# Supplementary Materials to

Boehm Titration Revisited (Part I): Practical Aspects for Achieving a high Precision in Quantifying Oxygen-Containing Surface Groups on Carbon Materials

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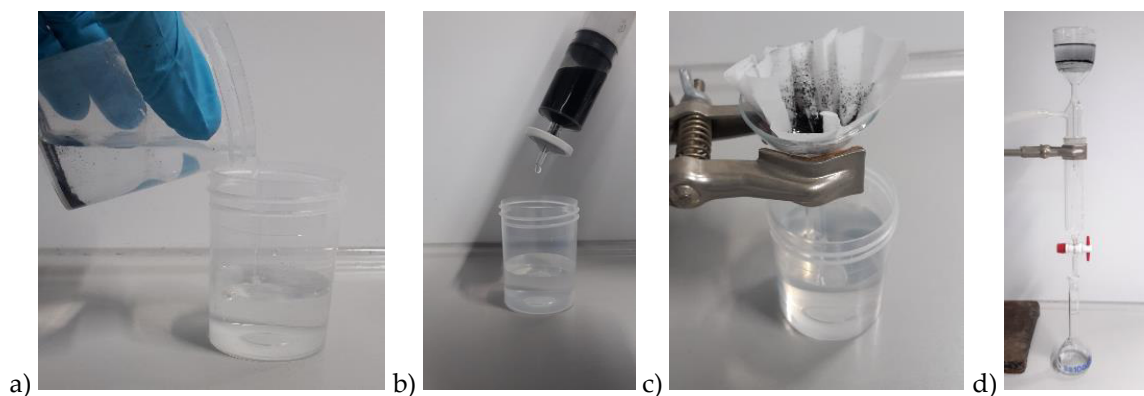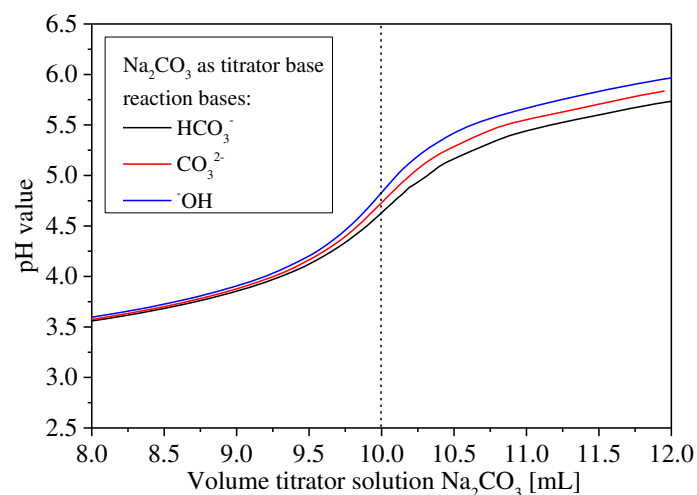
Figure S1. Illustration of the CNT removal methods: (**a**) decanting, (**b**) syringe filters, (**c**) folded filters and (**d**) suction through round filter.
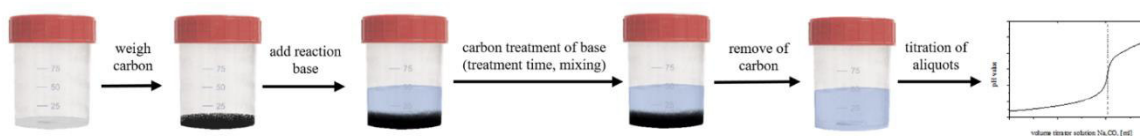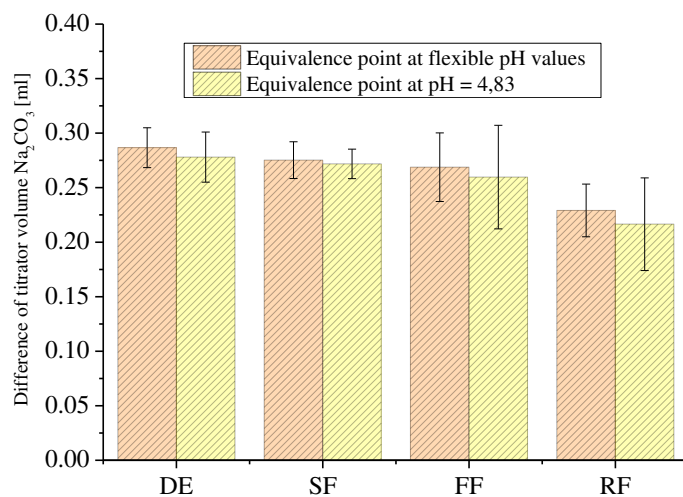

Figure S2. Required working steps for Boehm titration.

