preservation $HgCl_2$	0 32
anionic surfactants	no preservation acidified $HgCl_2$	0 0 32

Recommendations of the "Working Party on Stabilization of Samples from the Hydrochemistry Team of the German Chemists Association" (1981) for preservation of primary clarifier effluent for analyzing different parameters

Exercise: Sample preparation and sample division and its impact on the TOC analyse

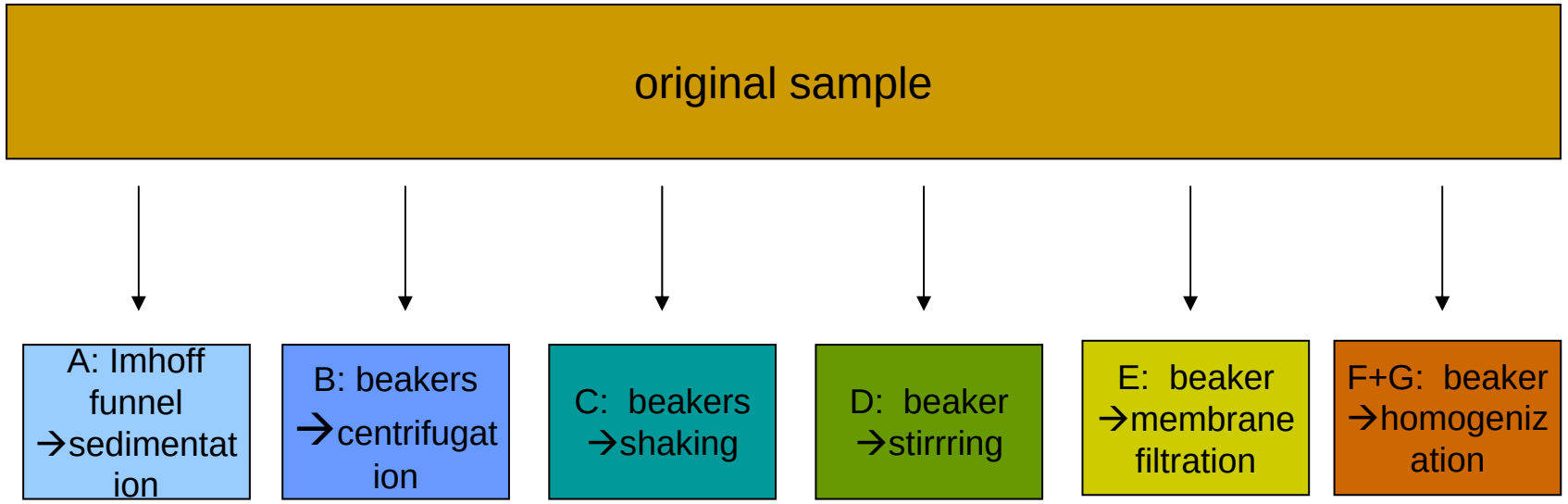
Introduction

Wastewaters usually contain particles. The kind of partitioning a wastewater sample will influence the result of the wastewater analyses. Usually not the entire sample shipped to the laboratory will be analysed for a particular wastewater parameter, but only a small part of the sample. The **kind of partitioning** will especially **influence the analytical results** when particles suspended in the wastewater contain analytes to be determined in a particular analytical procedure. When there are flocs with organic material present in the wastewater which will be either enriched or partially lost by partitioning the sample (which is an important step during sample preparation), organic sum parameters of the sample like TOC or COD will show higher or lower concentrations.

For showing these effects a wastewater sample with suspended particles has to be divided into 6 subsamples. These subsamples (A-G) will be pretreated differently and analysed for TOC.

Division in 6 subsamples

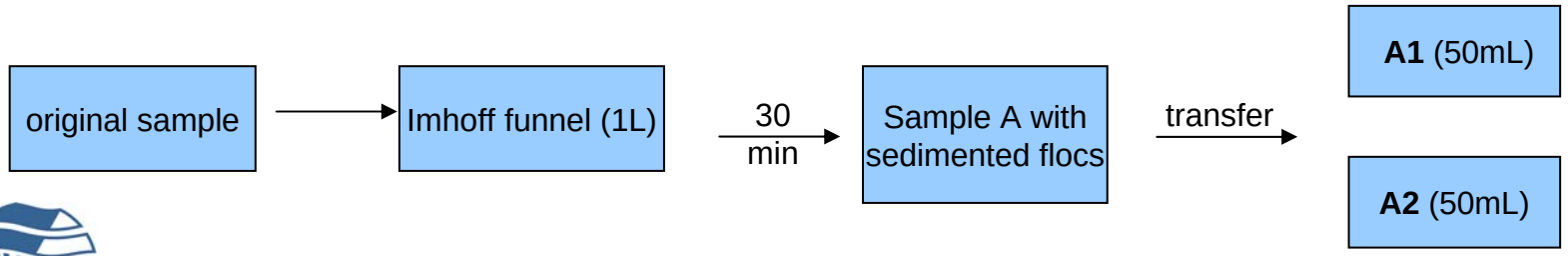
One sample was taken from a municipal wastewater treatment plant in a container. From this container sub-samples are poured into different receptacles. **Before each pouring of wastewater sample, the container has to be shaken vigorously** in order to ensure that the original sample is homogeneous before taking a sub-sample!



