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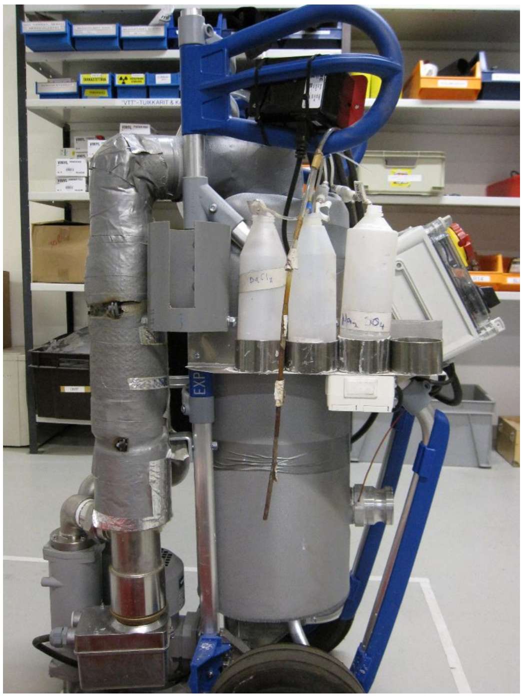

Characterisation of the produced particles by the IndMeas industrial flow calibration device

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Characterisation of the produced particles by the IndMeas industrial flow calibration device	
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Summary

A measurement (calibration) device designed by the IndMeas company for the calibration of industrial flow meters with the help of activated particles is studied and characterised. With this device it is also possible to check/evaluate, e.g. emissions and energy balances of an industrial facility. The method applies ^{137}Ba-tracer, whose $t_{d,1/2}$=153 s.

Particle number concentration (PNC) during the normal pulsed particle generation with the standard $BaCl_2 + Na_2SO_4$ + silica reagent varied between 1.0-1.4·10^7 1/cm^3, and the mass concentration between 215-465 mg/m^3. The aerodynamic count median diameter (CMD_{ae}) varied between 0.8-4 µm, and the mass size distribution peaked at 1-3 µm sized particles (aerodynamic size). The particles were large (>1 µm; the cut point of the cyclone is 1 µm) and almost spherical. The silica caused some "branching" and "porous" structure of the particles. Leaving out the silica ($BaCl_2 + Na_2SO_4$) did not change the particle number concentration much (0.6-1.2·10^7 1/cm^3), but the CMD_{ae} decreased to 0.9-2 µm. The mass concentration varied between 70-230 mg/m^3. The particle size did not seem to change much, but the structure becomes more compact (cobblestone), and the "branching" disappears.

During continuous particle generation (no cyclone collection) the formed particles were clearly smaller than with the pulsed production combined with cyclone collection. It also seemed that the particles were less "branched" and more compact. The size of these particles was too small (<1 µm) to be captured with the cyclone (cut point 1 µm).

As a conclusion, the IndMeas flow calibrator device is able to produce small particles (<< 1 µm), but these particles cannot be captured with the current cyclone with a cut point of 1 µm. To increase the yield of the signal (particles carrying the tracer ^{137}Ba) reaching the measurement target the produced particles should be small (preferably <1 µm) and as spherical as possible. This may be achieved by a suitable selection of the reagent(s). In order to capture the produced small particles a new collection device is needed. This could be, e.g. a small cylinder-type bag filter.

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1 Introduction

This study titled as “Production and dispersion of tracer particles for process flow measurements” is a part of the CLEEN MMEA (Measurement, monitoring and environmental efficiency assessment) research program going on during 2010-2014. The aim of the research program is “to combine the development of new measurement technologies, data quality assurance methods, modelling and forecasting tools, and information and communication technology (ICT) infrastructure (CLEEN MMEA factsheet, 2010).”

A measurement (calibration) device designed by the IndMeas company for the calibration of industrial flow meters with the help of activated particles is studied and characterised. With this device it is also possible to check/evaluate, e.g. emissions and energy balances of an industrial facility. The method applies ^{137}Ba-tracer, whose $t_{d,1/2}$=153 s. The aim of the research is to characterise the IndMeas-measurement method and to improve its performance. The main focus is to concentrate on thoroughly charactering the particles produced by the device, and on improving the properties of the particles, i.e. to reduce their adherence and decrease their size to reduce particle losses by ,e.g. deposition.

2 Methods

2.1 Principles of measurement devices

In the following section a short description of the experimental techniques and equipment used in this study is provided. For more thorough information the required references are provided.

An aspiration electron microscopy sampler (AEM sampler) was used to collect samples for morphology studies in scanning electron microscope (SEM). The sampler consists of an EM grid mounting head soldered with silver into 6 mm tubing and Swagelok fittings. The carbon coated copper grid (Holey carbon, d_{grid}=3.1 mm) is mounted on the grid mounting head with the help of a hollow screw, and a copper seal is mounted between the screw and the EM grid. The flow through the aspiration sampler is regulated to approximately 0.1 Nlpm with a critical orifice (CO). This sampler is designed and manufactured by VTT.

A Berner-type low-pressure Impactor (BLPI) was used to measure the mass size distribution of the particles. The BLPI has a total of 11 collection stages, where the aerosol is directed through orifices lying against a flat collection plate. The uppermost stage (11) collects particles whose Stokes diameter is larger than 10 µm and the lowest stage (1) particles whose Stokes diameter is 0.01-0.02 µm. When passing through several successive impactor stages the aerosol is classified into several different size classes (Berner and Lürzer, 1980; Berner et al., 1979; Hillamo and Kauppinen, 1991; Kauppinen, 1992).

An electrical low-pressure impactor (ELPI) was used to measure the particle number concentration and number size distribution. The base of the ELPI is a 12 stage cascade low-pressure impactor with a without a final filter stage. In these measurements the ELPI is equipped with a filter stage. In ELPI the particles are charged with a unipolar diode charger to a well-defined charge level prior entering the cascade impactor. Inside the impactor the particles are classified in to 12 size classes (from 30 nm to 10 µm) according to their aerodynamic diameter. When collected at the different collection stages the particles produce electric current that is measured with highly sensitive electrometers. The results may then be recorded to a PC equipped with a control software (Keskinen, et al., 1992; Baltensperger, Weingartner, Burtscher and Keskinen, 2001).

A tapered element oscillating microbalance (TEOM). A 1400a-type TEOM (Patashnick and Rupprecht, 1986; Patashnick and Rupprecht, 1991) was used to measure continuously the particle mass concentration. The particles were collected on a filter, which was placed on top of a transversely vibrating hollow rod. The sample flow was drawn through the filter and the rod with a pump. Because the rod oscillates as a harmonic oscillator the mass of the oscillating element (the hollow rod and the filter) can be calculated from the vibration frequency of the rod.

A porous tube diluter (PRD, dilution probe) was used to reduce particle deposition and total particle concentration suitable for the measurement devices. PRD is a coaxial cylindrical diluter in which the dilution air flows through a porous tube (pore size 20 µm) into the inner tube, thus sheeting the aerosol flow from deposition and thermophoresis (Auvinen et al., 2000).

A Fourier transform infrared spectrometer (**FTIR**) was used to measure and monitor the gas composition during the measurements. The degree of absorption of infrared radiation at each wavelength is quantitatively related to the number of absorbing molecules in the sample gas. Because there is a linear relationship between the absorbance and the number of absorbing molecules, multicomponent quantitative analysis of gas mixtures is feasible (Gasmet, 2001).

2.2 Studied process and measurement set-up

The IndMeas flow calibrator device (FCD) uses as a reagent/carrier $BaCl_2$ + Na_2SO_4 + silica, and some tracer ^{137}Ba ($t_{d,1/2}$=153 s) originating from the ion exchange column. In this case the eluent solution passing through the ion exchange column, and thus “capturing” (actually ion exchanging) the tracer ^{137}Ba is $BaCl_2$. The usual $BaCl_2$/silica mass relation is 10g/1.5g, respectively. Approximately 30 ml of the reagent mixture ($BaCl_2$ + Na_2SO_4 + silica) is fed for about 1 min to the ”drier”, where the reagents react to form ”wet” particles that are dried, i.e. the moisture is removed. The dried particles, approximately 2-3 µm in size are collected with a cyclone attached to drier exit. A fast and powerful ”blow” with air or N_2 (approx. 20 bar) through the line at the bottom of the collection cup of the cyclone makes the particles flow with the “blow”. The particles will the follow the flow to the measured target. (Fig. 1a, 1b). The particle production with the current set-up and reagents is approx. 2 g. IndMeas has estimated that approximately 10 % of this will reach the measured target when blowing the particles through the cyclone collection cup.

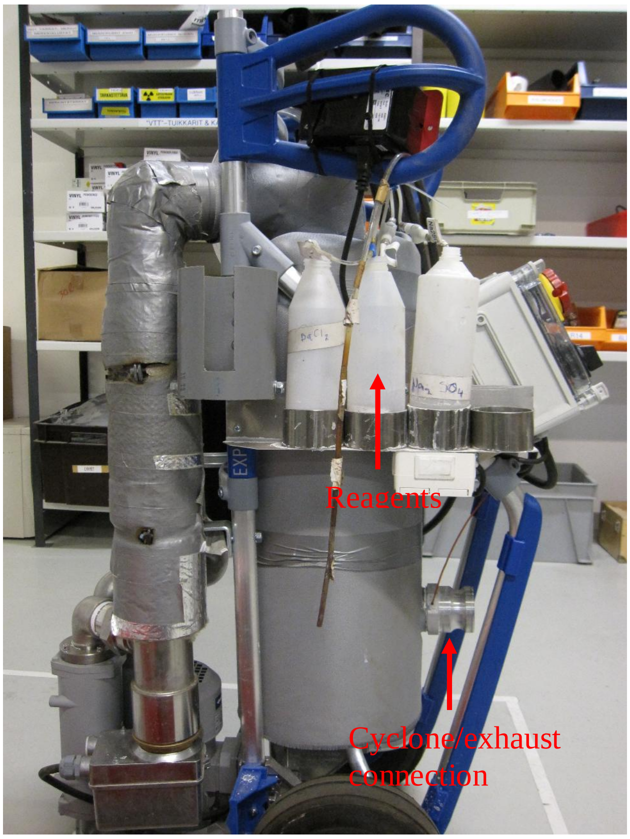

Fig.1a. The IndMeas flow calibrator.

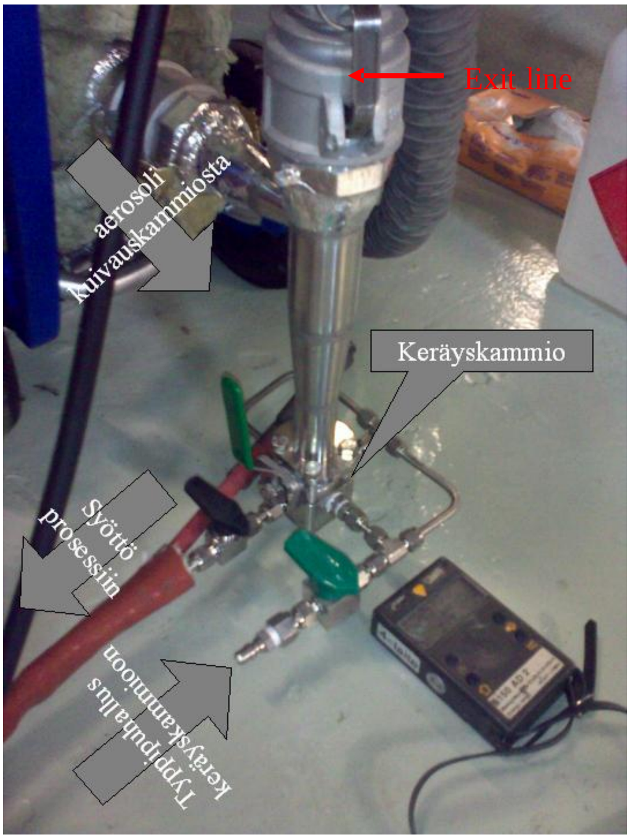

Fig. 1b. A photograph showing the cyclone and pressurised gas (N_2) inlet and outlet to the process under study connections.

To characterise the particles currently produced by the flow calibrator device (FCD) a measurement campaign was carried out to determine the particle number and mass concentration and number and mass size distribution and particle morphology and composition. The produced particles were collected in the cyclone and "blown" away with air or N_2 (pulsed generation), and the gas composition (mainly moisture of the gas) at the exit after the "drier" was measured at the same time (Fig. 2a and 2b). The inlet to the FTIR was heated to 150 °C to avoid moisture condensation. In addition, the generated particles were also measured and characterised during continuous particle production without the collection into the cyclone (continuous generation). The particles were sampled directly from the exhaust connection of the FCD (Fig. 1a and 2a). In addition, the generated particles were also measured at the exit line of the FCD during the pulsed generation. This indicates the number and size of the particles not captured by the cyclone.