Figure S3. Titration cup with analyte solution (left: addition tube, middle: stirrer, right: pH electrode).

Figure S4. Titration curves with Na₂CO₃ titrator solution at the different reaction bases after addition of the HCl excess.

Figure S5. Difference between reference reaction base and aCNTs treated reaction base after removing of the aCNTs with different methods (DE: decantation, SF: syringe filter, FF folded filter, RF: round filter) (0.01 N solutions, NaOH as reaction base, Na₂CO₃ as titrator base).
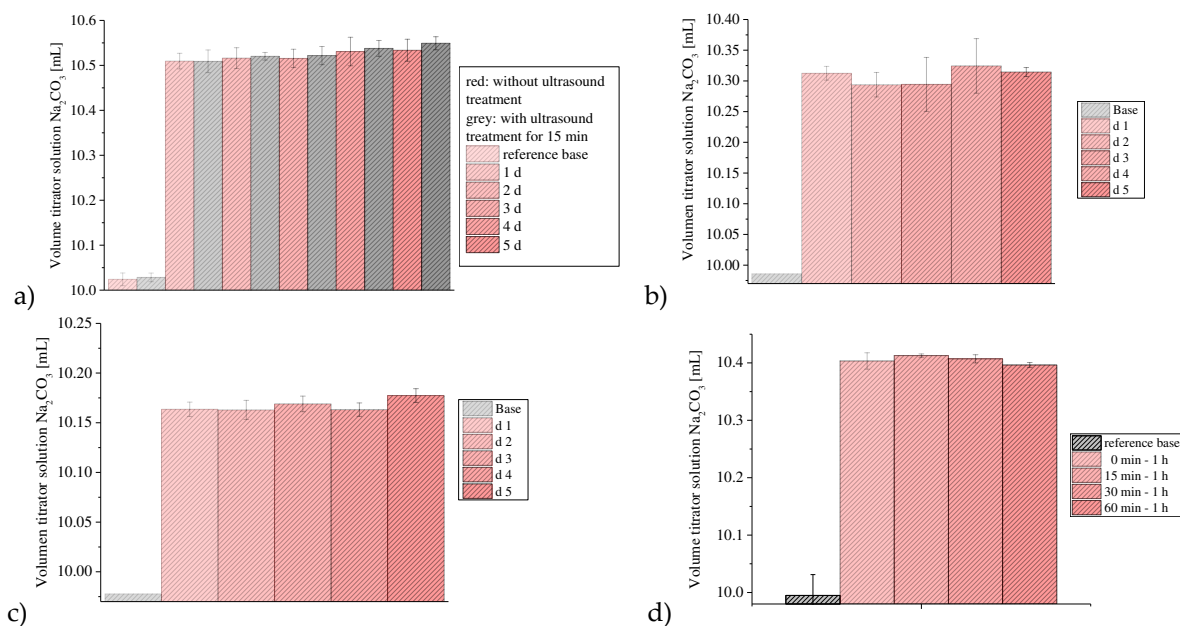
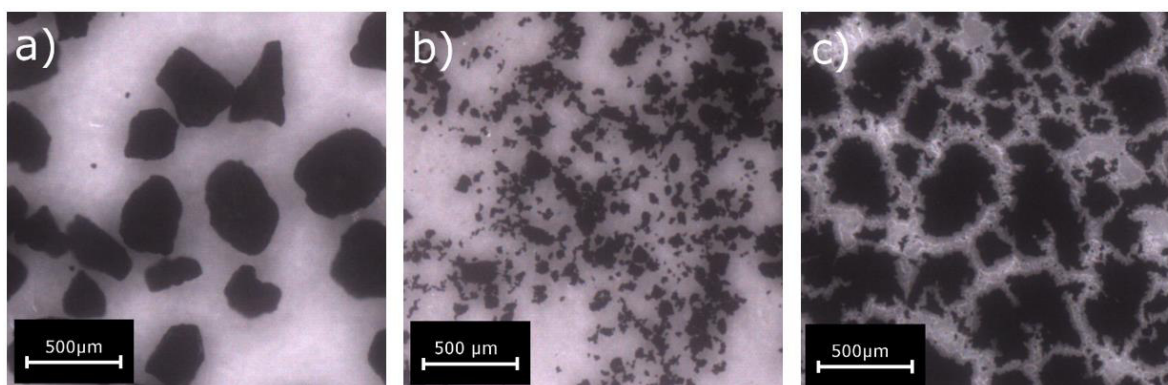**Figure S6.** Consumed volume of titrator solution Na₂CO₃ for reference and aCNT treated reaction base (**a**) NaOH, (**b**) Na₂CO₃ and (**c**) NaHCO₃ as a function of treatment time (1 – 5 d) and (**d**) after ultrasound treatment for 15 – 60 min.

