Condensation Particle Counter Calibration Procedures

Report to Department for Transport

Title	Condensation Particle Counter Calibration Procedures
Customer	Department for Transport
Customer reference	PPAD 9/33/99(B)
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File reference	netcen/ED48629001
Reference number	netcen/ED48629001/Issue 1

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1 Introduction

Condensation of supersaturated vapors has been used for more than a century to grow small aerosol particles to sizes that can be detected optically. Instruments that use condensation to detect particles can be divided into two categories:

- Expansion-type instruments (including the "Aitken" dust counters and the "Pollak" photoelectric nucleus counters).
- Steady-flow condensation particle counters (CPC).

The second category of instruments can be further subdivided according to the approach used to produce the saturated vapour:

- Forced convection heat transfer
- Mixing warm and cool vapour streams, or mixing two vapours that subsequently undergo multi-component condensation
- Segmented thermal diffusion

The majority of modern CPCs are of the forced convection heat transfer type and only this type of CPC will be considered here. Further information on the historical development and performance of all types of CPC can be found in the review produced by McMurry (2000).

2 Principle of Operation

On entering the CPC, particles pass through a saturator where the working fluid evaporates into the gas stream. The flow becomes saturated with vapour of the working fluid before passing into a condenser where supersaturation of the vapour occurs. Under this condition the vapour condenses onto the particles to form droplets larger in diameter than the original particles. The droplets pass through a laser on leaving the condenser, and light scattered by the droplets is collected and focused onto a photodetector. The photodetector converts the light signal to an electrical pulse that is recorded as a particle count.

The optimal working fluid for an instrument of this type requires a vapor pressure at typical ambient temperature (25–30°C) that is large enough to grow particles in the condenser to a size that can easily be detected optically (0.5–15 μm), yet not so large that particles would be lost by sedimentation or impaction. Vapor diffusivity, which determines the rate of vapor depletion to the condenser walls, is also an important consideration. It is desirable to choose a working fluid having a small diffusivity in air, thereby ensuring that particles are exposed to elevated supersaturation as long as possible during flow through the condenser.

The first commercially produced forced convection heat transfer CNC was developed by Agarwal and Sem (1980). This instrument operated in two modes: single-particle counting mode for concentrations below ~1000 cm^{-3} and "photometric" mode for concentrations higher than this. The single particle counting mode involved the detection of forward-scattered white light from a halogen lamp. The photometric mode involved measurement of the d.c. level of light scattered by the aerosol cloud at the exit of the condenser. While the single-particle count mode was considered to provide an absolute measurement of concentration, the photometric mode required an empirical calibration. Butanol was selected as the working fluid because it was found to absorb water more slowly than isopropanol, which was used initially. Absorbed water led to a decrease in the amount of alcohol vapor added to the aerosol, and therefore affected the instrument response.

A number of refinements in the design of continuous flow CPCs have been reported since (*e.g.* Wilson *et al.* (1983a, 1983b), Stolzenburg and McMurry (1991)).

3 Primary Calibration Method

The current calibration method for CPCs is based on the method developed by Liu and Pui (1974). The electrostatic classifier is used to deliver singly charged, monodisperse calibration aerosols of known size and composition. An aerosol electrometer and the CPC under calibration sample this aerosol in parallel downstream of the classifier. The concentration is obtained from the aerosol electrometer current.

This approach has been adopted as a calibration standard in many laboratories (*e.g.* Liu *et al.* (1975), Liu and Kim (1977), Agarwal and Sem (1980), Marshall and Dickens (2000)) and in numerous calibration workshops (*e.g.*, Liu *et al.* (1982), Bartz *et al.* (1985), Wiedensohler *et al.* (1997)).

This is the method used by most CPC manufacturers to determine CPC performance, including lower size detection limit, counting efficiency and linearity of response. It will also form the basis of the calibration method for CPCs within the ISO standard currently under development by ISO Technical Committee 24, Sub-Committee 4 "Particle Sizing by Methods Other Than Sieving" (ISO (2005)).

Two potential complications with this method have been mooted:

- multiply charged particles having the same mobility as the desired singly charged particles may be included within the aerosol leaving the electrostatic classifier, leading to a more complicated relationship between current and concentration, and

- the detection limit of the aerosol electrometer limits the concentrations at which the calibration can be performed to those greater than ~10^3 particles cm^{-3}.