In both sampling cases the aerosol flow (produced particles) from the FCD was diluted with a porous tube diluter (PRD; Fig. 2a and 2b) in order to reduce particle deposition and total particle concentration suitable for the measurement devices. The dilution gas was air, and the dilution flow was set to 80 Nlpm, and controlled with a Brooks 5800-series mass flow meter. A digital pressure gauge and temperature meter were also installed in the sampling line to find out the possible pressure peak caused by the "particle blow" from the cyclone collection cup. To ensure adequate mixing of the aerosol flow from the FCD and the dilution air the length of the sampling line was set to >0.5 m. In addition, a by-pass line was installed in the sampling line to pass the "excess" flow not aspirated by the measurement devices to the exit (Fig. 2b).

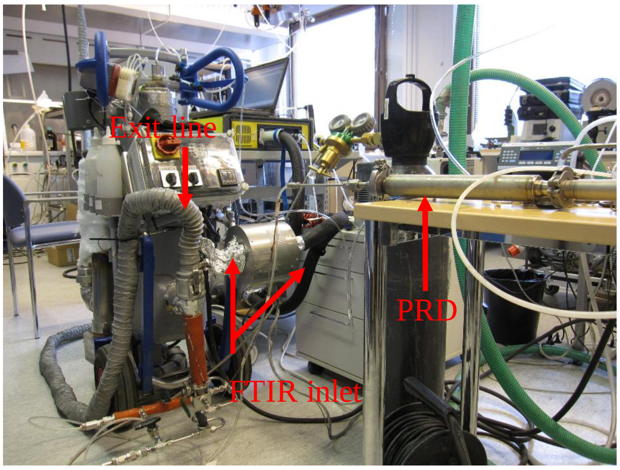

Fig. 2a. Measurement set-up for the particle characterisation measurements.

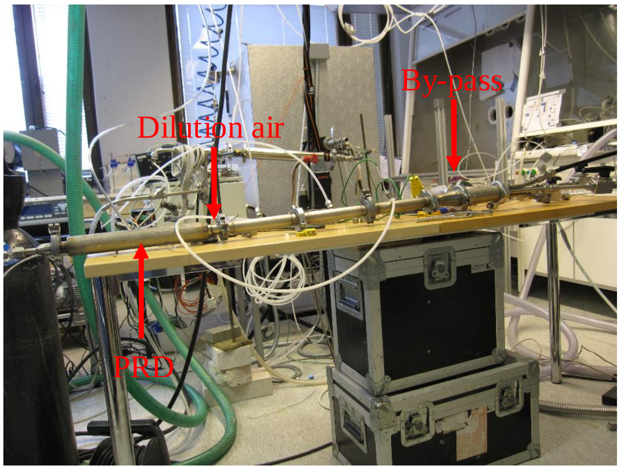

Fig. 2b. Measurement set-up for the particle characterisation measurements. The inlets for the particle measurement devices are on the left.

2.3 Experimental matrix

Table 1. Measurement matrix. Used reagents, processes (charges (pulses) or continuous production), BLPI and electron microscopy sample collection times. During "charges" and "continuous" process ELPI and TEOM were measuring after the porous tube diluter and FTIR from the exhaust (Fig. 1a and 2a), and during "continuous" FTIR was left out.

Date	Reagent(s)	Time	Process	BLPI	SEM
11.5.2010	$BaCl_2$+Na_2SO_4+Si	9:41-10:46	Pulses	10:40-10:46	10:35
		10:48-10:54	Continuous		
		11:17-11:40		11:23-11:31	11:34
		13:45-14:11	Pulses+ bullet		
		15:02-15:31		15:29-15:38	15:17
		15:49-15:54	Pulses		
12.5.2010	$BaCl_2$	10:05-10:26	Pulses	10:07-10:26	10:26
		10:57-11:02	Pulses+ bullet		
		12:30-12:44	Continuous exhaust		
	$BaCl_2$+Si	13:19-13:27			
		13:46-13:53	Pulses		
		14:06-14:15	Pulses+ bullet		
		14:39-14:43	Pulses		14:43
14.5.2010	$BaCl_2$+Na_2SO_4	10:10-10:26	Pulses		
	$BaCl_2$+Na_2SO_4+Si	10:35-10:52			10:38
		11:05-11:19	Continuous		
		12:48-13:04	Continuous exhaust		
	$BaCl_2$+Na_2SO_4	13:04-13:11			
	$BaCl_2$+Na_2SO_4+Si, Si:Ba=8:1	13:46-14:01	Pulses		14:00

The experimental matrix was roughly divided into two parts:

- The characterisation of the calibration particles at the moment.
- Change of the reagent proportions or reagents and/or increase the amount collected particles to the cyclone together with increase of ”blown” particles to the measurement target. This may be achieved by decreasing the particle size with e.g. installing an impaction plate (in this case a cone shaped like a “bullet”, Fig. 3) to the piping after the cyclone. When the particles hit the impaction plate in a suitable angle they may disintegrate into smaller ones. The change of reagent proportion included the change of $BaCl_2$/silika –mass proportion (now 10/1.5) and leaving Na_2SO_4 out of the reagents.

The experimental matrix is presented in Table 1.

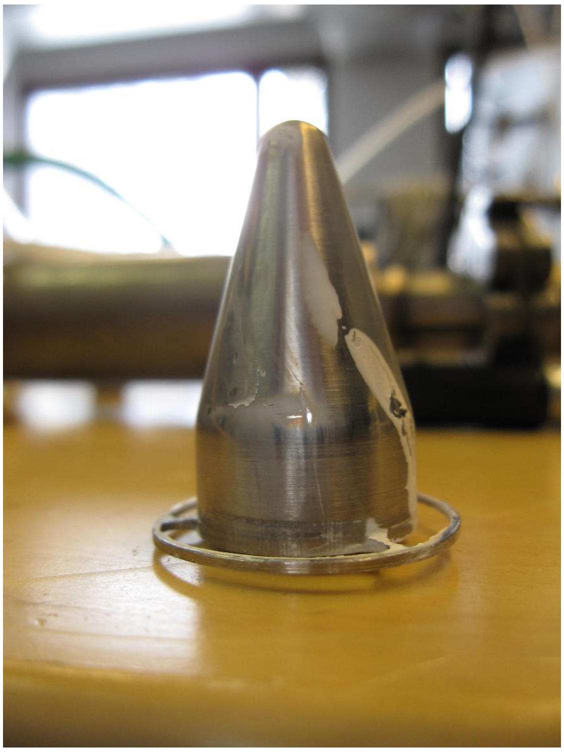

Fig. 3a. An impaction plate (in this case a cone shaped like a “bullet”, L=35 mm, d_{nose}=5 mm, d_{end}=19 mm) used in the experiments to decrease particle size.

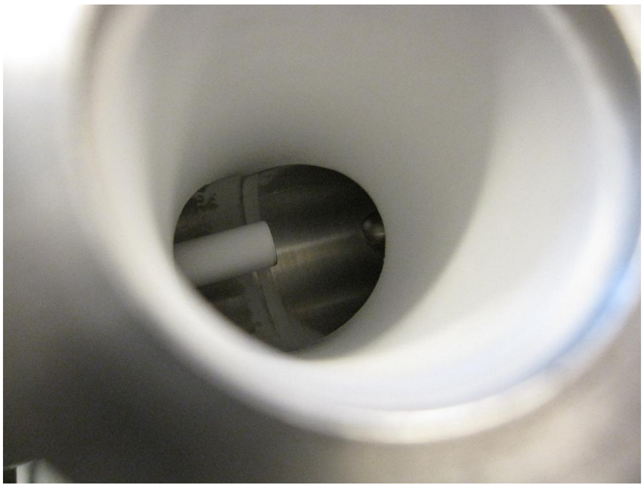

Fig. 3b. The impaction late installed in the flow channel of the experimental set-up. The nose of the plate (“bullet”) is seen on the right, and the tube where the produced particles are “blown” from the cyclone to experimental set-up on the left.

3 Results

3.1 $BaCl_2$+ Na_2SO_4 + silica and $BaCl_2$+Na_2SO_4

3.1.1 Particle number concentration and number size distribution

Particle number concentration and size distribution was measured with an ELPI. Typical particle number concentration during the normal pulsed particle generation with the standard **$BaCl_2$ + Na_2SO_4 + silica** reagent varies between 1.0-1.4·10^7 1/cm^3, and the aerodynamic count median diameter (CMD_{ae}) of the particles varies from 0.8 to 4 µm (Fig. 4a and 4b). The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as “spikes” in the total particle number concentration and in the CMD_{ae} of the particles. The number of pulses may thus be easily counted by counting the number "spikes" in the total number concentration graph(s). Leaving out the silica (**$BaCl_2$ + Na_2SO_4**) the particle number concentration varies between 0.6-1.2·10^7 1/cm^3, and the aerodynamic count median diameter (CMD_{ae}) of the particles varies from 0.9 to 2 µm (Fig. 6a). With added silica content **(Ba:Si=8:1)** the particle number concentration is higher varying from 1.4 up to 3.0·10^7 1/cm^3 (typically 2.0·10^7 1/cm^3). The aerodynamic count median diameter (CMD_{ae}) of the particles varies from 0.4-0.5 µm (Fig. 6b).

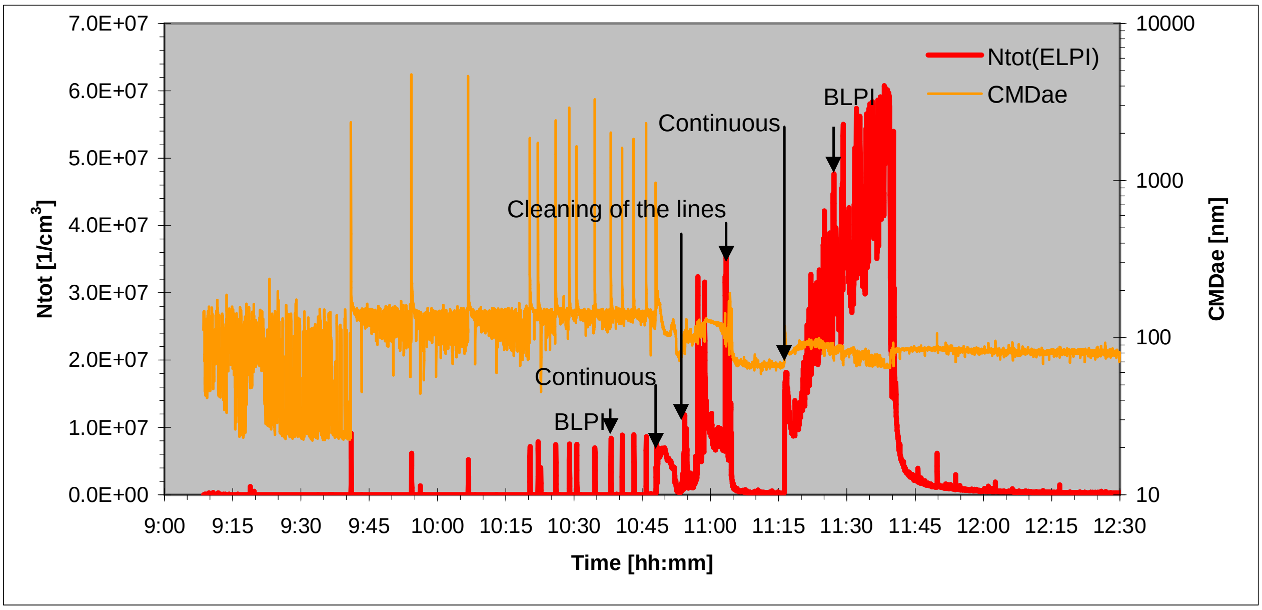

Fig. 4a. Total particle number concentration and aerodynamic count median diameter (CMD_{ae}) of the particles generated from $BaCl_2$ + NaS_2O_4 + silica reagent measured with ELPI on 11.5. 2010. The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as "spikes" in the total particle number concentration (red curve) and in CMD_{ae} of the particles (orange curve). "Continuous" means particle production without the cyclone collection.