Figure S7. Microscope images of oCNT-Agglomerates in 0.01 N NaOH: (**a**) Agglomerates obtained by synthesis, (**b**) ground agglomerates (through 250 µm sieve) and (**c**) ground agglomerates after ultrasound treatment.

Similarly to the observations of Oickle et al., the agglomerates of oCNTs also increased again after ultrasound treatment. This indicates that the agglomerate structures were broken down and the CNTs reconnected due to their hydrophobicity. However, when filtered through the syringe filter, the resistance is clearly increased and the CNTs are distributed more finely. The CNTs in the newly formed agglomerates seems less strongly connected.

Table S1. Aliquot mass for eight HCl aliquots of the accuracy measurement at various titrator bases as well as the titrated consumption of titrator base (upper part: real measured consumption, lower part: consumption multiplied by factor 10 mg / aliquot mass).

NaOH as titrator base		Na_2CO_3 as titrator base		$NaHCO_3$ as titrator base	
Aliquot mass [mg]	Consumption [ml]	Aliquot mass [mg]	Consumption [ml]	Aliquot mass [mg]	Consumption [ml]
9.97321	10.06964	9.97957	10.04928	9.96716	9.96387
9.96400	10.03430	9.97375	10.00290	9.96284	9.99433
9.96096	10.02459	9.98232	9.99575	9.97282	10.01170
9.97148	10.00569	9.97896	9.99408	9.96651	9.98131
9.95890	10.00150	9.97513	9.98379	9.98509	10.01146
9.96880	9.93973	9.97784	9.98792	9.98158	10.01654
9.97153	9.94607	9.97886	9.98698	9.97765	10.02968
9.98060	9.97849	9.97888	9.99929	9.97357	9.99111
Aliquot mass [mg]	Consumption [ml] corrected by aliquot mass	Aliquot mass [mg]	Consumption [ml] correlated by aliquot mass	Aliquot mass [mg]	Consumption [ml] correlated by aliquot mass
9.97321	10.09669	9.97957	10.06986	9.96716	9.99670
9.96400	10.07055	9.97375	10.02923	9.96284	10.03161
9.96096	10.06388	9.98232	10.01346	9.97282	10.03899
9.97148	10.03431	9.97896	10.01515	9.96651	10.01484
9.95890	10.04278	9.97513	10.00868	9.98509	10.02641
9.96880	9.97084	9.97784	10.01010	9.98158	10.03502
9.97153	9.97446	9.97886	10.00814	9.97765	10.05215
9.98060	9.99788	9.97888	10.02046	9.97357	10.01759

Error propagation:

(a) For addition of random errors $(y = k + k_a\sigma_a + k_b\sigma_b + \ldots)$: $\sigma_y = \sqrt{\sigma_a{}^2 + \sigma_b{}^2 + \ldots}$

(b) For muliplication of random errors $\left(y = k\,\dfrac{a\,b}{c\,d}\right)$: $\sigma_y = y\sqrt{\left(\dfrac{\sigma_a}{a}\right)^2 + \left(\dfrac{\sigma_b}{b}\right)^2 + \left(\dfrac{\sigma_c}{c}\right)^2 + \left(\dfrac{\sigma_d}{d}\right)^2}$

$$n_{lactone} = \left(\frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g] \,\times\, \frac{1}{5}} - \frac{\left(V_{sample,\,NaHCO_3} - V_{reference,\,NaHCO_3}\right)}{weight_{CNT}\,[g] \,\times\, \frac{1}{5}} \right) (titer \times c)_{titrator\ base}$$