These issues have been addressed by Osmondson *et al.* (2004). They generated a quasi-monodisperse calibration aerosol by electrospraying emery oil and measured the size distribution after electrostatic classification to confirm the absence of any larger multiply charged particles. Thereafter they calibrated four TSI Model 3010 CPCs against a reference aerosol electrometer over a concentration range from 2,000 to 11,000 particles cm^{-3}. A further data point was recorded for each calibration at a particle concentration of zero. Excellent agreement was achieved between concentrations measured by the CPCs and the aerosol electrometer, with correlation plots yielding gradients in the range from 0.953 to 0.973 and correlation coefficients greater than

0.998. Figure 1 is an example of such a correlation plot. Thus, with correlation plot gradients close to unity, correlation coefficients greater than 0.998 and good agreement at zero particle concentration, it is unnecessary to undertake calibration measurements at particle concentrations less than ~1000 particle cm^{-3}, below the detection limit of the reference aerosol electrometer. There is no plausible reason why CPC performance should be any different between zero and ~ 1,000 particles cm^{-3} than it is above 1,000 particles cm^{-3}. Osmondson *et al.* also undertook an analysis of the traceability of critical parameters affecting the performance of the reference aerosol electrometer, *viz.* flow rate, charge per particle and electrometer current. Osmondson and Liu (2005) also demonstrated that the collection efficiency of the filter within the aerosol electrometer is greater than 99.999% for 50 nm particles.
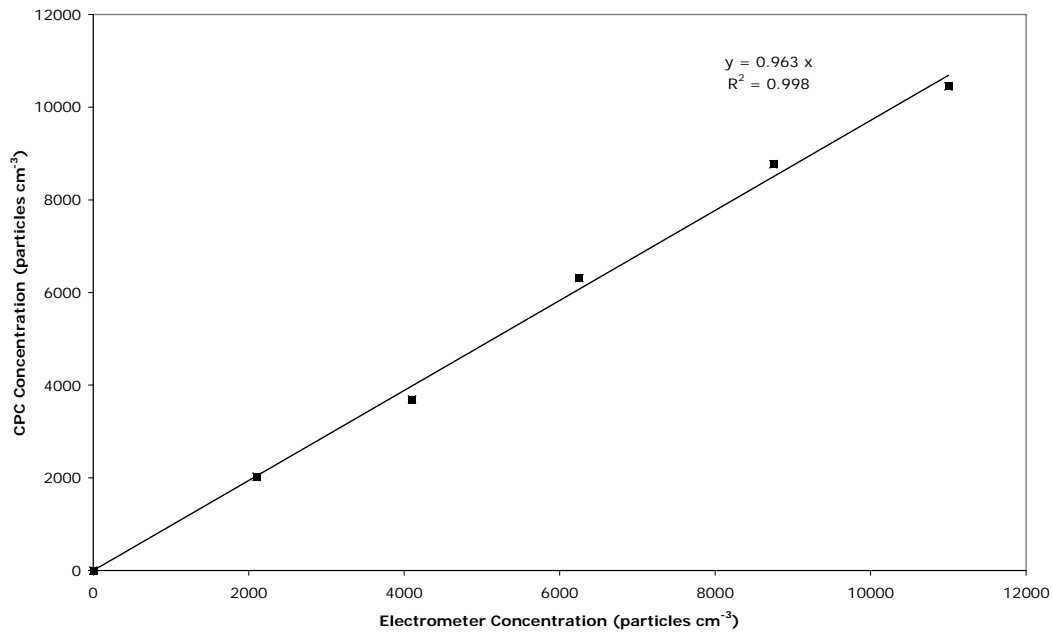
Figure 1   Example of Reference Aerosol Electrometer and CPC Concentration Correlation