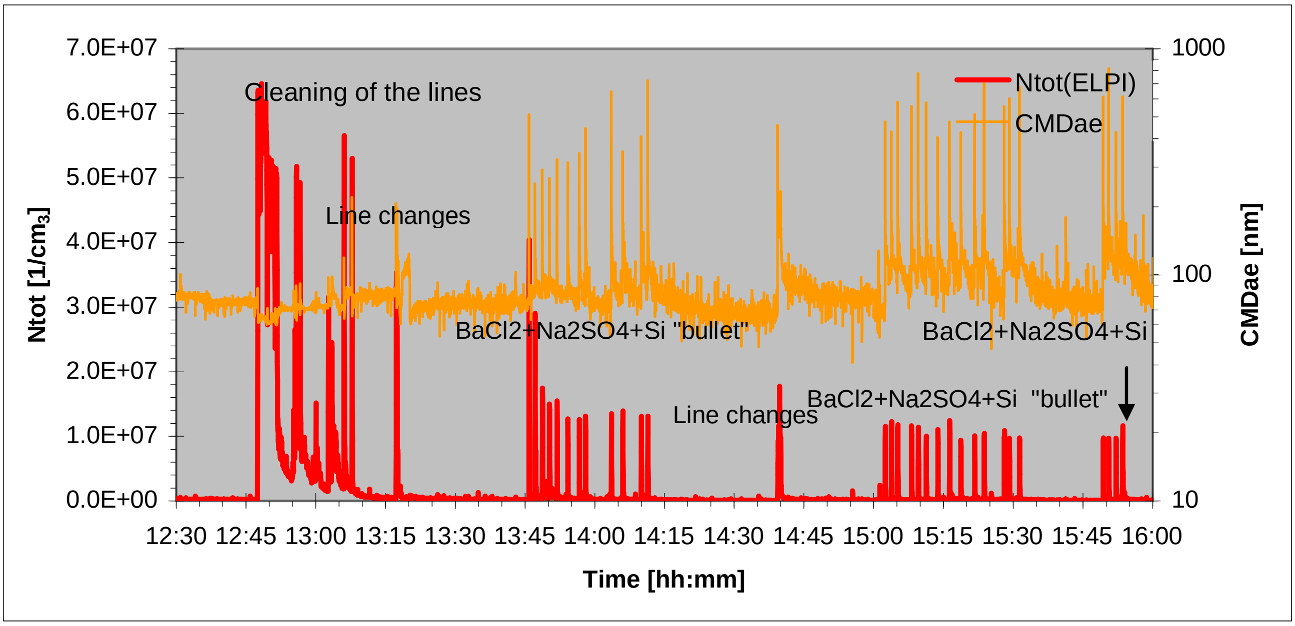

Fig. 4b. Total particle number concentration and aerodynamic count median diameter

(CMD_{ae}) of the particles generated from $BaCl_2$ + NaS_2O_4 + silica reagents measured with ELPI on 11.5.2010. The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as "spikes" in the total particle number concentration (red curve) and in CMD_{ae} of the particles (orange curve). The "bullet" is an impaction plate (shaped as a bullet, Fig. 3) in the flow channel near the exit tube of the particles blown out of the cyclone (Fig. 1b and 2a). The impaction plate was tested if it had any effect on the particle size.

During continuous particle generation (no cyclone collection) with the **$BaCl_2$ + Na_2SO_4 + silica** reagent the total particle number concentration increases during the measurement period 11:17-11:40 from approximately 1.2 to $6.2 \cdot 10^7$ 1/cm^3. At the same time the particle CMD_{ae} decreases from approximately 100 to 70 nm (Fig. 4a). Similar behaviour is also observed in the repetition experiment (Fig. 6a). The increase in the particle number concentration may have been caused by the increase in temperature of the exit of the "drier". The generated particles are thus clearly smaller during continuous generation than during pulsed generation with the cyclone collection. An obvious reason for this is the cut point of 1 µm of the cyclone: the particle generation system is able to produce small particles (< <1µm) but the cyclone is not able to collect them. It also possible that if the collected particles have a "sticky" surface, they may even further grow during cyclone collection because of agglomeration and aggregation.

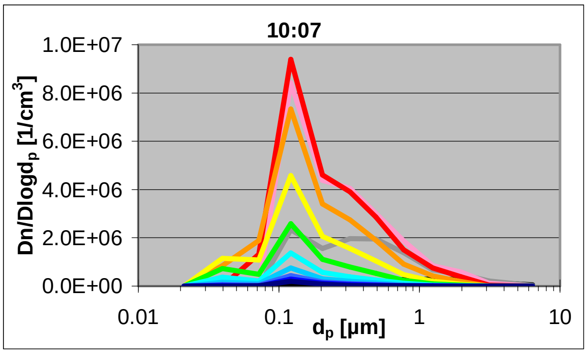

Fig. 5a. The evolution of the number size distribution during one pulse at 10:07 (Fig. 4a), reagent $BaCl_2$+Na_2SO_4+silica.

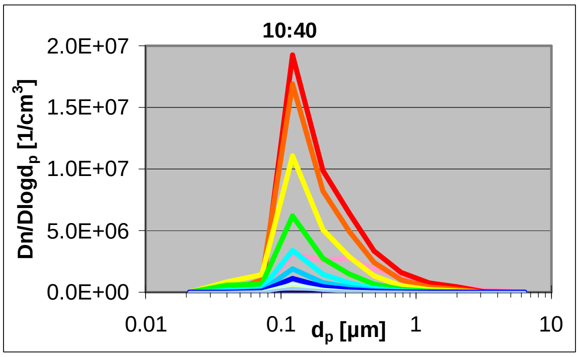

Fig. 5b. The evolution of the number size distribution during one (pulse at 10:40 (Fig. 4a), reagent $BaCl_2$+Na_2SO_4+silica.

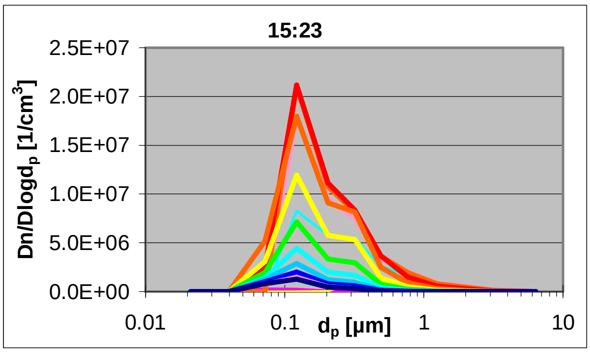

Fig. 5c. The evolution of the number size distribution during one pulse at 15:23 (Fig. 4b), reagent $BaCl_2$+Na_2SO_4+silica with "bullet".

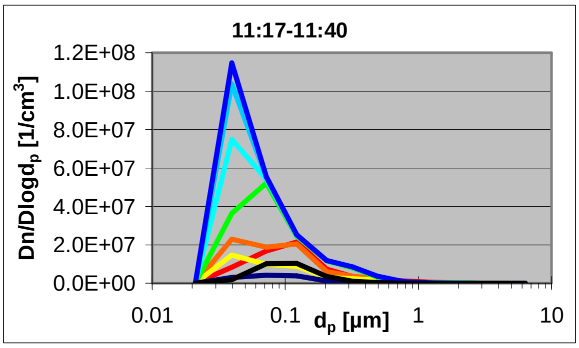

Fig. 5d. The evolution of the number size distribution during continuous production of particles at 11:17-11:40 (no cyclone, Fig. 4a), reagent $BaCl_2$+Na_2SO_4+silica.

Typical particle number concentration in the exhaust flow (Fig. 2a, i.e. particles that are not collected by the cyclone and are "wasted") during continuous particle generation with the **$BaCl_2$ + Na_2SO_4 + silica** reagent is approximately $3.0 \cdot 10^6$ $1/cm^3$, and the aerodynamic count median diameter (CMD_{ae}) of the particles about 130-140 nm. Without the silica (**$BaCl_2$ + Na_2SO_4**) the number concentration decreases to $0.8\text{-}0.9 \cdot 10^6$ $1/cm^3$, and the aerodynamic count median diameter (CMD_{ae}) of the particles increases to 180-190 nm (Fig. 6b). This indicates that the silica particles may act as condensation nuclei for the other forming particles (mostly $BaSO_4$).

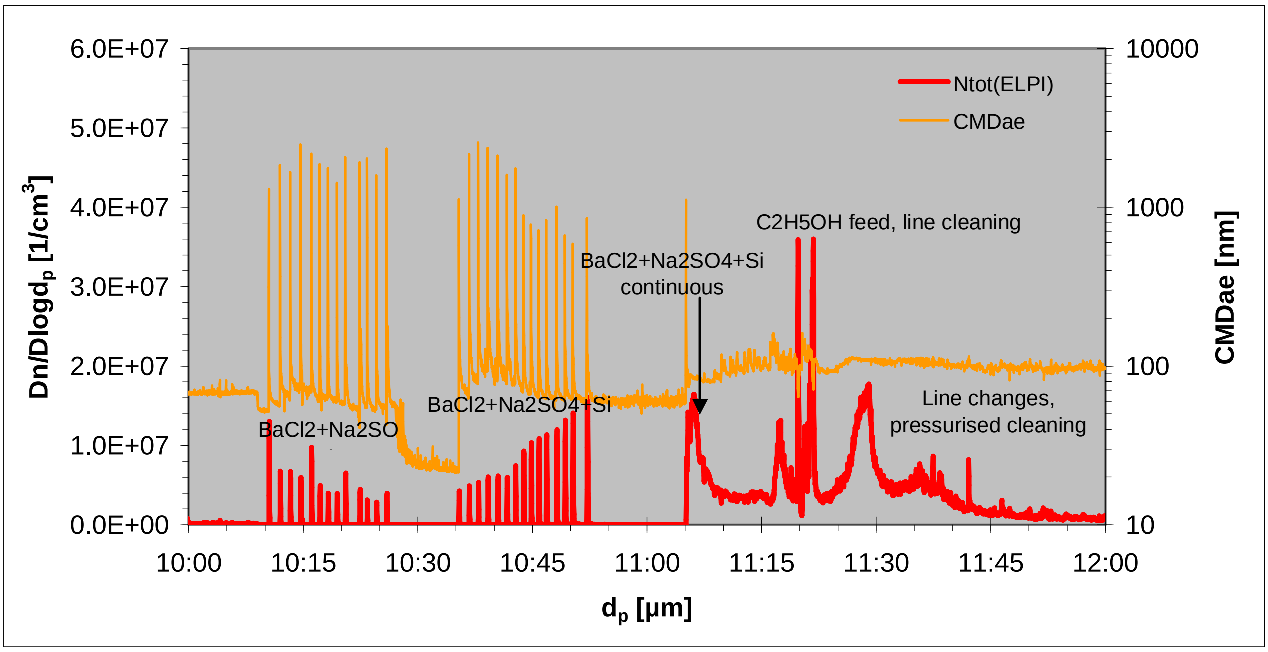

Fig. 6a. Total particle number concentration and aerodynamic count median diameter (CMD_{ae}) of the particles generated from $BaCl_2$ + NaS_2O_4 and $BaCl_2$ + NaS_2O_4 + silica reagents measured with ELPI on 14.5. 2010. The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as "spikes" in the total particle number concentration (red curve) and in CMD_{ae} of the particles (orange curve; compare to Fig. 4). "Continuous" means particle production without the cyclone collection.

The number size distribution (NSD) with **$BaCl_2$ + Na_2SO_4 + silica** reagent during one single pulse with cyclone collection of the particles is typically unimodal with a peak at approx. 150 nm. However, the NSD is sometimes rather wide at the beginning (Fig. 5a-b) and starts to narrow towards the end of the pulse duration. Leaving out the silica (**$BaCl_2$ + Na_2SO_4**) the number size distribution during one single pulse with cyclone collection of the particles is typically bimodal with peaks at approx. 50-60 nm and 400-600 nm (Fig. 7a). With increased silica content (**Si:Ba=8:1**) the NSDs are rather similar to standard case with $BaCl_2$ + NaS_2O_4 + silica (Fig. 7b). The colours indicate the phase of the pulse: red indicates the highest number concentration at the beginning of the pulse and the "colder" (darker) colours the evolution of the pulse towards the end. The time resolution is 1s.