Sample A

First, one liter of the original sample is poured from the container to an Imhoff funnel A. At this time a stop-watch is started. Then the Imhoff funnel is allowed to stand quietly in a wooden rack. After exactly 30 min the volume of flocs sedimented to the bottom of the funnel is read. Moreover, two time 50 ml of the supernatant in the funnel close to the liquid surface are transferred to two TOC analyser sampling tubes by means of a 50ml glass pipette and a Peleus ball. The glasses are marked with "A1" and "A2". Later these glasses with sub-samples are put into the autosampler of a TOC analyser.

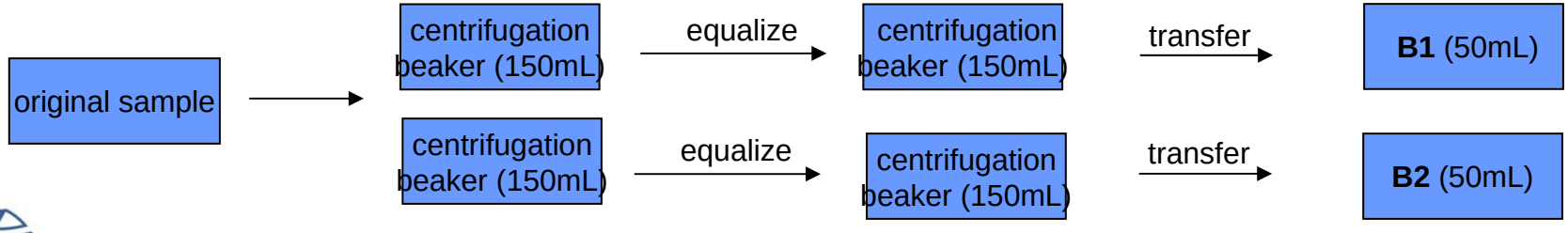
TOC Analyser



Sample B

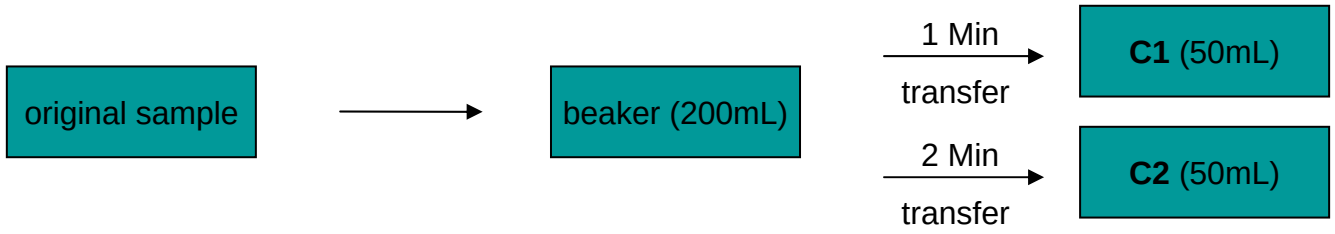
150 ml of the sample are transferred to two polyethylene centrifugation beakers each by means of a graduated cylinder. The centrifugation beakers are then closed with their screw caps, inserted opposite one another into the rotor by means of particular fixing devices, and finally centrifuged for 15 min at 4000 rounds per minute. After the rotor has come to a standstill, the centrifugation beakers are taken out from the rotor very carefully in order to avoid mixing of the pellet with the supernatant. From the supernatant of each beaker 50 ml are transferred to TOC sampling glasses (marked "B1" and "B2") by a glass pipette.