Sakurai *et al.* (2005) describe the adoption of a very similar method using a reference aerosol electrometer as the national Japanese standard against which CPCs are calibrated.
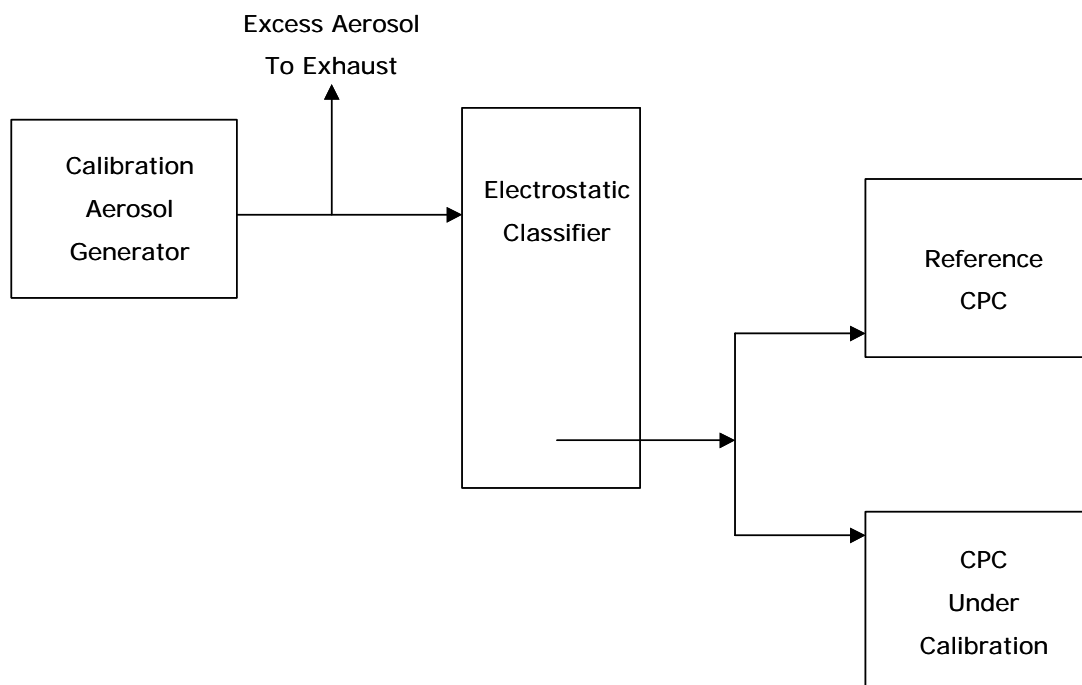
4 Secondary Calibration Method

Any CPC calibrated by the primary calibration method described in Section 3 can be utilised as a transfer standard against which the performance of other CPCs can be compared.

4.1   EXAMPLE

This approach has been adopted to calibrate the Golden CPC currently being used in the PMP Interlaboratory Comparison Exercise. A TSI Model 3010 CPC (S/N: 2005) calibrated by TSI according to the primary method was used as the transfer standard.

The experimental set-up is illustrated in Figure 2.

