Evaluation of Uncertainties in the Calibration of the Volatile Particle Remover

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1. Introduction

The European Union has decided to regulate particles from automobiles by their number, and efforts have been made to develop an accurate and reliable instrument for the number measurement, as well as its calibration and testing methods.   One component of the measurement instrument is a condensation particle counter (CPC, or PNC).   For assuring the measurement accuracy of the CPC, a few mechanisms have been built.   One is the calibration services in several countries that is traceable to a national standard of aerosol particle number concentration.   Another effort for such a mechanism is the development of an ISO standard for the method of calibrating CPCs which was initiated recently.

Another important component of the measurement instrument for the EU's number regulation is the volatile particle remover (VPR).   The VPR is a pre-conditioner to eliminate volatile particles before they enter the CPC.   Another function of the VPR is to dilute non-volatile particles so that the concentration of those particles becomes low enough for accurate measurement by the CPC.

For accurate determination of the number concentration of non-volatile particles, the VPR requires calibration and testing of its performance.   The calibration includes determination of the reduction factor of the concentration of non-volatile particles (the particle concentration reduction factor; PCRF) which is mainly determined by the factor of dilution, but is also significantly affected by losses of particles that are dependent on particle size.   While many efforts have been made so far, there may be still some unidentified sources of errors in the determination of the PCRF.   By evaluating uncertainties in a systematic way, through identification of sources of biases and fluctuations both in the VPR itself and also in the calibration system, and through quantification of the magnitude of the biases and fluctuations, we may be able to find the most influencing sources of error.   Such findings would allow us to revise the calibration and testing methods for determination of the performance of the VPR with smaller errors.

We recently started uncertainty evaluations in the VPR calibration.   So far, we have been focusing on evaluation of uncertainties in determining the PCRF in two aspects.   One is the concentration linearity of the CPC(s) used in the PCRF determination, and the other is the chemical composition of the particles used in determination of PCRF values.   Some initial results are presented in this poster.

2. VPR Evaluation

We built a VPR evaluation system by following the latest PMP procedure[1].   To measure the upstream and downstream concentrations of the VPR, we used two CPCs of the same model from the same manufacturer; the sampling flow rate of 0.3 L/min and single-counting mode operation up to about 10^4 cm^{-3}.

The VPR used in this investigation was Model PMS-M2 of Tsukasa Sokken Co. Ltd. (Tokyo, Japan). This VPR can be connected to various PNCs of different flow rates, while dilution ratios do not get affected by the PNC that is attached to it, which is a unique characteristics as a diluter.   Because of this, we were able to use the CPCs of the sampling flow rate of 0.3 L/min in the PCRF determination without any problem. The VPR uses critical nozzles to regulate precisely flow rates (and hence dilution ratios) of the diluters in the VPR system, and can be operated at nominal dilution factors of 100, 200, 500, and 1000.

We generated two kinds of particles to be used in the VPR evaluation.   One was sodium chloride (NaCl), which was generated by nebulization of aqueous salt solution.   The other was soot generated by Combustion Aerosol Standard 2 (CAST-2; Matter Engineering, Switzerland).   For experiments at 30 nm, the CAST was set in 30 nm mode while experiments at 50 and 100 nm, the CAST was set in 60 nm mode.

3. Uncertainties due to CPC's Linearity

It is often the case that we can expect good linearity in concentration measurement by a CPC when it

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[1] Sandbach, E. (2007). Volatile Particle Remover Calibration and Validation Procedures, AEA/ED47382004/VPR/Issue 5.

operates in single-counting mode while counting losses by coincidence are insignificant. However, since obtained PCRF values would have errors if the CPCs used in the PCRF determination have poor linearity, we investigated the linearity of the CPCs used in our study.

The linearity evaluation was made in two ways with different references. The first was with the Japanese primary standard for aerosol particle number concentration. This gave the absolute detection efficiency, but the linearity was studied only in the range of 3000 to 30000 cm^{-3} because of the limitation of the concentration range of the standard at 0.3 L/min. The second was with another "reference" CPC, the linearity of which was checked separately in two ways, i.e., by calibration with the primary standard and by experiments with a rotating-disk diluter, which is also a linearity reference. Readings of the reference CPC agreed with the concentration change made by the rotating-disk diluter within 1 % in the 500-20000 cm^{-3} range. The linearity was investigated with both sodium chloride and soot.