Development of $\sigma_{Lactone}$ with equation (a) and (b):

with (b):
$$\sigma_{lactone} = \left(\frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g] \,\times\, \frac{1}{5}} - \frac{\left(V_{sample,\,NaHCO_3} - V_{reference,\,NaHCO_3}\right)}{weight_{CNT}\,[g] \,\times\, \frac{1}{5}} \right)(titer \times c)_{titrator\ base} \sqrt{\left(\frac{\sigma\left(\frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} - \frac{\left(V_{sample,\,NaHCO_3} - V_{reference,\,NaHCO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}}\right)}{\left(\frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} - \frac{\left(V_{sample,\,NaHCO_3} - V_{reference,\,NaHCO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}}\right)} \right)^2 + \left(\frac{\sigma_{titer \times c}}{titer \times c} \right)^2 }$$

with (a):
$$\sigma\left(\frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} - \frac{\left(V_{sample,\,NaHCO_3} - V_{reference,\,NaHCO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} \right) = \sqrt{ \left(\sigma\left(\frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} \right) \right)^2 + \left(\sigma\left(\frac{\left(V_{sample,\,NaHCO_3} - V_{reference,\,NaHCO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} \right) \right)^2 }$$

with (b):
$$\sigma\left(\frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} \right) = \frac{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} \sqrt{ \left(\frac{\sigma\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)}{\left(V_{sample,\,Na_2CO_3} - V_{reference,\,Na_2CO_3}\right)} \right)^2 + \left(\frac{\sigma_{weigh_{CNT}\,[g]}}{weight_{CNT}\,[g]\,\times\,\frac{1}{5}} \right)^2 }$$

with (a):
$$\sigma\left(V_{sample,\,Na2CO3} - V_{reference,\,Na2CO3}\right) = \sqrt{ \left(\sigma_{V_{sample,\,Na2CO3}} \right)^2 + \left(\sigma_{V\ reference,\,Na2CO3} \right)^2 }$$

Example for:

σ_V	0.015	mL	$V_{sample\ NaHCO3}$	10,5	mL
σ_{weight}	0.0005	g	$V_{sample\ Na2CO3}$	11	mL
weight	0.1	g	titer $\times$ c	0.01	mmol/mL
$V_{reference\ NaHCO3,\ Na2CO3}$	10	mL	$\sigma_{titer} \times c$	0.000015	mmol/mL

$$\sigma_{\left(V_{sample,\ Na2CO3}\ -\ V_{reference,\ Na2CO3}\right)}=\sqrt{(0.015\text{mL})^2+(0.015\text{mL})^2}=0.021213\ \text{mL} \qquad \text{and} \qquad \sigma_{\left(V_{sample,\ NaHCO3}\ -\ V_{reference,\ NaHCO3}\right)}=\sqrt{(0.015\ \text{mL})^2+(0.015\ \text{mL})^2}=0.021213\ \text{mL}$$

$$\sigma_{\left(\frac{\left(V_{sample,\ NaHCO3}\ -\ V_{reference,\ NaHCO3}\right)}{weight_{CNT}\ [g]\ \times\frac{1}{5}}\right)}=\frac{(11\text{mL}\ -\ 10\text{mL})}{0.1\ g\ \times\ \frac{1}{5}}\sqrt{\left(\frac{0.021213\text{mL}}{11\text{mL}\ -\ 10\text{mL}}\right)^2+\left(\frac{0.0005g}{0.1g}\right)^2}=1.068000\ \frac{\text{mL}}{\text{g}} \quad \text{and} \quad \sigma_{\left(\frac{\left(V_{sample,\ NaHCO3}\ -\ V_{reference,\ NaHCO3}\right)}{weight_{CNT}\ [g]\ \times\frac{1}{5}}\right)}=\frac{(11\text{mL}\ -\ 10\text{mL})}{0.1\ g\ \times\ \frac{1}{5}}\sqrt{\left(\frac{0.021213\text{mL}}{10.5\text{mL}\ -\ 10\text{mL}}\right)^2+\left(\frac{0.0005g}{0.1g}\right)^2}=1.06095\ \frac{\text{mL}}{\text{g}}$$