Figure 2 Secondary Calibration Method

The aerosol generator consisted of a ceramic crucible heated via an electric Bunsen (Figure 3). The bulk material (sodium chloride) was placed in the ceramic crucible and heated to near its boiling point. A small flow was introduced into the crucible to displace vapour from the surface of the bulk material to a cooler region of the generator where
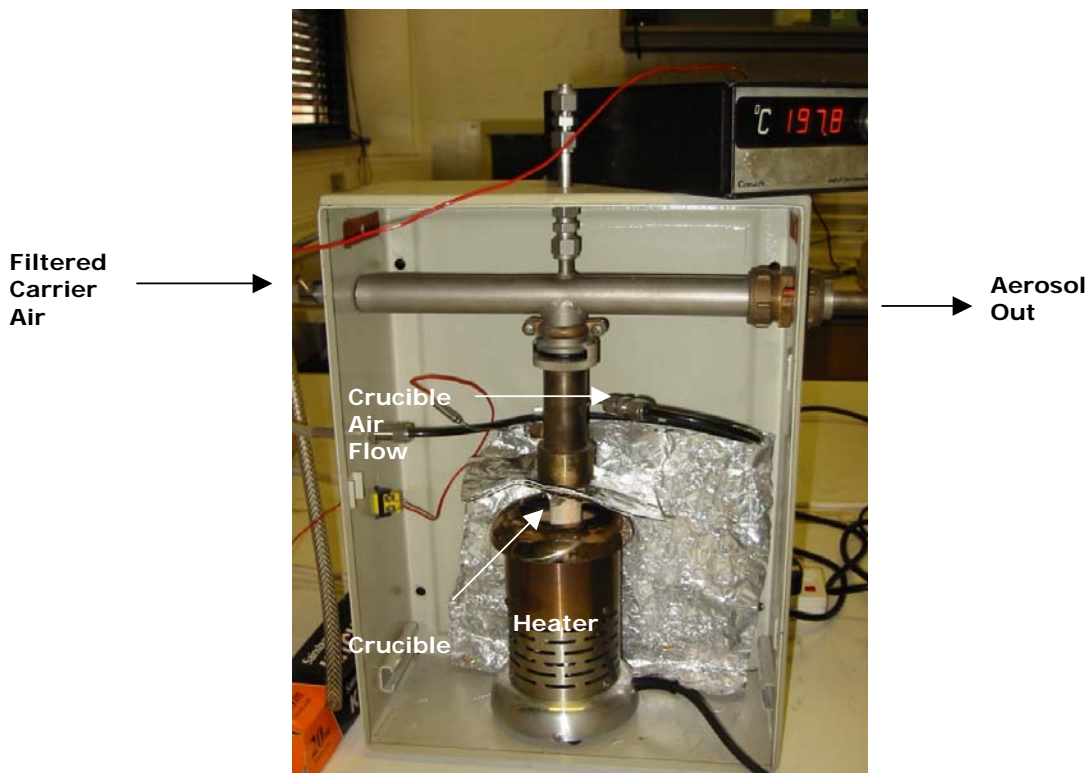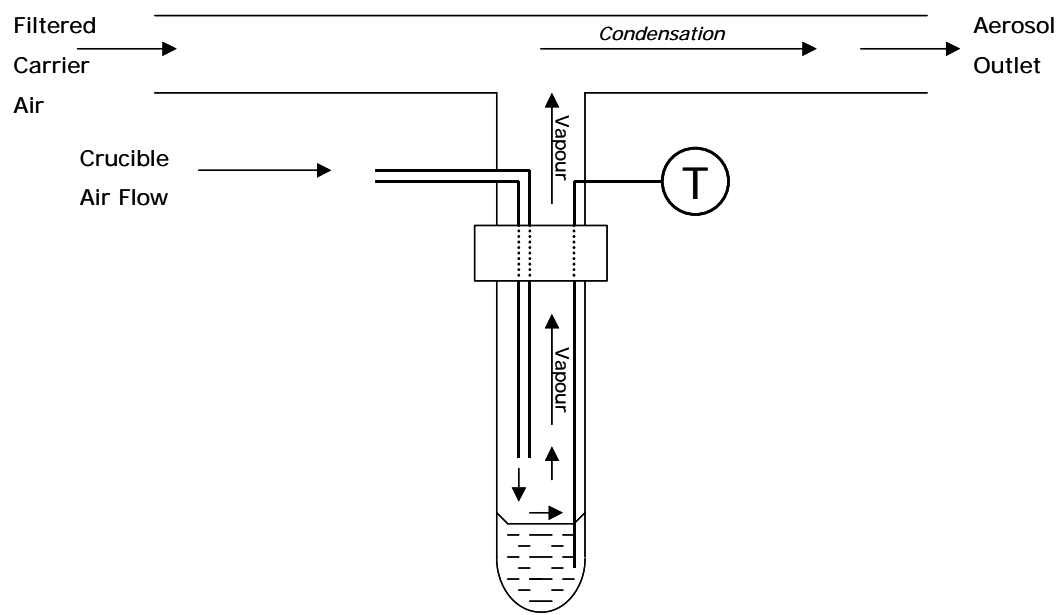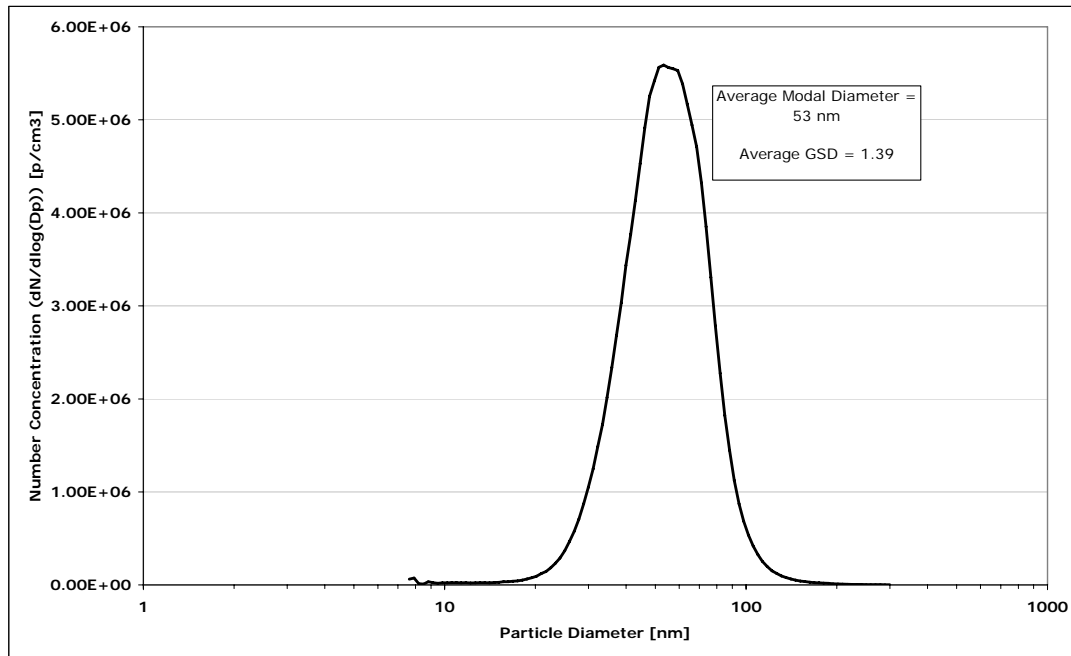
Figure 3   Condensation Aerosol Generator