With continuous generation with **$BaCl_2$ + Na_2SO_4 + silica** reagent the peak in the NSD starts to shift to clearly smaller particles, from 150 nm to 50 nm (Fig. 5d). The increase in the particle number concentration and decrease in particle size may have been caused by the increase in temperature of the exit of the "drier". In similar repetitive experiment the particle NSD is clearly bimodal (Fig. 7c). The location of the peaks are, however, similar, and in this case there was no temperature increase at the exit of the “drier”. With pulsed production of particles but measured from the **exit line of the FCD** (Fig. 1c) the number size distribution is again bimodal but the peaks are located at larger particles at 80-90 nm and at 300-400 nm. These are particles that are not captured by the cyclone, and are thus “wasted” (Fig. 7d).

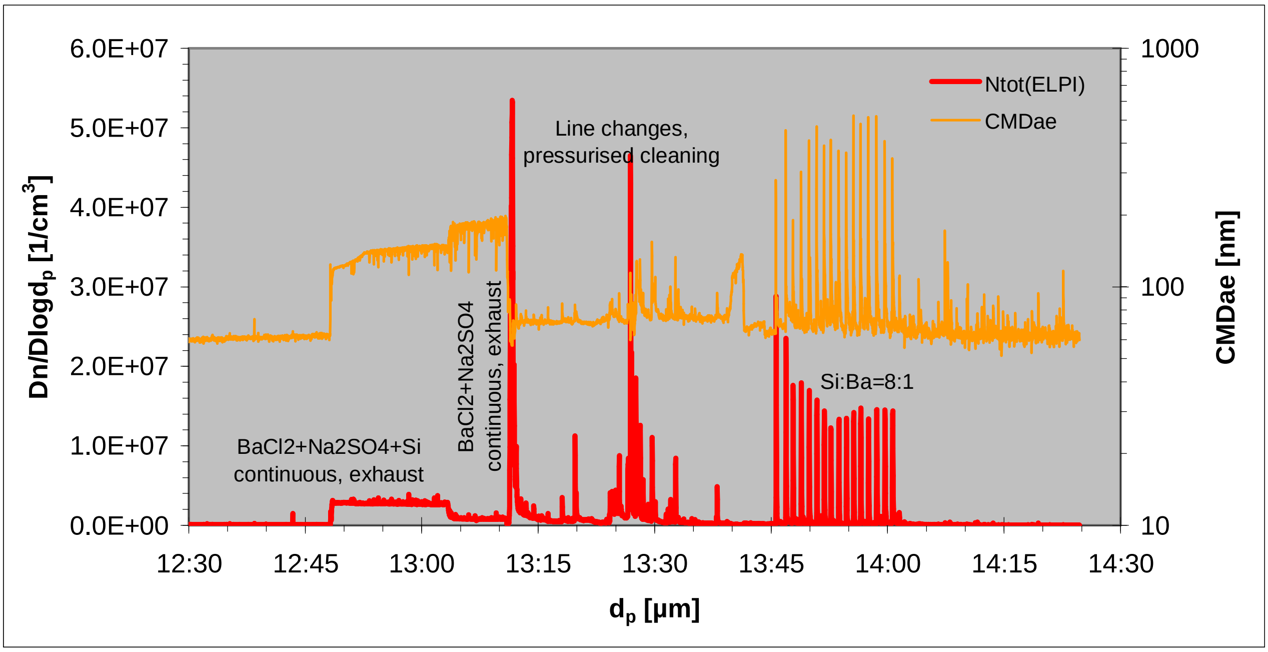

Fig. 6b. Total particle number concentration and aerodynamic count median diameter (CMD_{ae}) of the particles generated from $BaCl_2$ + NaS_2O_4 and $BaCl_2$ + NaS_2O_4 + silica reagents measured with ELPI on 14.5.2010. The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as “spikes” in the total particle number concentration (red curve) and in CMD_{ae} of the particles (orange curve; compare to Fig. 4). “Continuous, exhaust” means particle production with the cyclone collection followed by the “blow”, but the measurements were carried out at the exit line of the IndMeas FCD (Fig. 1b).

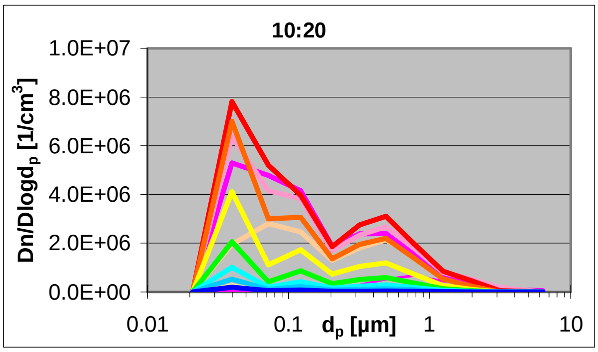

Fig. 7a. The evolution of the number size distribution during one pulse at 10:20 (Fig. 6a), reagent $BaCl_2$+Na_2SO_4.

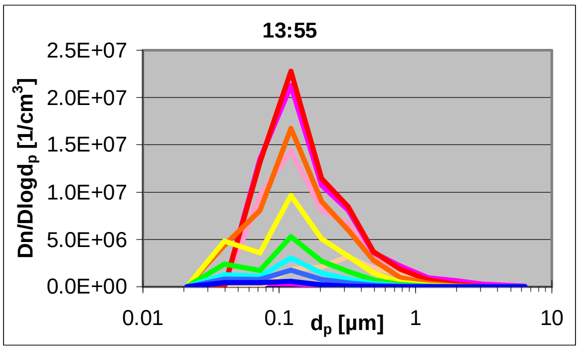

Fig. 7b. The evolution of the number size distribution during one pulse at 13:55 (Fig. 6b), reagent $BaCl_2$+Na_2SO_4+silica, Si:Ba=8:1.

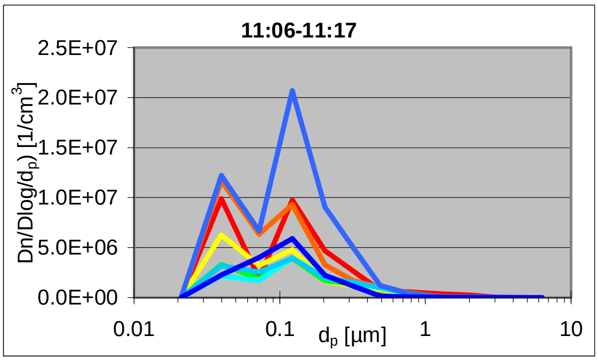

Fig. 7c. The evolution of the number size distribution during continuous production of particles at 11:06-11:17 (no cyclone, Fig. 6a), reagent $BaCl_2$+Na_2SO_4+silica.

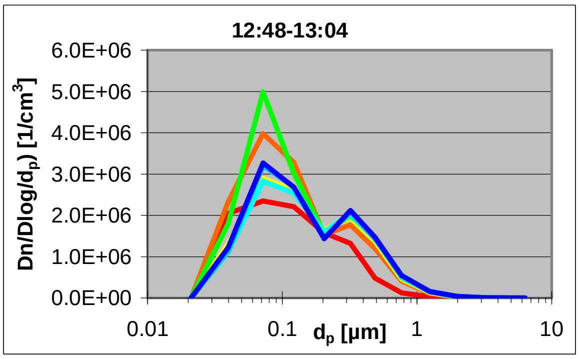

Fig. 7d. The evolution of the number size distribution during pulsed production of particles but measured from the exit line of the FCD (Fig. 1c) at 12:48-13:04 (Fig. 6b), reagent $BaCl_2$+Na_2SO_4+silica.

The effect of an impaction plate to possibly disintegrate the particles collected by the cyclone and "blown" away from the collection cup with N_2 was also tested with **$BaCl_2$ + NaS_2O_4 + silica** reagent. With the tested set-up (Fig. 3) no significant effect on the particle size is found (Fig. 4b; Fig. 5a-c). The reason for this is probably too aerodynamically designed impaction plate ("bullet" shaped) so that the particles do not actually impact to it but just flow pass by. Another cause may be the too large a distance between the impaction plate ("bullet") and the exit of tube where the particles enter the measurement system (Fig. 3b).

3.1.2 Particle mass concentration and mass size distribution

The particle mass concentration was measured online with TEOM. The particle mass concentration during the normal pulsed particle generation with the standard **$BaCl_2$ + Na_2SO_4 + silica** reagent varies between 215-465 mg/m^3. Because of the longer time constant (10s) compared to ELPI the individual pulses are not observed as peaks but they are averaged out (Fig. 8a). Comparable mass size distributions measured with BLPI indicate that the total mass concentration is 102 and 111 mg/Nm^3. It should be noted that BLPI and TEOM results are not directly comparable, because they were measured on a different day, BLPI on 11.5.201 and TEOM on 14.4.2010, respectively. In addition, the sampling times for the BLPI were 6 and 9 min: the results are thus averages over the sampling time. The BLPI mass size distributions peaked at 1-3 µm sized particles (Fig. 9). Leaving the silica out (**$BaCl_2$ + Na_2SO_4**) the particle mass concentration varies between 70-230 mg/m^3. Thus the mass concentration is at least two times higher with the silica than without it (Fig. 8a). Increasing the amount of silica (**Si:Ba=8:1**) increases the particle mass concentration very strongly: it varies between 240-930 mg/m^3 (Fig. 8b).

Typical particle mass concentration in the exhaust flow (Fig. 2a, i.e. particles that are not collected by the cyclone and are "wasted") during the normal pulsed particle generation with the standard **$BaCl_2$ + Na_2SO_4 + silica** reagent is about 24 mg/m^3. Leaving the silica out (**$BaCl_2$ + Na_2SO_4**) again decreases the particle concentration to 12 mg/m^3, approximately half of that with the silica (Fig. 8b).

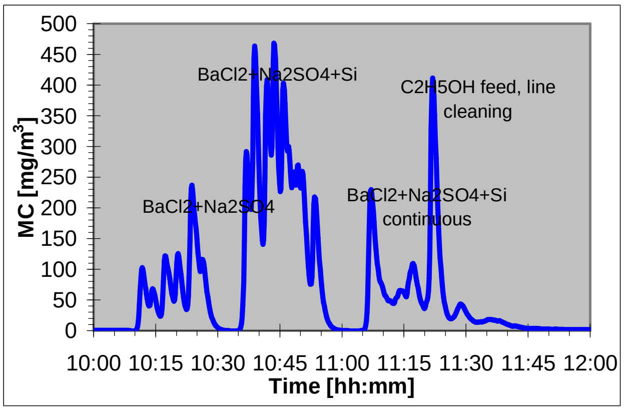

Fig. 8a. Mass concentration of the particles generated from $BaCl_2$ + NaS_2O_4 and $BaCl_2$ + NaS_2O_4 + silica reagents measured with a TEOM (See Fig. 6a and 9).

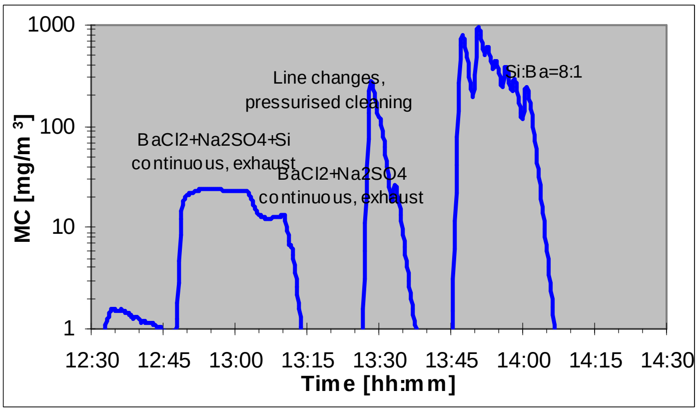

Fig. 8b. Mass concentration of the particles generated from $BaCl_2$ + NaS_2O_4 and $BaCl_2$ + NaS_2O_4 + silica reagents measured with a TEOM (See Fig. 6b and 9). "Continuous, exhaust" means particle production with the cyclone collection followed by the "blow", but the measurements were carried out at the exit line of the IndMeas FCD (Fig. 1b).

