

Further Data Validation of NO₂ and PAN Data

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Background

CE-CERT built eight analyzers to measure nitrogen dioxide (NO₂) and peroxyacetyl nitrate (PAN) for use in the CCOS 2000 summer measurement study. Under separate contract CE-CERT installed and calibrated the analyzers, trained operators, reviewed data and QC during the study period, provided technical support for operations, and removed the equipment. Although CE-CERT was not responsible for data validation, a significant amount of validation was performed under the “technical support” component. This was necessary since the analyzers, which were built in an extremely short period of time due to contractual delays, showed peculiarities that would best be done by those who were most familiar with the instrument. Funding for such validation was limited since this task was not in the original scope of work. This resulted in NO₂ data being submitted for the entire field sampling period, but PAN data was only submitted for the intensive periods. There were two primary problems that were difficult to resolve during the initial data validation, the shifting of retention times due to changes in the temperature of the shelter and a sinusoidal response due to the pulsing of the liquid luminol pump. These variables affected the PAN data much more than the NO₂ since the latter is found at much higher concentration. Since each 1-minute chromatogram was stored in the analyzer’s computer we were able to manually calculate the PAN peak height to determine concentration. This laborious method, which is not as accurate as determining peak area, was carried out only for the intensive days and for only one injection for each 10-minute reporting interval.

Objective

The NO₂ and PAN data accuracy and precision could be improved if software could be applied to the chromatograms to determine peak area as the retention times and baselines shifted. This would also allow PAN to be determined for all injections and for the entire field measurement program duration.

Approach

The following steps were used to process the data to meet the project objectives:

- Assembled previously collected data from the NO₂/PAN gas chromatograph.
- PAN data were reviewed to apply timing gates for the PAN peaks.
- Periods of zero/span checks (which were done at two hour intervals for twenty-minute periods starting at midnight) and calibrations were removed from the data set.
- All periods that did not have valid NO₂ data were removed from the data set.
- The detector background was determined by fitting an equation to the response after the elution of the PAN peak (the last 36 seconds of the 60 second chromatogram) and back calculating the background at the time of peak elution.
- The net detector response was determined by subtracting the background and summing the responses over the timing gate period.

- The ratio of the PAN calibration factor compared to the NO₂ calibration factor from the initial calibration was calculated.
- For each chromatogram the PAN calibration factor was determined by multiplying the above ratio by the NO₂ factor used at the time of the chromatogram (the NO₂ factor was previously determined from the span check conducted every two hours).
- The PAN concentrations were calculated by multiplying the response by the calibration factor.
- Data higher than 10ppb and lower than -1ppb were reviewed and resulted in all such data being removed as outliers.
- Data were then either reported or flagged as missing data (MD).

Results

Due to the constraints of processing unstable data, some of the data periods previously reported by manual inspection and peak height determination may not be reported in the data set reported here. All PAN data from the automated processing were submitted as EXCEL spreadsheets. Data for the months (all or part) at the following sites were reported:

Bethel Island: July, August, September

Sunol: August, October

Granite Bay: July, August, September, October

Pacheco Pass: July, August, September, October

Parlier: July, October

Spot checks of these overlapping periods did show good agreement. Figure 1 is an example of a comparison of the data derived manually compared to this data set that used automated peak selection and background removal. During the five days the concentrations were derived manually, the trends and peak concentrations are similar to the automated data. Detectable levels of PAN were observed on the non-intensive days, especially on the 27th and 28th, which lead up to the intensive day on the 29th. There is more apparent noise because, as expected, manual analysis provides a better level of judgment than the automated process. Another reason for the wider scatter with the automated data processing is that there is a data point for every 1-minute chromatogram, rather than one determined manually six times per hour. Also note that the automated data often is below zero, which is a natural reflection of uncertainty near the detection limit. For the manually-derived data zero response was assigned when not chromatographic peak could be discerned.

Conclusions

The results provided show that additional useful PAN data were obtained for non-intensive CCOS measurement periods. This data may be useful in analyzing buildup to intensive days and modeling non-intensive days that generated significant pollutant concentrations.

Figure 1. Comparison of PAN concentrations determined by manual and automated calculations.