$$\sigma_{\left(\frac{\left(V_{sample,\ NaHCO3}\ -\ V_{reference,\ NaHCO3}\right)}{weight_{CNT}\ [g]\ \times\frac{1}{5}}-\frac{\left(V_{sample,\ NaHCO3}\ -\ V_{reference,\ NaHCO3}\right)}{weight_{CNT}\ [g]\ \times\ \frac{1}{5}}\right)}=\sqrt{\left(1.068000\ \frac{\text{mL}}{\text{g}}\right)^2+\left(1.06095\ \frac{\text{mL}}{\text{g}}\right)^2}=1.5054\ \frac{\text{mL}}{\text{g}}$$

$$\sigma_{lactone}=\left(\frac{(11-10)\text{mL}}{0.1g\ \times\frac{1}{5}}-\frac{(10.5-10)\text{mL}}{0.1g\ \times\frac{1}{5}}\right)0.01\ \frac{\text{mmol}}{\text{mL}}\sqrt{\left(\frac{0.060216\ \frac{\text{mL}}{\text{g}}}{\left(\frac{(11-10)\text{mL}}{0.1g\ \times\frac{1}{5}}-\frac{(10.5-10)\text{mL}}{0.1g\times\frac{1}{5}}\right)}\right)^2+\left(\frac{0.000015\ \frac{\text{mmol}}{\text{mL}}}{0.01\ \frac{\text{mmol}}{\text{mL}}}\right)^2}=0.0155\ \frac{\text{mmol}}{\text{g}}$$

$$n_{lactone}\ =\ 0.2500\ \frac{\text{mmol}}{\text{g}}\ ;\ \sigma_{lactone}=0.0155\ \frac{\text{mmol}}{\text{g}}$$

$$\sigma_{lactone}\ =\ 6.2\%$$

Standard Operating Procedure
Boehm titration

Provided by:
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Purpose   Carry out a valid quantification of acidic oxygen containing groups on carbon surfaces via acid-base titration

Responsibilities _____
To implement the SOP in your institute, add a qualified person.

Scope   As analyte, any sort of carbon with a minimal hydrophilic character can be used. $NaHCO_3$, Na_2CO_3 and $NaOH$ are used as reaction bases to quantify mainly carboxyl acids, lactones and phenols.

Prerequisites   To determine the most suitable amount of carbon for Boehm titration samples, we suggest measuring the surface area and the whole oxygen amount of the carbon material with elemental analysis and physisorption with N_2. With respect to low surfaces and low oxygen amounts, a high mass of carbon is necessary for accurate Boehm titration measurements (e.g. 500 – 1000 mg). For high surfaces and high oxygen amounts, less than 200 mg should be used so that the whole base is not consumed. Pretests with one sample are suggested before measuring the whole sample series.

Required instruments:
- 1 x 10 mL, 1 x 20 mL, 1 x 50 mL volumetric pipette class A (+ pipette bulbs)
- 1 x 1 L, 1 x 100 mL volumetric flask
- 4 x 1 L PE flask (for stock solutions)
- 2 x 3 L PE flask (for reaction bases)
- 2 x 5 L PE flasks (for HCl and titrator solution Na_2CO_3)
- 9 sealable PE beakers per carbon sample within a sample series + 3 sealable beakers per reference base
- 50 mL syringes (luer-lock) + syringe filters
- autotitrator + pH electrode + titrator beakers
- shaking plate or stirrer
- micro scale

All instruments should be new and/or it should be ensured that they work correctly. This includes testing the transferred volume for each volumetric pipette, volumetric flask, etc. Please follow the instrument maintenance

instructions to avoid changes (e.g., no heating for drying for all volumetric glass instruments).

All instruments, vessels and beakers should be cleaned carefully. We describe the suggested cleaning in **Step 2** in the part of the procedure.

It should be tested, whether the carbon material generates a suspension or settle down in the base solutions. If the carbon floats on the surface of the water phase, the carbon material is to hydrophobic and an analysis via Boehm titration is not possible due to the missing penetration of the base into the carbon material.

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Procedure

Step 1: Preparation of solutions
- 0.1 N HCl stock solution: We recommend purchasing a commercial solution.
- 0.1 N Base stock solutions: Transfer the dried base (4 g NaOH, 5.3 g Na_2CO_3 or 8.4 g $NaHCO_3$) in a 1 L volumetric flask quantitatively and fill it up with deionized water. Store the final solution in PE bottles (NaOH could otherwise react with SiO_2 of the glass). Close the bottles carefully to avoid evaporation of water and thereby an increase of the base concentration.
- For the acid and the bases, dilute the 0.1 N stock solutions by a factor of 10. Store the solutions in PE or PP vessels. It is important to plan carefully how much solution is necessary for the whole sample series to avoid multiple titer determination.
  (For about 10 carbon samples, generate 5 L titrator solution (0.01 M Na_2CO_3) and 5 L HCl (0.01 N). For each of the reaction base, 2 L are enough (triplet determination with 50 mL reaction base on 10 carbon samples + 3 references needs 1.65 L per reaction base).