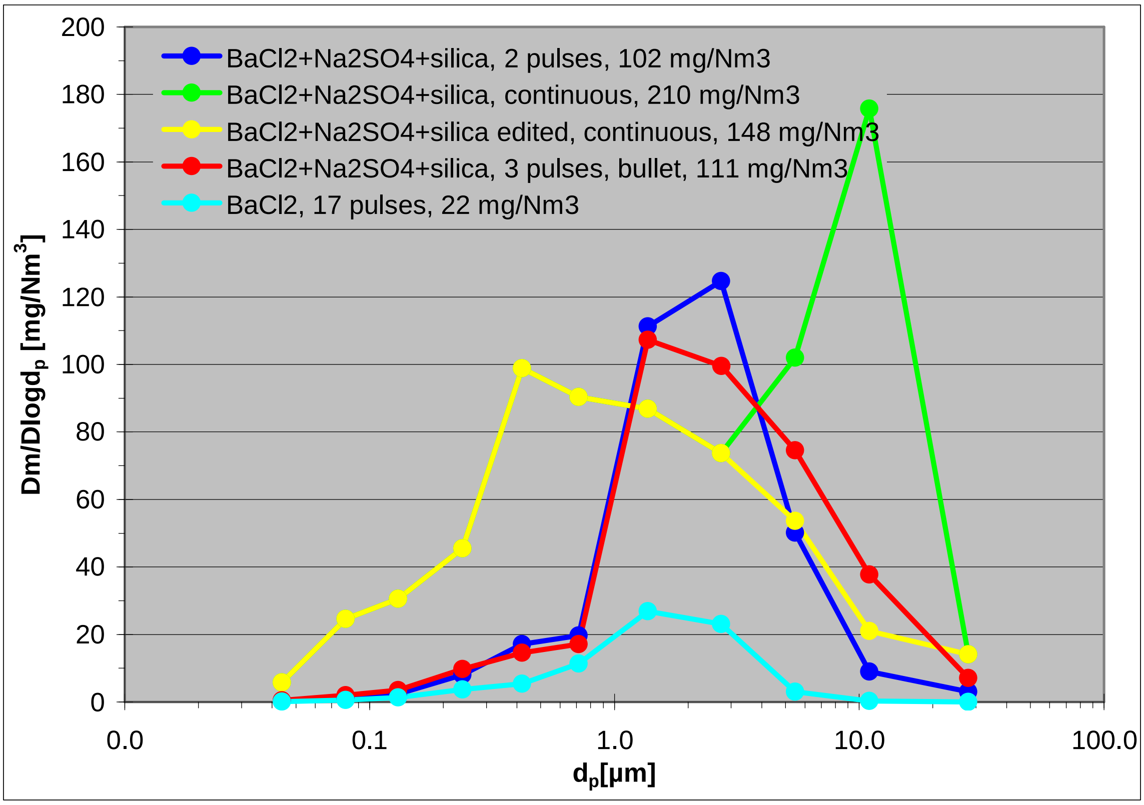

Fig. 9. Mass concentration of the particles generated from $BaCl_2$ + NaS_2O_4 + silica (and $BaCl_2$) reagent(s) measured with a BLPI. "Continuous" means particle production without the cyclone collection. During the measurement of "$BaCl_2$ + NaS_2O_4 + silica, continuous" (green curve) a large particle cluster was noticed to enter the measurement system. The effect of omitting this cluster is seen on the yellow curve (the average of the blue and red curves after the stage 8, at approx. 3 µm).

3.1.3 Particle morphology

The individual particle samples were collected with an aspiration electron microscopy sampler (AEM sampler). With the **$BaCl_2$ + Na_2SO_4 + silica** reagent during the normal pulsed generation the particles are large (>1 µm; the cut point of the cyclone is 1 µm) and almost spherical. The silica also causes some “branching” of the particles (Fig. 10a). With higher magnification the surface of the spherical particles is seen to consist of even smaller, almost spherical particles approx. 30-50 nm in diameter (Fig. 10b). Leaving the silica out (**$BaCl_2$ + Na_2SO_4**) the particle size does not seem change much, but the structure becomes more compact, and the “branching” disappears (Fig. 10c). With higher magnification the more compact surface structure of the particles is clearly visible, and reminds the structure of cobblestones. There are also some very small particles (diameter approx. 10-20 nm) on the surfaces of these cobblestones (Fig. 10d). Increasing the amount of silica (**Si:Ba=8:1**) seems to cause even more “branching” to the particles than with the normal silica amount (Fig. 11a). The increased silica amount thus seems to cause the formation of chain-like structures.

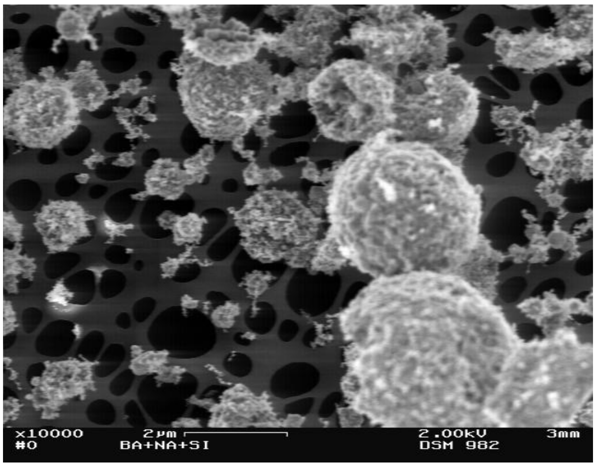

Fig. 10a. The generated particles with $BaCl_2$ + NaS_2O_4 + silica reagent collected with cyclone and “blown“ away. Large particles (>1 µm) are almost spherical.

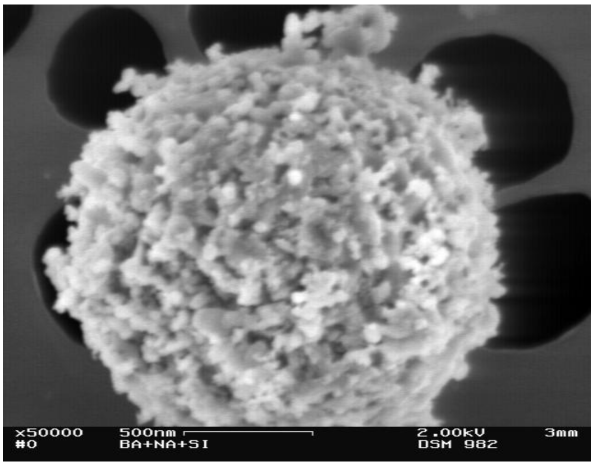

Fig. 10b. A detail of a spherical particle. The surface consists small particles, of which some are almost spherical (diameter approx. 30-50 nm).

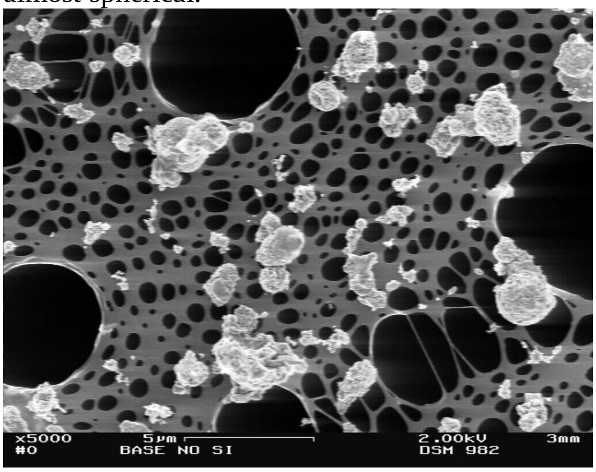

Fig. 10c. The generated particles with $BaCl_2$ + NaS_2O_4 reagent collected with cyclone and “blown“ away. Particle structure is more compact than with silica.

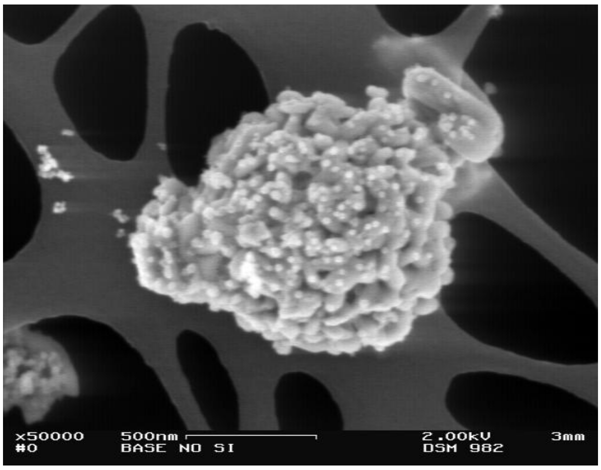

Fig. 10d. A detail of an almost spherical particle. There are very small spherical, primary particles (diameter approx. 10-20 nm) on the surface of a cobble-stone structure.

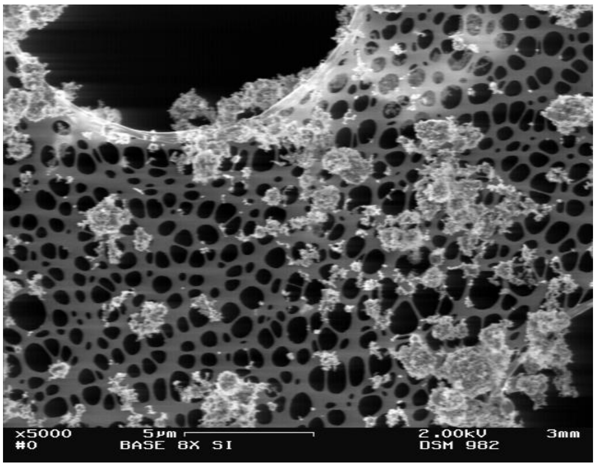

Fig. 11a. The generated particles with $BaCl_2$ + NaS_2O_4 + silica with Si:Ba=8:1 reagent collected with cyclone and "blown" away. The particles look more "branched" than with the normal silica amount (Fig. 10a).

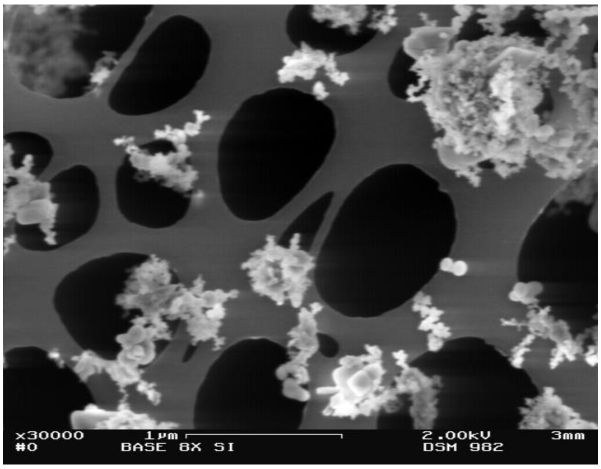

Fig. 11b. A detail of the collected particles. The "branched" structure of the particles is clearly visible..

During continuous particle generation (no cyclone collection) with the **$BaCl_2$ + Na_2SO_4 + silica** reagent the formed particles are clearly smaller than with the pulsed production combined with cyclone collection. It also seems that the particles are less "branched" than with pulsed production (Fig. 12a). Also the structure of the particles seems to be more compact than with pulsed production (Fig. 12b).

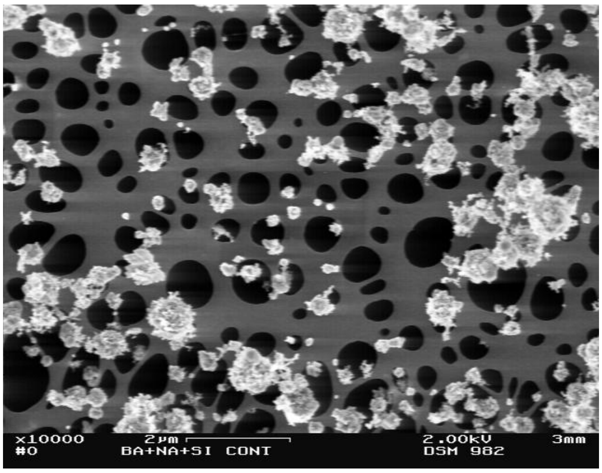

Fig. 12a. The generated particles with $BaCl_2$ + NaS_2O_4 + silica reagent with continuous production (no cyclone collection). The particles are clearly smaller than with cyclone collection.

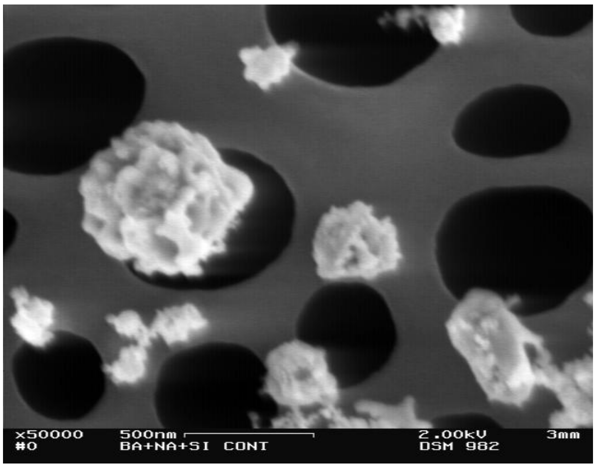

Fig. 12b. A detail of almost spherical particles. The structure of the particles is compact.