Centrifuge



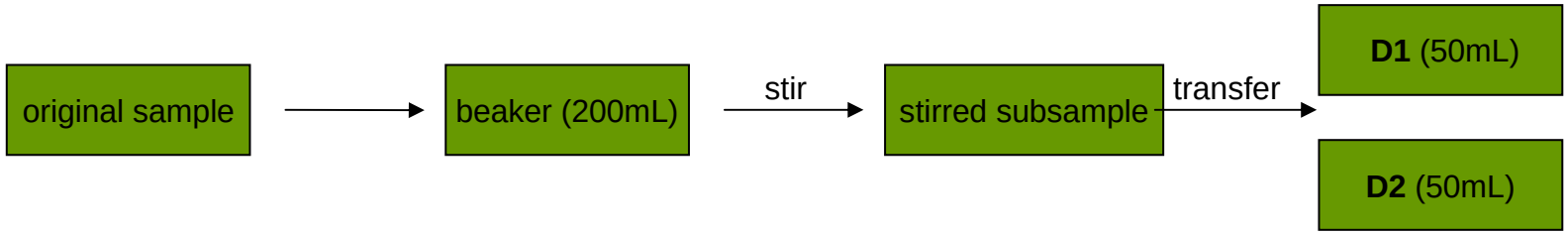
Sample C

200 ml of the sample are poured into beaker C. The sample in the beaker is not agitated at all in this experiment! After about one minute a 50 ml sample is pipetted from the beaker into the TOC sampling glass "C1", after another minute without agitation, another 50 ml sample is transferred to TOC sampling vial "C2" by means of a glass pipette. Also these samples will be analyzed for their TOC concentration later on.



Sample D

200 ml of the sample are poured into beaker D (using the 200 ml mark of the beaker). In contrast to beaker C, beaker D contains a magnetic stirrer bar and is placed on a magnetic stirrer. From this stirred sub-sample 50 ml are transferred to TOC sampling glasses "D1" and "D2" each being analysed in the TOC analyser later on.

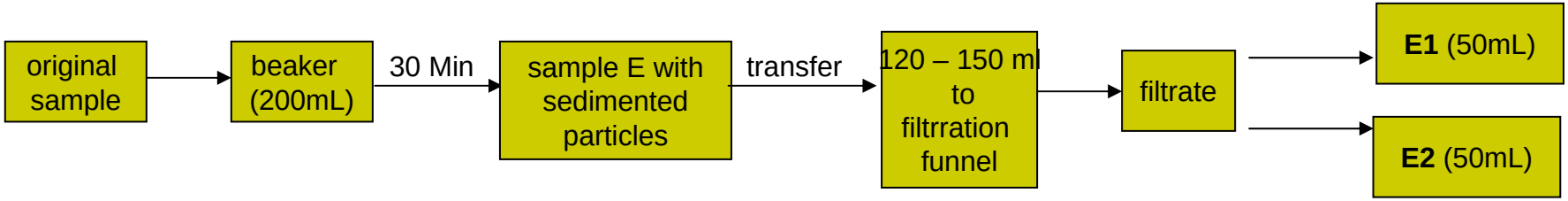


Sample E

200 ml of the sample are poured into beaker E. This beaker is not stirred and is allowed to stand for a 30 min for sedimentation of particles before about 120 to 150 ml of the supernatant with low particle content are transferred to a filtration funnel containing a cellulose acetate or cellulose nitrate membrane filter (pore width: 0.45 µm).

When membrane filtration is complete, from the filtrate 50 ml are transferred to TOC sampling glasses "E1" and "E2" each.