Step 2: Suggested cleaning of beakers
- An important issue to consider is the difference between the usage of HCl or base solutions with regard to the evaporation for not sealed solutions. In the case of the base solution, the water evaporates and the base remains as a solid. When an HCl solution is not sealed, the acid as well as the water evaporates completely. Accordingly, vessels with base solutions must be washed more carefully. We strongly recommend a drying with cellulose paper after washing. This allows a fast drying, which includes a complete transfer of the solution into the paper. In this way, the whole base should be removed without remaining a solid residue. This also allows a reuse of beakers in a short time.
- For all instruments, it is important to avoid the use of strong detergents and to remove any detergents carefully by multiple rinse of water. Remaining detergents would change the surface tension of the solution and thereby the formation of the meniscus in the volumetric flasks and volumetric pipettes. Also a compartment drier should not be used. Volumetric flasks and pipettes would be changed by heat, so that an exact determination of volumes is not possible anymore.

Step 3: Preparation of carbon
- If the carbon material is inhomogeneous or the agglomerates are bigger than 1 mm^3, we suggest a grinding. By doing this, it can be ensured obtaining a representative sample, which allows a calculation of the whole amount of oxygen containing groups on the material.

Step 4 – 7 are illustrated on **Page 9**

Step 4: Treatment of carbon with bases
- Weigh nine times a useful and constant amount per carbon sample (check **prerequisites**, e.g., 100 – 300 mg for MWCNTs) in closeable 100 mL beakers.
- Add 50 mL of the base solution via volumetric pipette to three beakers per reaction base (triple determination).
(The addition should take place in a tempered lab because all volumetric instruments are calibrated at 20 °C. The base should be stored in that lab before or produced with tempered water.)
- Weigh and record the mass of the base (to adjust the results later regarding the actually weighted mass).
- Transfer also three times 50 mL per reaction base via volumetric pipette in similar beakers without carbon (reference samples).
- Seal all beakers carefully to avoid loss of water through evaporation
- All samples should be transferred on a shaker at least 24 h. We recommend shaking the samples for three days.

    The reference samples should be stored in the same rooms and treated exactly as the normal samples. Even the filtration steps should be done as in the normal samples, to ensure the same influences on the solutions.

Step 5: Remove of carbon from the base solution
- After shaking, rotate the beakers to homogenize the solution and collect all solution droplets which were possibly generated on the walls or the cap. The droplets could arise through evaporation and condensation on the surfaces (**Fig. SOP 3**). Another reason can be the rip of the solution film on the polymer surface of the beaker. These droplets would cause a different concentration und must be collected with the main solution.
- Transfer the majority of the solution in a 50 mL syringe with Luer Lock. It is not necessary to transfer all of the solution or the whole carbon material. The less carbon is in the syringe the easier the filtration will be. Then screw the filter on the syringe (e.g. Whatman FP30/0.45 CA).
(We suggest cleaning up the beaker and use it again for the base without carbon. When the solution is in the syringe, the remaining carbon can be washed out and separated for a reuse. The empty beaker should be washed multiply times to remove the rest of the base and then dried by cellulose papers (check **step 2**).)
- Press nearly all the solution through the filter into the beaker. Based on the carbon material it needs much strength and time. We used a lever apparatus to make this step more comfortable.
- After transferring the solution, close and seal the beaker carefully to avoid evaporation of water. Afterwards, store the solution in the tempered lab where the titration should take place.

Step 6: Aliquot preparation
- We strongly recommend an indirect titration of the base amount (please see the related manuscript). Therefore, take four 10 mL aliquots of the base solution via volumetric pipette and transfer them in the corresponding beakers from the autotitrator. Add 20 mL 0.01 N HCl via volumetric pipette in each of these beakers. Then, it is possible to add water to the beaker so that the pH-electrode will be fully encased during titration.
- Measure the produced aliquots within the next hour to avoid evaporation of the HCl. To protect the aliquots from external influences, cover the beakers till the titration is carried out.
  (We cleaned the autotitrator beakers like the storage beakers with cellulose papers after use (check **step 2**).)