3.1.4 Gas composition

The gas composition at the exhaust line of the FCD (Fig. 2a) was measured with a FTIR. Here an example case of the results of the measurements is presented for the $BaCl_2$ + NaS_2O_4 + silica reagent. During the pulses similar "spikes" as in the number concentration measured with ELPI (Fig. 4a) are observed in H_2O and in O_2 concentration (Fig. 13). During these "spikes" the H_2O increases to 5 V.%, and O_2 concentration decreases to 13 V.%. Thus the moisture concentration of the exhaust flow during the pulses is 5 V.%. This also holds for continuous operation (no cyclone). Similar results are obtained for other conditions and reagents.

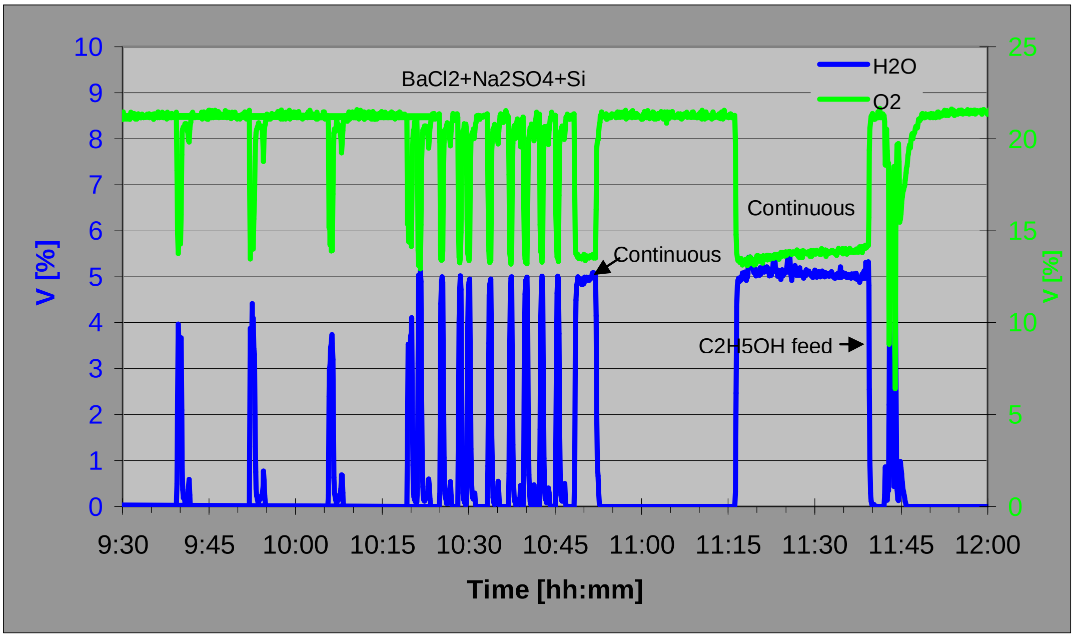

Fig. 13. Gas composition at the exhaust line of the FCD measured with a FTIR on 11.5.2010 with $BaCl_2$ + NaS_2O_4 + silica reagent (See Fig. 4a). The charges (pulses) generated by the powerful blow of N_2 through the cyclone are clearly seen as “spikes” in the H_2O (blue curve) and in O_2 concentration (green curve). “Continuous” means particle production without the cyclone collection. Other reagents and conditions are similar.

3.2 $BaCl_2$ + silica and $BaCl_2$

3.2.1 Particle number concentration and number size distribution

Particle number concentration and size distribution was measured with an ELPI. Typical particle number concentration during the normal pulsed particle generation with the **$BaCl_2$** reagent varies between 2.5-6.5·10^6 1/cm^3, which less than half compared to $BaCl_2$ + Na_2SO_4 + silica reagent (1.0-1.4·10^7 1/cm^3). The aerodynamic count median diameter (CMD_{ae}) of the particles varies between 1-4 µm (Fig. 14a), which is almost the same as for $BaCl_2$ + Na_2SO_4 + silica reagent (0.8-4 µm). Again, the pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as “spikes” in the total particle number concentration and in the CMD_{ae} of the particles. Adding an impaction plate to the flow channel does not seem to have any significant effect on the particles (Fig. 14a). This is similar to previous cases with other reagents. Adding silica to the $BaCl_2$ (**$BaCl_2$ + silica**) increases the particle number concentration: during the first set of pulses the number concentration varied between 0.6-1.6·10^7 1/cm^3, and during the second 1.9-4.7·10^7 1/cm^3. The CMD_{ae} of the particles varies between 1-2.5 µm and 0.3-2.4 µm. With the impaction plate (“bullet”) the number concentration varies between 1.1-6.3·10^7 1/cm^3, and CMD_{ae} of the particles between 0.6-2 µm (Fig. 14b). The increased number concentration with impaction plate and during the second set of $BaCl_2$ + silica (Fig. 14b) is probably caused by the variation in the particle production.

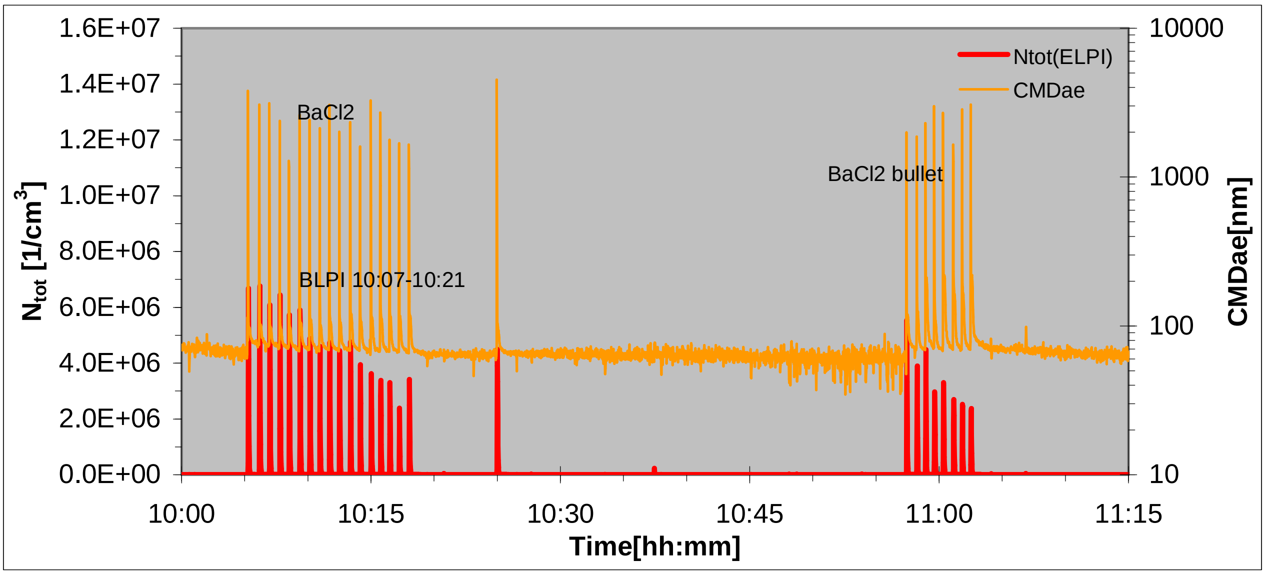

Fig. 14a. Total particle number concentration and aerodynamic count median diameter (CMD_{ae}) of the particles generated from $BaCl_2$ reagent measured with ELPI on 12.5. 2010. The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as "spikes" in the total particle number concentration (red curve) and in CMD_{ae} of the particles (orange curve). "Bullet" is an impaction plate installed in to the flow channel to disintegrate large particles in to smaller ones (Fig. 3).

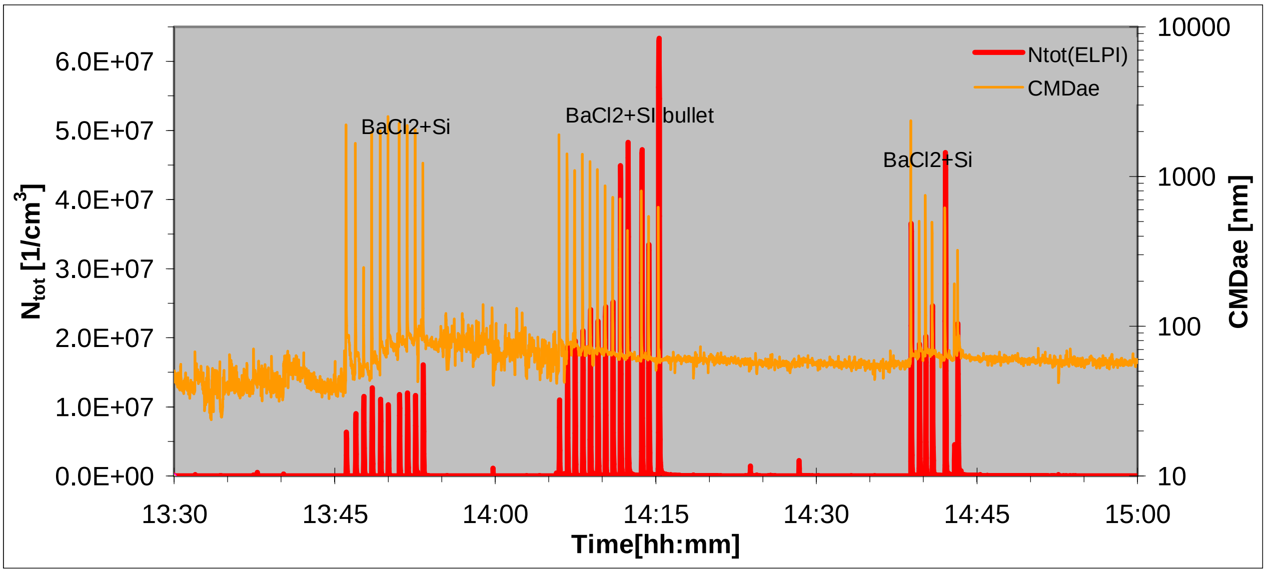

Fig. 14b. Total particle number concentration and aerodynamic count median diameter (CMD_{ae}) of the particles generated from $BaCl_2$ and $BaCl_2$ + silica reagent measured with ELPI on 12.5. 2010. The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as "spikes" in the total particle number concentration (red curve) and in CMD_{ae} of the particles (orange curve). "Bullet" is an impaction plate installed in to the flow channel to disintegrate large particles in to smaller ones (Fig. 3).

Typical particle number concentration in the exhaust flow (Fig. 2a, i.e. particles that are not collected by the cyclone and are "wasted") during pulsed particle generation with the **$BaCl_2$** reagent varies between $0.4\text{-}1.1 \cdot 10^6$ 1/cm^3, and the aerodynamic count median diameter (CMD_{ae}) of the particles about 140-170 nm disregarding a few high peaks (Fig. 14c). Adding silica to the $BaCl_2$ (**$BaCl_2$ + silica**) increases the particle number concentration to $4.9\text{-}8.7 \cdot 10^6$ 1/cm^3, and the aerodynamic count median diameter (CMD_{ae}) of the particles varies about 130-150 nm disregarding a few high peaks (Fig. 14c). The number concentration is thus at least 9 times higher with the added silica.