condensation occurred. Particle diameters could be varied by controlling the rate of vapour transport from the crucible (via the crucible air flow) and/or the subsequent cooling rate of the vapour (via the carrier air flow). A typical size distribution of a generated aerosol is presented in Figure 4.
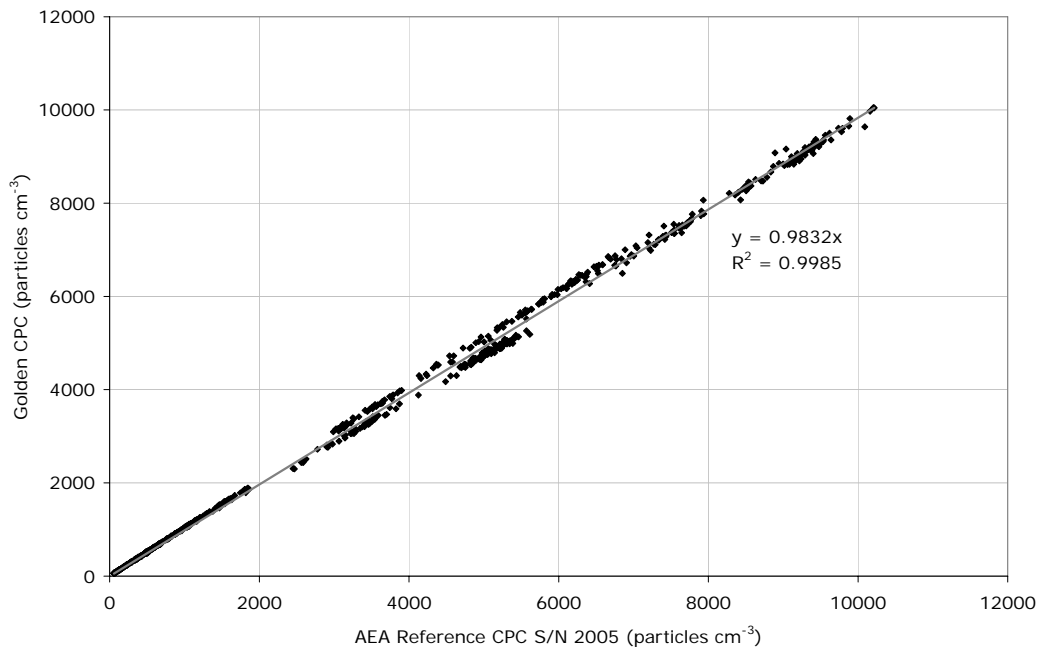

Figure 4   Typical Size Distribution of a Sodium Chloride Calibration Aerosol

The electrostatic classifier was used to select monodisperse fractions of the polydisperse sodium chloride calibration aerosol and deliver concentrations in the range from zero to 10,000 particles cm^{-3} to the CPCs, while simultaneously logging the concentrations reported by both CPCs. The electrostatic classifier was simply used to vary the concentration of particles reaching the CPCs, in contrast to the primary method where the electrostatic classification delivers singly charged particles to allow measurement with the reference aerosol electrometer.