Step 7: Titration
- At the beginning, purge the autotitrator with the titrator solution to achieve a constant concentration of the titrator solution in the autotitrator tubes. Repeat this daily before the first titration.
  There should be enough titrator solution for each sample within a sample series. In this way, external influence on the solution are excluded during the whole sample series. After a series, produce a new titrator solution and determine the titer before titration.
- The first aliquot after a titration break should be a base sample, which is neither a sample nor a reference sample, but it should contain a similar base concentration. This is important to purge the volumetric pipettes and to equilibrate the pH-electrode.
- After finishing a titration, remove the sample quickly. Otherwise the solution in the beaker can diffuse in the addition tube and reduces the titrator solution concentration in the tube (**Fig. SOP 5**). Rinse the stirrer, the pH-electrode and the outside of the addition tube carefully before a new sample is added at the autotitrator to avoid a cross-contamination of the new with the last sample.
- We recommend measuring first one sample per triplet determination for each carbon material and then start from the beginning with the second sample for each carbon material until all three samples are measured. (C1-S1, C2-S1, C3-S1…; C1-S2, C2-S2, C3-S2…; C1-S3, C2-S3, C3-S3…)
  If only one base sample per carbon material should be measured, we recommend a random order of all samples with one reaction base if they are related to each other (e.g. NaOH). This enables the finding of trends over time due to changes of titers.
  Do not change the bases among themselves often to reduce the contamination of the instruments.

Step 8: Evaluation

- Autotitrators usually detect the equivalence point automatically. However, it is advisable to check the pH-value for each equivalence point to find and to correct outliers. This can be done by calculating the average of the pH-values at similar samples and then detect the titrator volume on this pH-value for the outlier.
- At fast titration times, the equivalence point is usually found at lower pH values than the theoretical pH value for the titration of HCl with Na_2CO_3 (pH = 5.1). We receive values between 4.6 and 4.8. The pH value is slightly affected by the reaction bases (please see the related manuscript).
- The first aliquot of a sample should be observed. In most of the cases this aliquot shows divergent values. This can be due to the insufficient purging of the volumetric pipettes or the standing time before the reuse of the pipettes.
- The base consumption through carbon should always be calculated by the difference of the carbon treated samples and the reference samples. These values can be corrected by the weight of the reaction base and the weight of carbon. Usually, the correction influences the values not significantly.
- The reference or the titer should always be determined by the same titration method as the samples. Accordingly, systematically errors should affect the reference and the samples in the same way. Therefore, these errors are corrected by the subtraction of the titration values during the calculation.

Procedure for Deviation

The major deviations occur through not exact use of the volumetric instruments or cross contaminations. The latter leads mostly to an outlier of the first aliquot. This can also be caused by longer standing times of the volumetric pipette, which slightly influences the releasing of the solution. That is the reason why later aliquots usually shows a higher accuracy. In this case, the first aliquot can be axed for the calculation.

When all aliquots of one base sample shows higher or lower values than the other samples of the triplet determination, the carbon material could be inhomogeneous or a failure during the carbon-base treatment has occurred. If the deviating values cannot be traced back to too less amounts of reaction base or too less amounts of carbon (compare with the reported masses), the sample should be axed.

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Attachments

Fig. SOP 1: Example of a workplace for Boehm titration

Fig. SOP 2: Base samples after filtration through syringe filter (left), carbon residue after removing of the base by syringe (middle), carbon base suspensions with different suspension stabilities (right)

Fig. SOP 3: Generation of droplets through evaporation/condensation or rip of solvent film on the beaker wall

Fig. SOP 4: Base MWCNT suspension 60 s after shaking

Fig. SOP 5: Titration beaker with addition tube (left), stirrer (middle) and pH- electrode (right)

Fig. SOP 6: Remove of carbon from the base solution with syringe filter

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amount of carbon should be related to the oxidation degree (0.1 - 1 g)

+ 50 mL reaction base (0.01 N) $NaHCO_3, Na_2CO_3, NaOH$

treatment time 3 d shaking

filtration with syringe filter

10 mL base (4 aliquots)