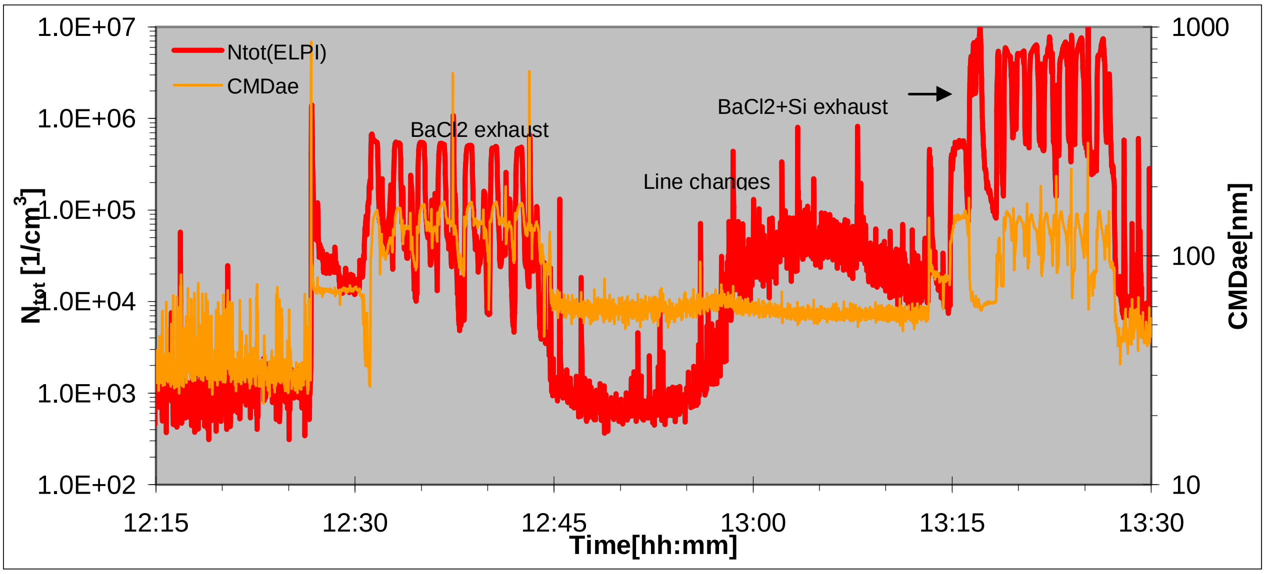

Fig. 14c. Total particle number concentration and aerodynamic count median diameter (CMD_{ae}) of the particles generated from $BaCl_2$ and BaCl2 + silica reagents measured with ELPI from the exhaust of the FCD on 12.5.2010. The pulses generated by the powerful blow of N_2 through the cyclone are clearly seen as "wide spikes" in the total particle number concentration (red curve) and in CMD_{ae} of the particles (orange curve). "Exhaust" means particle production with the cyclone collection followed by the "blow", but the measurements were carried out at the exit line of the IndMeas FCD (Fig. 1b).

The number size distribution (NSD) with **$BaCl_2$** reagent during one single pulse with cyclone collection of the particles is typically unimodal with a peak at approx. 70 nm (Fig. 15a). Compared to $BaCl_2$ + Na_2SO_4 + silica case (≈150 nm; Fig. 5a-b) this is approx. a half of that. With $BaCl_2$ + Na_2SO_4 reagent the number size distributions are bimodal with peaks at approx. 50-60 nm and 400-600 nm, and thus much "wider" (i.e. larger geometric standard deviation GSD; Fig. 7a) than in the case of $BaCl_2$. Adding silica to $BaCl_2$ reagent (**$BaCl_2$ + silica**) makes the number size distribution clearly wider, and towards the end of the pulse the NSD also has bimodal character (Fig. 15b). This is caused by the silica "building bridges" ("branching") between the particles.

Typical particle number distribution in the exhaust flow (Fig. 2a, i.e. particles that are not collected by the cyclone and are "wasted") during pulsed particle generation with the **$BaCl_2$** reagent is rather wide having bimodal character with a peak at approx. 120 nm and 320 nm (Fig. 15c). Adding silica to $BaCl_2$ (**$BaCl_2$ + silica**) does not seem to change the position of the peak at 120 nm, but the second peak is almost disappeared leaving only an indication of a peak, a shoulder (Fig. 15d).

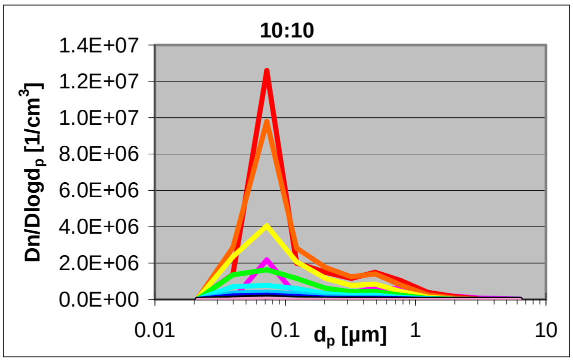

Fig. 15a. The evolution of the number size distribution during one charge (pulse) at 10:10 (Fig. 14a), reagent $BaCl_2$.

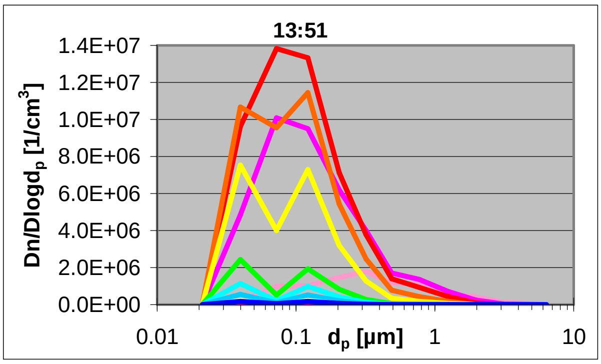

Fig. 15b. The evolution of the number size distribution during one charge (pulse) at 13:51 (Fig. 14b), reagent $BaCl_2$+silica.

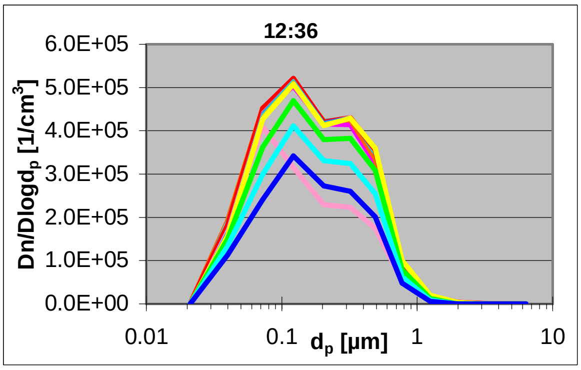

Fig. 15c. The evolution of the number size distribution during pulsed production of particles at 12:36 measured at the exhaust of the FCD, reagent $BaCl_2$ (Fig. 14c).

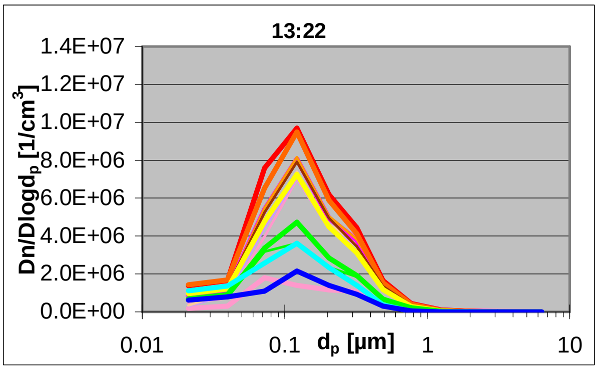

Fig. 15d. The evolution of the number size distribution during pulsed production of particles but measured from the exit line of the FCD (Fig. 1c), reagent $BaCl_2$+silica (Fig. 14c),.

3.2.2 Particle mass concentration and mass size distribution

The particle mass concentration was measured online with TEOM. Typical particle mass concentration during the normal pulsed particle generation with the **$BaCl_2$** reagent varies between 22-31 mg/m^3. Because of the longer time constant (10s) compared to ELPI the individual pulses are not observed as peaks but they are averaged out. During the TEOM measurement a BLPI sample of 14 min (22 mg/Nm^3) was also measured, and it matches well with TEOM measurement. Adding an impaction plate ("bullet") in to the flow channel seems to approx. double the mass concentration to 42-53 mg/m^3 (Fig. 16a). It is not probable that is caused by the impaction plate itself. Adding silica to $BaCl_2$ (**$BaCl_2$ + silica**) increases the mass concentration to 76-119 mg/m^3, and in a repetition experiment to 126-153 mg/m^3. An impaction plate causes in this case, a similar phenomenon as in the case of $BaCl_2$: the mass concentration increases to 94-192 mg/m^3 (Fig. 16b). Similar trends are observed in number concentration (Fig. 14a-b).

Typical particle mass concentration in the exhaust flow (Fig. 2a, i.e. particles that are not collected by the cyclone and are "wasted") during the normal pulsed particle generation with the **$BaCl_2$** reagent varies between 2.7-6.0 mg/m^3. Adding silica to $BaCl_2$ (**$BaCl_2$ + silica**) increases the mass concentration to 16-22 mg/m^3, which is at least 4 times higher than without the silica (Fig. 16c).

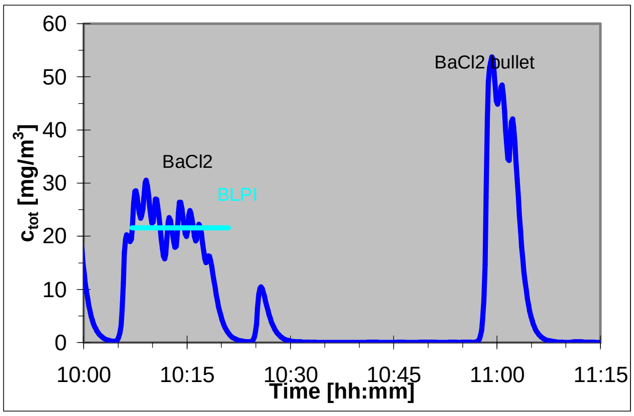

Fig. 16a. Mass concentration of the particles generated from $BaCl_2$ reagent measured with a TEOM (See Fig. 14a and 9). A BLPI sample (14 min) was collected during TEOM measurement.

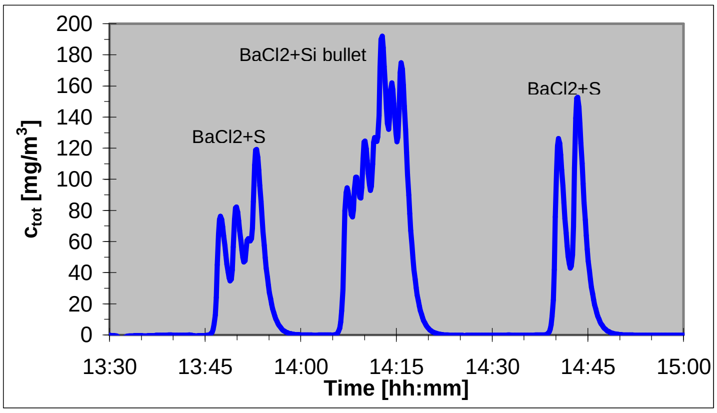

Fig. 16b. Mass concentration of the particles generated from $BaCl_2$ + silica reagent measured with a TEOM (See Fig. 14b).

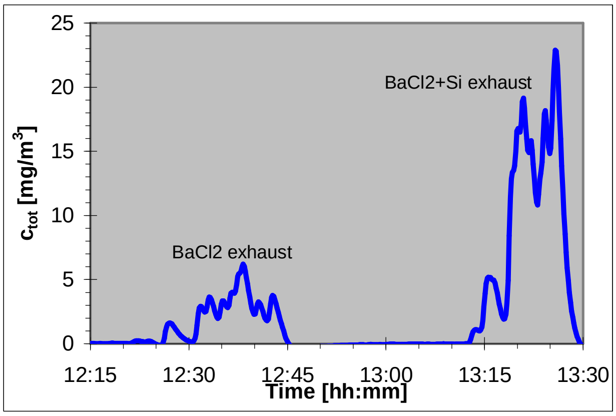

Fig. 16c. Mass concentration of the particles generated from $BaCl_2$ and $BaCl_2$ + silica reagent measured with a TEOM from the exhaust of the FCD (See Fig. 14b).

3.2.3 Particle morphology

The individual particle samples were collected with an aspiration electron microscopy sampler (AEM sampler). With the **$BaCl_2$** reagent during the normal pulsed generation the particles are, generally, 2 µm or smaller in diameter. The structure of the particles is compact (Fig. 17a). The surface the formed particles reminds slightly that of the $BaCl_2$ + Na_2SO_4 reagent particles (Fig. 10c-d): it has similar cobblestone structure, but the small spherical particles on the surface are missing (Fig. 17b). Again, the silica (**$BaCl_2$ + silica**) also causes some "branching" and more porous structure of the particles (Fig. 17c-d).

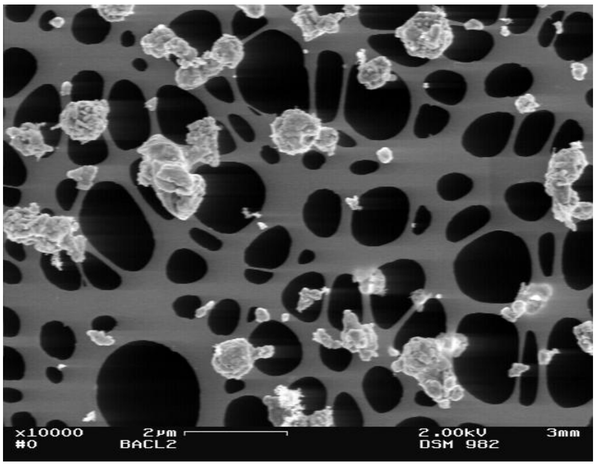

Fig. 17a. The generated particles with $BaCl_2$ reagent collected with cyclone and "blown" away. Particles are, generally smaller than 2 µm.