The results showed that both of the two CPCs used in the VPR evaluation behaved similarly with each other, and were very linear in the concentration range between ~1 and ~3000 cm^{-3} for ~3 orders of magnitude. However, we observed poor linearity (as fluctuations of the detection efficiency relative to references) in both of the CPCs between ~4 x 10^4 and ~2 x 10^4 cm^{-3}, while the two CPCs behaved very similarly. The deviation from the detection efficiency in the low concentration range was as large as ~ 5 %, if we look at the concentration range only up to 10^4 cm^{-3}. (The deviation was even greater at concentrations slightly above 10^4 cm^{-3}.) We do not know the exact reason for this, and speculate that coincidence correction did not function very well in this concentration range for the two CPCs.

The detection efficiencies relative to the reference CPC increased slightly as the particle size increased. This was either due to increase of the detection efficiency of CPC1 and CPC2, or due to decrease of that of the reference CPC. The relative detection efficiencies were identical between sodium chloride and soot.

With the CPCs with these linearity characteristics, we can still make accurate measurements. One way to do it is to limit the usage of the CPCs in the concentration range of less than 3 x 10^3 cm^{-3}., which would be simplest because basically no corrections are needed, and hence give smallest uncertainties, though the concentration downstream of a VPR would be very low, which would require long measurement periods to count enough particles. Another is to use the linearity data to correct for the detection efficiency. This is expected to work fine too. The sharp oscillating changes of the detection efficiency in the concentration range between 8000 and 12000 cm^{-3}, however, would produce some uncertainty and also would require very stable particle generation. There is also an option not to correct for the observed linearity at all, while the VPR's upstream may be around 4000-10000 cm^{-3}. In this case, uncertainties in the VPR upstream concentration of up to ~5 % need to be accounted for.

4. Uncertainties due to the Particle Composition

The PCRF values determined with the two kinds of particles were essentially the same at 50 and 100 nm. However, at 30 nm, the PCRF values with soot were greater than those with sodium chloride by about 3-5 %. These stand for greater mean PCRFs with soot by 1-2 % than with sodium chloride.

The reason for the greater PCRF values with soot is not known. As seen in the previous section, the detection efficiencies of the CPCs between sodium chloride and soot were the same. Therefore, the difference in PCRF was produced in the VPR. We speculate that 30-nm soot particles from the CAST generator was somewhat volatile and may have shrunk when heated in the evaporation tube of the VPR. This would reduce the size of the particles, and therefore losses may increase before the particles exit the VPR, which would be observed as increased PCRFs.

The data obtained in this study indicates that, if the particle composition is different, results of the PCRF evaluation would be different. Our study showed the difference of about 1-2 % in the mean PCRFs, which is not too large, but we do not know if these values are common with other VPRs, or unique to the VPR used in this study.

5. Conclusions

We investigated two sources of uncertainties in PCRF evaluation of the VPR, i.e., the CPC concentration linearity and the particle composition.

The concentration linearity of the two CPCs used in our VPR evaluation was investigated in the range from 1 to ~10^4 cm^{-3}. While the linearity was good for ~3 orders of magnitude between 1 and 3 x 10^3 cm^{-3}, the linearity was poor above ~4 x 10^3 cm^{-3}. Depending on how the actual linearity is taken into account, PCRF values could have errors of up 5 %.

The mean PCRF value with soot was greater by 1-2 % compared to NaCl. If the material in the PCRF evaluation is not specified, there could be errors of a similar magnitude. The error may be VPR dependent.
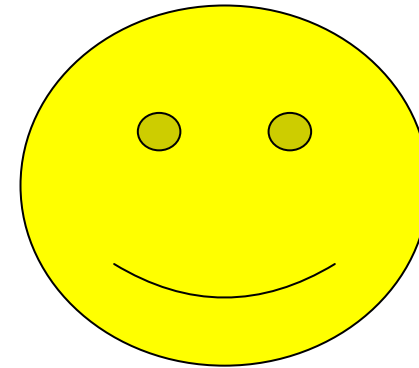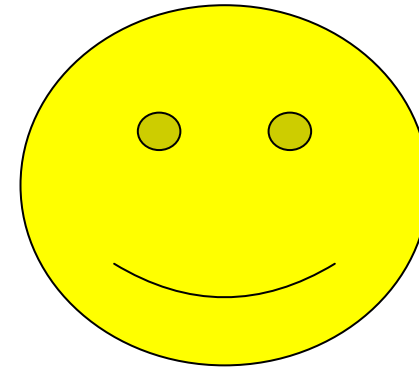
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Purpose of the study

- Evaluate uncertainties in determination of the particle concentration reduction factor (PCRF) of the volatile particle remover (VPR) in two aspects: the concentration linearity of the CPC(s) and the particle composition.