+ 20 mL HCl (0.01 N)

titration with Na_2CO_3 (0.01 N)

reaction bases 42-50 mL: $NaHCO_3, Na_2CO_3, NaOH$ (reference: 0.01 N) (sample: < 0.01 N)

10 ml aliquot (reference: 0.1 mmol base) (sample: < 0.1 mmol base)

30 ml aliquot (reference: 0.1 mmol HCl) (sample: > 0.1 mmol HCl)

Results with constant accuracy for all reaction bases (± 0.025 mL) (reference: 10 mL Na_2CO_3) (sample: > 10 mL Na_2CO_3)
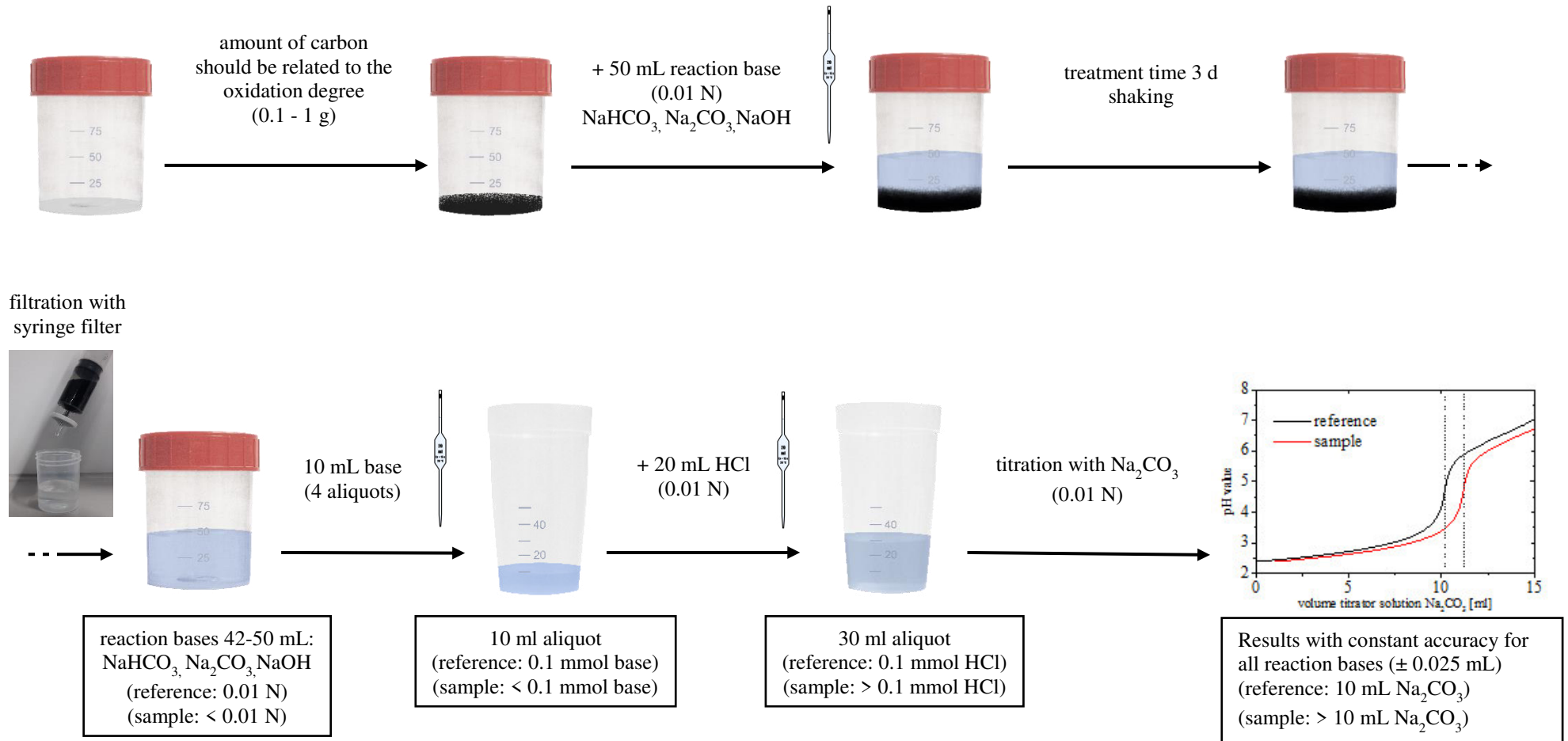
Fig. SOP 7: Schematic depiction of the Boehm titration working steps