Filtration funnel

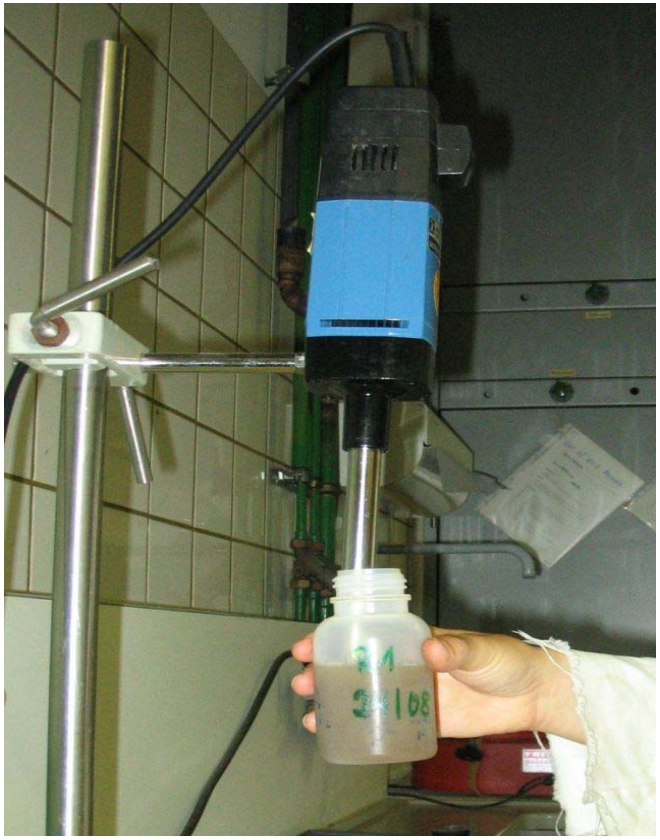


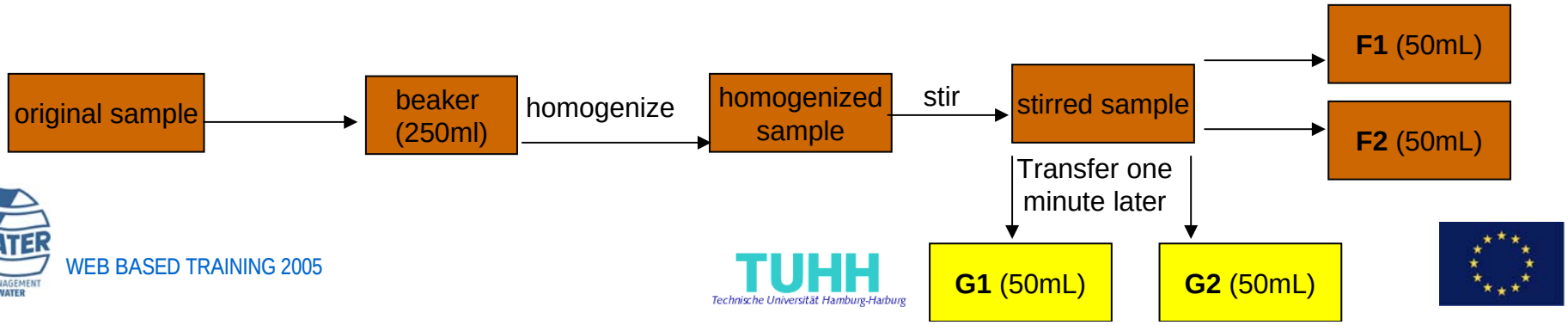
Sample F and G

250 ml of the original wastewater sample are poured into beaker F. Into this sub-sample a homogenizer with rapidly rotating blades ("Ultraturrax") is inserted.

The Ultraturrax is operated for 2 min decreasing the particle size of the coarse suspended wastewater particles (consequently leading to smaller sedimentation velocities). After removing the Ultraturrax from the beaker a magnetic stirrer bar is added to the homogenized sub-sample, the beaker placed on a magnetic stirrer and stirred. From the stirred homogenized sub-sample 50 ml are transferred to TOC sampling glasses "F1" and "F2" each. The stirrer is switched of and after about one minute another sub-sample is transferred to a TOC sampling glass ("G1"). Another minute later once more 50 ml are transferred from the non-stirred homogenized sub-sample to TOC sampling glass "G2".

Homogenizer





Results

The following results have been obtained in the laboratory for the different sample division methods with these three different wastewaters.

Sample	TOC [mg/l] Wastewater Sample #1	TOC [mg/l] Wastewater Sample #2	TOC [mg/l] Wastewater Sample #3
A1	35.7	54.1	34.3
A2	37.2	51.5	32.3
B1	20.9	18.7	27.7
B2	21.5	17.8	19.9
C1	753	583	83.7
C2	69.8	370	56.8
D1	458	736	621
D2	467	742	567
E1 (not analysed in duplicate)	20.1	19.6	17.7
F1	415	643	620
F2	445	721	596
G1	129	1,114	889
G2	102	149	330

Questions and solutions

Calculate means of TOC concentrations analysed in duplicate!

Calculate coefficients of variation.

(This is done usually with more analyses!)

	Wastewater Sample #1		Wastewater Sample #2		Wastewater Sample #3	
	Mean Mg/l	**Coefficient of variation**	**Mean** mg/l	**Coefficient of variation**	**Mean** mg/l	**Coefficient of variation**
A	36	2.9%	53	3.5%	33	4.2%
B	21	2.0%	18	3.5%	24	23.2%
C	411	117.4%	477	31.6%	70	27.1%
D	463	1.4%	739	0.6%	594	6.4%
E						
F	430	4.9%	682	8.1%	608	2.8%
G	116	16.5%	75	139.3%	610	64.9%

Note: coefficient of variation is: standard deviation / mean

Questions and solutions

Interprete different TOC means measured for one sample!

You can see that there are very high variations possible depending on the type of preparing and sampling.

e.g. The TOC analyses of A and B (supernatant after sedimentation and centrifugation) are very low because most of the particles are missing. The main TOC is located in the particles. The analyses of C and D show high coefficients of variations because they are not homogenised.

The analyses of E and B are relatively close together. So if the membran filtration is too complicated, it is also possible to centrifuge the sample. In the supernatant there are almost no particles. With analysing the supernatant, the mistake is very low compared to membrane filtration.

Questions and solutions

Calculate part of TOC associated to particles! Which types of sample preparation/division are appropriate for this calculation?

F is the most representative analyse for the original total COD of the sample and E is the membrane filtrated sample which means analyse without particles. So the difference of F and E is the part of TOC that is associated to the particles.

If you have further considerations about the experiment, please write a message and post it in Forum A!

The End