VPR used in this investigation

- Model PMS-M2 by Tsukasa Sokken Co. Ltd. (Tokyo, Japan)
- Can be operated at nominal dilution factors of 100, 200, 500, and 1000.
- Uses critical nozzles to regulate precisely flow rates (and hence dilution ratios) of the diluters in the VPR system.
- The PNC flow rate does not necessarily have to be 1 L/min. The VPR can be operated with a PNC of the sampling flow rate of 0.3 L/min too.

VPR evaluation setup at AIST

- Uses two CPCs of the same model; one upstream, the other downstream of the VPR; the sampling flow rate of 0.3 L/min, single-counting mode up to ~10^4 cm^{-3}
- Aerosol generation: Sodium chloride (NaCl) and Soot
    - Sodium chloride (NaCl) by nebulization of aqueous salt solution
    - Soot by CAST-2
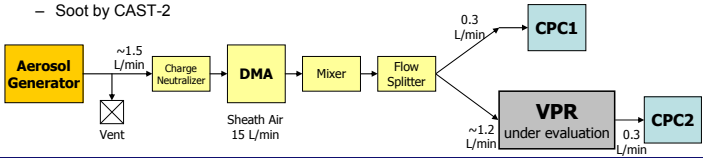

Why does the linearity matter?
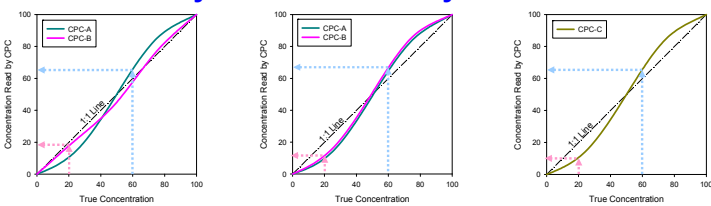
If CPCs have poor linearity, PCRF determined by the CPCs will have errors. If two CPCs have the linearity curves above, comparison between the two tells that something is wrong in the linearity, at least in one of the two CPCs.

In the above case, comparison between the two CPCs does not tell the poor linearity.

The issue is not due to the use of two CPCs. Having (and using) only a single CPC may suffer from the same problem.

**The CPC linearity needs to be checked with good linearity references.**

Calibration by the Japanese primary standard
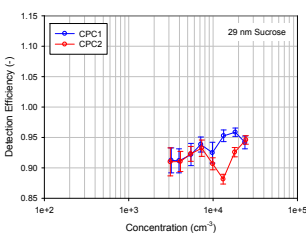
- Detection efficiency oscillates by a few % between ~4 x 10^3 and ~2 x 10^4 cm^{-3}
- The two CPCs behave similarly with each other except the range between 10^4 and 2 x 10^4 cm^{-3}.
- Coincidence correction does not seem to be functioning very well.
- The concentration range that can be calibrated with the primary standard (i.e., aerosol electrometer) is too limited, while data of a wider concentration range are needed.

Reference CPC →

- This CPC works in single counting mode up to 10^4 cm^{-3} with coincidence correction.
- The detection efficiency is not 100 %, but is about constant; therefore coincidence correction seems to be functioning well, which is crucial for good linearity.
- This CPC seems to be suitable as a reference to study the linearity of CPC1 and CPC2 between 10^3 and 10^4 cm^{-3}.
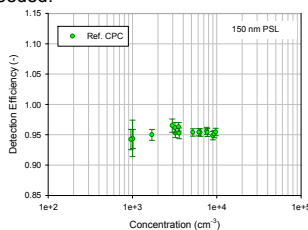

Linearity double-check with a rotating-disk diluter

Experiments with the reference CPC and a rotating-disk diluter (Matter Engineering Model MD19-1i) indicated that the agreement between the two linearity references was good within 1 % at all three particle sizes (30, 50, and 100 nm) under the conditions below:

Ref. CPC:	Rotating-disk diluter (in potentiometer setting):
500 – 20000 cm^{-3}	30 – 100 % with 10-cavity disk
	40 – 100 % with 8-cavity disk