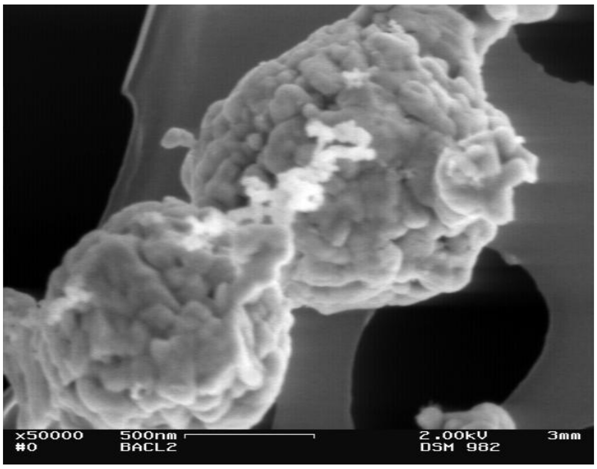

Fig. 17b. A detail of a spherical particle. The surface reminds cobblestone structure also found with $BaCl_2$+Na_2SO_4 reagent.

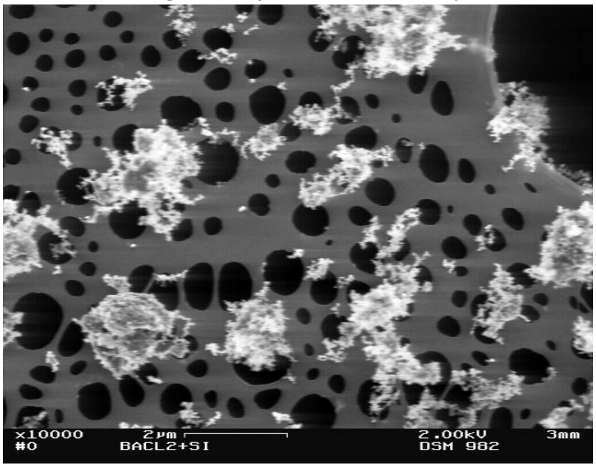

Fig. 17c. The generated particles with $BaCl_2$ + silica reagent collected with cyclone and "blown" away. Silica causes "branching of the particles.

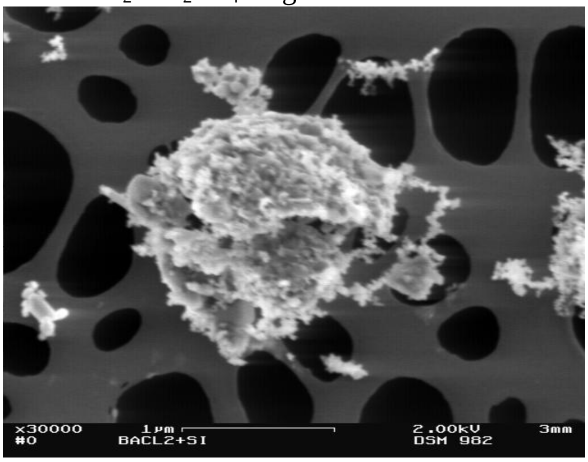

Fig. 17d. A detail of a particle. The "branching" and more porous structure caused by the silica is clearly visible.

3.2.4 Gas composition

The gas composition at the exhaust line of the FCD (Fig. 2a) was measured with a FTIR. Here an example case of the results of the measurements is presented for the $BaCl_2$ + silica reagent. During the pulses similar "spikes" as in the number concentration measured with ELPI (Fig. 14b) are observed in H_2O and in O_2 concentration (Fig. 18). During these "spikes" the H_2O increases to 5 V.%, and O_2 concentration decreases to 13 V.%. Thus the moisture concentration of the exhaust flow during the pulses is 5 V.%. This also holds for continuous operation (no cyclone). Similar results are obtained for other conditions and reagents.

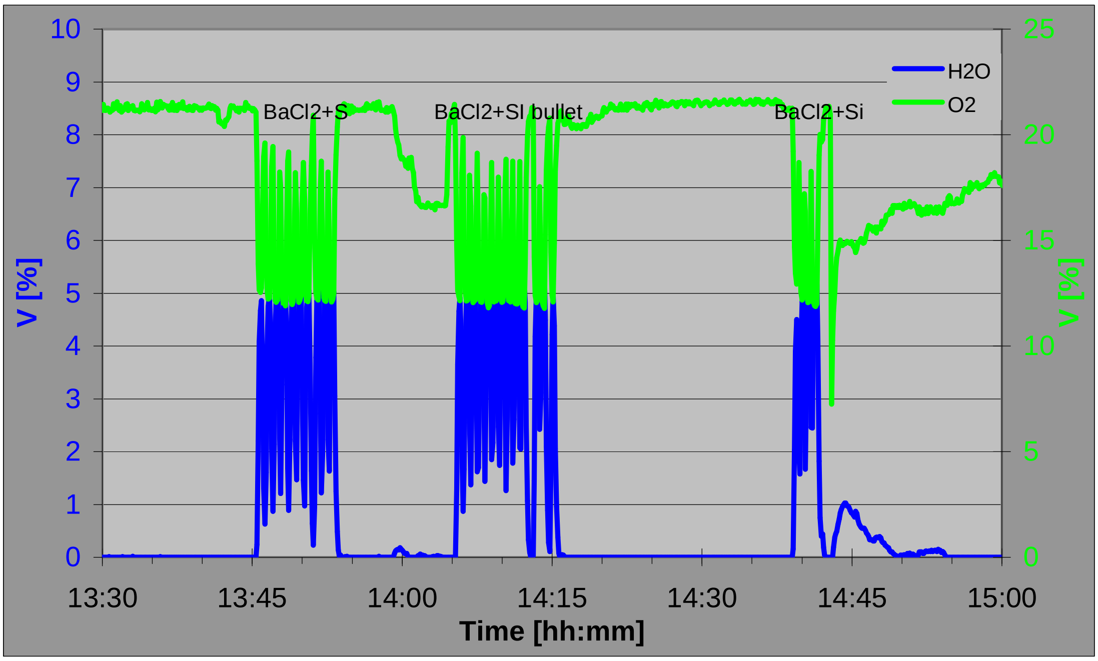

Fig. 18. Gas composition at the exhaust line of the FCD measured with a FTIR on 12.5.2010 with $BaCl_2$ + silica reagent (See Fig. 14b). The charges (pulses) generated by the powerful blow of N_2 through the cyclone are clearly seen as “spikes” in the H_2O (blue curve) and in O_2 concentration (green curve). Other reagents and conditions are similar.

4 Summary and conclusions

In this study the IndMeas flow calibrator device (FCD) using as a reagent/carrier $BaCl_2$ + Na_2SO_4 + silica, and some tracer ^{137}Ba ($t_{d,1/2}$=153 s) originating from the ion exchange column was studied and characterised. To characterise the particles currently produced by the flow calibrator device (FCD) a measurement campaign was carried out to determine the particle number and mass concentration and number and mass size distribution and particle morphology and composition. The produced particles were collected in the cyclone and “blown” away with air or N_2 (pulsed generation), and the gas composition (mainly moisture of the gas) at the exit after the “drier” was measured at the same time. In addition, the generated particles were also measured and characterised during continuous particle production without the collection into the cyclone (continuous generation). The particles were sampled directly from the exhaust connection of the FCD. In addition, the generated particles were also measured at the exit line of the FCD during the pulsed generation. This indicates the number and size of the particles not captured by the cyclone.

Particle number concentration (PNC) during the normal pulsed particle generation with the standard **$BaCl_2$ + Na_2SO_4 + silica** reagent varied between 1.0-1.4·10^7 1/cm^3, and the mass concentration between 215-465 mg/m^3. The aerodynamic count median diameter (CMD_{ae}) varied between 0.8-4 µm, and the mass size distribution peaked at 1-3 µm sized particles (aerodynamic size). Leaving out the silica (**$BaCl_2$ + Na_2SO_4**) did not change the particle number concentration much (0.6-1.2·10^7 1/cm^3), but the CMD_{ae} decreased to 0.9-2 µm. The mass concentration varied between 70-230 mg/m^3, and was thus at least two times higher with the silica than without it. Adding more silica **(Ba:Si=8:1**) increased PNC to 1.4-3.0·10^7 1/cm^3 (typically 2.0·10^7 1/cm^3), but the size (CMD_{ae}) decreased to 0.4-0.5 µm. Also the mass concentration increased strongly: 240-930 mg/m^3.

The particles with the **$BaCl_2$ + Na_2SO_4 + silica** reagent during the normal pulsed generation were large (>1 µm; the cut point of the cyclone is 1 µm) and almost spherical. The silica caused some "branching" of the particles. The surface of the spherical particles consisted of even smaller, almost spherical particles approx. 30-50 nm in diameter. Leaving the silica out (**$BaCl_2$ + Na_2SO_4**) the particle size did not seem to change much, but the structure becomes more compact (cobblestone), and the "branching" disappears. Increasing the amount of silica (**Si:Ba=8:1**) seemed to cause even more "branching" of the particles than with the normal silica amount.

During continuous particle generation (no cyclone collection) with the **$BaCl_2$ + Na_2SO_4 + silica** reagent the total particle number concentration increases during the measurement period 11:17-11:40 from approximately 1.2 to 6.2·10^7 1/cm^3. At the same time the particle CMD_{ae} decreases from approximately 100 to 70 nm. The generated particles are thus clearly smaller during continuous generation than during pulsed generation with the cyclone collection. An obvious reason for this is the cut point of 1 µm of the cyclone: the particle generation system is able to produce small particles (< <1µm) but the cyclone is not able to collect them.

During continuous particle generation (no cyclone collection) with the **$BaCl_2$ + Na_2SO_4 + silica** reagent the formed particles were clearly smaller than with the pulsed production combined with cyclone collection. It also seemed that the particles were less "branched" than with pulsed production. Also the structure of the particles seems to be more compact than with pulsed production. The size of these particles is too small to be captured with the current particle collection device (i.e. cyclone, cut point 1 µm).

Typical particle number concentration during the normal pulsed particle generation with the **$BaCl_2$** reagent varied 2.5-6.5·10^6 1/cm^3, which less than half compared to $BaCl_2$ + Na_2SO_4 + silica reagent (1.0-1.4·10^7 1/cm^3). The mass concentration was 22-31 mg/m^3. A BLPI measurement of 14 min resulted to 22 mg/Nm^3, and the mass size distribution peaked at 1-3 µm being the same as for $BaCl_2$ + Na_2SO_4 + silica. The aerodynamic count median diameter (CMD_{ae}) of the particles varied between 1-4 µm, which is almost the same as for $BaCl_2$ + Na_2SO_4 + silica reagent (0.8-4 µm). Adding silica to the $BaCl_2$ (**$BaCl_2$ + silica**) increased the particle number concentration to approx. 1.0-4.7·10^7 1/cm^3. The CMD_{ae} of the particles varied between 0.3-2.5 µm. The mass concentration increased to 76-153 mg/m^3.

With the **$BaCl_2$** reagent during the normal pulsed generation the particles were, generally, 2 µm or smaller in diameter and compact. The surface the formed particles reminded slightly that of the $BaCl_2$ + Na_2SO_4 reagent particles (cobblestone). The silica (**$BaCl_2$ + silica**) also caused some "branching" and more porous structure of the particles.

As a conclusion, the IndMeas flow calibrator device (FCD) is able to produce small particles (<< 1µm), but these particles cannot be captured with the current collection device (a cyclone with a cut point of 1 µm). This was clearly discovered when the measurements were carried out with the cyclone collection or without it from the measurement line. Adding silica to the reagent(s) caused particle "branching", bridge building between the particles, and the "porosity", particle roughness increases. This may increase particle agglomeration, and therefore, increase the particle size. This was also discovered here in some cases. On the other hand, particles may also agglomerate/aggregate during cyclone collection. To increase the yield of the signal (particles carrying the tracer Ba^{137}) reaching the measurement target the produced particles should be small (preferably <1µm) and as spherical as possible. This may be achieved by a suitable selection of the reagent(s). In order to capture the produced small particles a new collection device is needed. This could be, e.g. a small cylinder-type bag filter.

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