Identical flow paths were used to deliver the calibration particles from the electrostatic classifier to both CPCs, thus ensuring any losses within the pipe work were the same for both units. Care was also taken to ensure that the voltages selected on the electrostatic classifier were such that the particles delivered to the CPCs were significantly bigger than the lower size detection limit of either CPC. This was particularly important in this example as the PMP Golden CPC had been modified to provide lower size detection limits of 23±3 and 37±4 nm for 50 % detection efficiency (D_{50}) and 90 % detection efficiency

(D_{90}) respectively. The reference CPC was unmodified having a D_{50} of 9.5±0.5 nm and D_{90} of 13.5±0.5 nm. Thus significant differences between the concentrations reported by both CPCs would be expected if the calibration particles were smaller than ~40 nm.

An example of the results of such a comparison is shown in Figure 5.

The chart shows data with fit line labelled:

$$y = 0.9832x$$
$$R^2 = 0.9985$$

Y-axis: Golden CPC (particles cm^{-3})

X-axis: AEA Reference CPC S/N 2005 (particles cm^{-3})

Figure 5   **PMP Golden CPC Calibration by the Secondary Method**

4.2   PROCEDURE

The procedure for performing a CPC calibration against a reference CPC according to the secondary calibration method is described below.

Prepare both CPCs for use:
- Position the CPCs as illustrated in Figure 2, but do not connect them to the electrostatic classifier.
- Fill with working fluid to the specified level and avoid moving the CPCs thereafter
- Switch on and allow the saturator and condenser to reach their specified temperatures
- Apply an external vacuum source if the CPC is not fitted with an internal pump

- Do not proceed unless all indicators show correct instrument status (*e.g.* temperature, liquid level, temperature, laser intensity *etc.*).
- Check the inlet flow rate with an appropriate calibrated flow meter
- Check that zero concentration is reported when a HEPA filter is attached to the inlet. The CPC requires attention from the manufacturer if non-zero concentrations are reported

Connect the CPCs to the remainder of the apparatus (Figure 2):

- Ensure that the particle residence time in the pipe work from the electrostatic classifier to both CPCs is identical. Take into account the inlet flow to each CPC and the internal diameter and length of the interconnecting pipe work. Take particular care if the inlet flows into each CPC are different. This will require either different path lengths with pipe work of the same internal diameter or the same path length with pipe work of different diameters.
- Set the electrostatic classifier flows such that the monodisperse aerosol flow leaving the classifier is sufficient for the total inlet flow of both CPCs.

Make arrangements to log data from both CPCs simultaneously at the same sampling rate.

Set the electrostatic classifier voltage to zero volts and begin logging CPC data. Both CPCs should report zero particle concentration, having already been checked with a HEPA-filtered inlet. If either CPC reports non-zero concentrations, check the apparatus for leaks. It is important that leaks are eliminated. Any particles leaking into the system downstream of the classifier may be of a size smaller than the D_{90} of either CPC which will invalidate the comparison.

Generate the calibration aerosol and select a voltage on the electrostatic classifier corresponding to a particle diameter larger than the D_{90} of either CPC. Continue logging CPC data and ensure that neither CPC is reporting a concentration above its maximum concentration limit. If not, adjust the electrostatic classifier voltage until the reported concentration is below the maximum limit. Thereafter, gradually adjust the electrostatic classifier voltage to vary the concentration delivered to the CPCs. Allow the CPC reported concentration to stabilise at each electrostatic classifier voltage to allow for possible differences in response time between the two CPCs.

Analyse the resulting data in terms of the correlation between the reported concentrations from both CPCs (as illustrated in Figure 5) with the reference CPC on the x axis and the CPC under calibration on the y axis, to establish the gradient and the linearity (R^2 coefficient).

The linearity of response in terms of the R^2 coefficient must be greater than 0.98, else the CPC under calibration does not respond linearly over the measured concentration range. The gradient of the calibration plot must be within the range from 0.95 to 1.05 (unity signifies complete agreement between the two CPCs). A gradient outside this range could be used as a calibration factor, but this is not to be encouraged. It is preferable that the concentrations reported by the CPC under calibration are correct without further manipulation.

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