Linearity tests

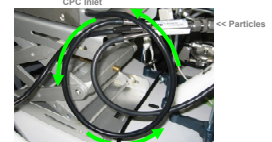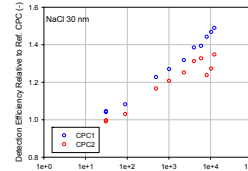Comparison against Ref. CPC at various concentrations
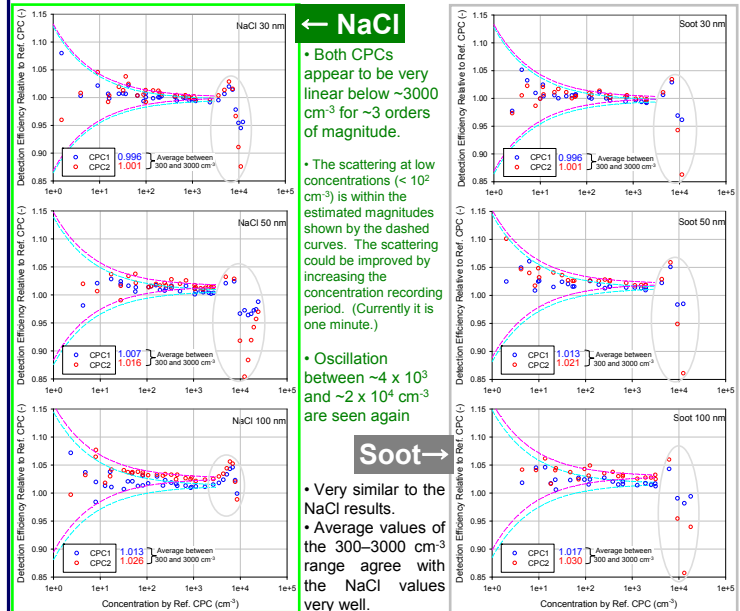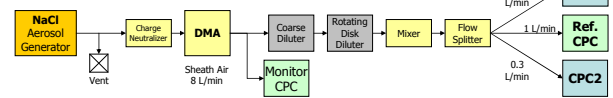
← NaCl

- Both CPCs appear to be very linear below ~3000 cm^{-3} for ~3 orders of magnitude.
- The scattering at low concentrations (< 10^2 cm^{-3}) is within the estimated magnitudes shown by the dashed curves. The scattering could be improved by increasing the concentration recording period. (Currently it is one minute.)
- Oscillation between ~4 x 10^3 and ~2 x 10^4 cm^{-3} are seen again

Soot→

- Very similar to the NaCl results.
- Average values of the 300–3000 cm^{-3} range agree with the NaCl values very well.

- With the linearity data above, we can estimate uncertainties in PCRF evaluation for several scenarios: For example, if we do not make corrections for the non-ideal linearity, errors of up to 5 % should be taken into consideration as an uncertainty.

Lessons learned

- The linearity of Ref. CPC seemed very poor in this measurement: Reason not exactly known, but how to generate NaCl particles seems to play some role.
- **Lesson: Linearity can not be assumed to be good without experimental evaluation.**

- Observed losses of 30-nm NaCl particles in a straight 60-cm conducting tube at 0.3 L/min: **~2 %** (losses estimated to be ~4 % by Gormley & Kennedy)
- Additional losses when the tube was in a circular shape: **~4 %**
- **Lesson: Not only the tube length, but also the shape (bent) of tubing connection matters !!**

NaCl vs. soot in PCRF values
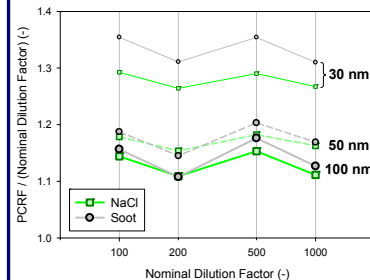
- For each size, the ratios of PCRF to the nominal dilution factor are about constant.
- The PCRF values of 50 and 100 nm are essentially identical between NaCl and soot.
- The PCRF values of 30 nm were noticeably different between the two materials: Soot gave larger PCRF values by about 0.04 – 0.07 (3 – 5 % of PCRF of 1.3).

- Note that this is not the difference in CPC detection efficiency, based on the similarity in CPC performance between NaCl and soot in the above linearity data.
- This results in a larger mean PCRF value for soot by 1 – 2 %.
- The difference between NaCl and soot may be dependent on the VPR design.

Conclusions

- We investigated two sources of uncertainties in PCRF evaluation of the VPR, i.e., the CPC concentration linearity and the particle composition.
- The concentration linearity of the two CPCs used in the VPR evaluation was investigated in the range from 1 to 10^4 cm^{-3}. While the linearity was good for ~3 orders of magnitude between 1 and 3 x 10^3 cm^{-3}, the linearity was poor above ~4 x 10^3 cm^{-3}. Depending on how the actual linearity is taken into account, PCRF values could have errors of up to 5 %.
- The mean PCRF value with soot was greater by 1 – 2 % compared to NaCl. If the material in the PCRF evaluation is not specified, there could be errors of this magnitude. The error may be VPR dependent.