

Comparison of NO₂ measurements using new Cavity Attenuated Phase Shift (CAPS) technology, with traditional chemiluminescent measurements.

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With recent US EPA equivalency approval of instruments utilising Cavity Attenuated Phase Shift (CAPS) technology for direct NO_2 measurements, it is important to perform intercomparisons with traditional chemiluminescent analysers to understand differences and ensure valid comparisons of long term data sets are possible and accurate.

This study compares ECOTECH'S new Serinus 60 CAPS analyser with the Serinus 40 chemiluminescent analyser in a near roadside application to investigate the differences in performance as well as its advantages and disadvantages.

NO₂ concentrations were measured during January 2017 in Knoxfield, a suburb of Melbourne, with vehicular traffic as a significant emission source.

The specifications for both instruments show a similar response time, based on standard tests between zero and span levels, however when the concentration is changing only by a small amount, the CAPS measurement and its inherent accuracy make it much faster to respond.

The sharp decrease in NO_2 at 21:18 in *Graph 3* shows a change over 5 minutes, while the response of the Serinus 40 takes a total of 14 minutes, largely due to the filtering required to remove the inherent noise from the switching chemiluminescent process. The main limitation on the CAPS response time is the volume of the measurement cell which depends on the flow rate; in the standard Serinus 60 this equates to about 30 seconds.



NO, ZERO MEASUREMENTS IN PPB (1 MINUTE AVERAGES)



Graph 1 : Daily average NO $_2$ measurements during the 3 week measurement campaign

As can be seen from *Graph 1*, there is a high degree of correlation in the results, though the Serinus 60 reads slightly lower on average than the Serinus 40 (except during calibration). We believe this discrepancy is due to the conversion and measurement of other nitrogen species such as NO₃ in the NO₂ converter of the chemiluminescent analyser.

Looking at the data for a single day in *Graph 2*, we see rapidly varying levels of NO₂ between about 4am and midday, with more stable levels outside these hours. The measurement site is located near a set of traffic lights that banks traffic up past the station during the inbound peak, but outbound traffic in the afternoon is both further away, and banked in the opposite direction away from the station, allowing for greater mixing and dispersion before it reaches the sample inlet. Traffic volumes, wind direction and other meteorological conditions obviously account for day to day variation in the pattern.

NO, MEASUREMENTS 17 JANUARY 2017 (5 SECOND DATA)



Graphs 4 & 5 : 3 hours of Zero and Span calibration measurements highlight the significantly lower noise in the CAPS measurements.



Looking at *Graphs 2 & 3,* the Serinus 60 CAPS analyser appears more "noisy" at low concentrations. However, looking at the span and zero measurements in *Graphs 4 & 5*, we can see that with a known stable source of NO2, the opposite is actually the case: the Serinus 60 is significantly less noisy. The Serinus 60 measurement is actually a more accurate measurement compared to the smoothed chemiluminescent response.



Graph 6 shows the response of the two instruments during a period of rapidly changing readings. Both instruments clearly show that the level of NO_2 is changing from minute to minute, and generally agree on the levels. This graph however shows a very important difference between the two technologies' capability to track rapid changes. The chemiluminescent analyser is continually switching between measuring NO and NO_X , then subtracting to calculate NO_2 . This process takes 12 seconds per cycle, limiting the time based resolution of readings to 5 changes per minute. In a near roadside site such as this, the concentration of NO₂ can be changing more quickly than this, leading to missed peaks.

Since the CAPS analyser is continuously measuring NO_2 directly, no peaks are missed. Peaks may not show the aboslute maximum reached at any single second due to the averaging effect of the cell volume, but this still leads to accurate averages over any 30 second period. The CAPS trace in *Graph 6* clearly shows multiple extra peaks and troughs compared to chemiluminescent measurements, highlighting the superior time resolution of the technology.



NO, MEASUREMENTS 17 JANUARY 2017 (5 SECOND DATA)



Graph 3 : Looking more closely at low, stable readings. Note the filter delay and significant smoothing in the chemiluminescent analyser. Graph 6 : Looking more closely at rapidly changing readings. Note the CAPS tends to measure rapid changes with greater resolution.

Historically most ambient stations have used Nitric Oxide (NO) to calibrate chemiluminescent based analysers and then mixed in Ozone (O_3) to determine converter efficiency. However with direct Nitrogen Dioxide (NO_2) measurement, such calibration is no longer possible.

If an accurately calibrated ozone source is available at the station, then mixing NO and a lower concentration of O_3 will generate a known quantity of NO₂ that can be used to calibrate the CAPS analyser. However this limits the accuracy of the calibration to that of the Ozone photometer.

Mixing excess ozone (with the aim of converting a known quantity of NO calibration gas) results in the generation of a number of other nitrogen species such as NO_3 that will reduce the amount of NO_2 generated to significantly less than the NO calibration gas (this is not so evident with a chemiluminescent analyser where the converter is less selective).

We recommend using an NO₂ calibration gas directly to avoid these limitations, though experience has shown that intercomparison of certified bottles of NO and NO₂ in a laboratory is advisable with many suppliers not yet as reliable with NO₂ certification.

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