UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards (OAQPS)
Research Triangle Park, North Carolina 27711

MEMORANDUM

SUBJECT: The effect of measurement error on 8-hour ozone Design concentrations.

FROM: William M. Cox and Louise Camalier, EPA-OAQPS, Air Quality Data Analysis Group

TO: Ozone NAAQS Review Docket (OAR-2005-0172)

DATE: July 7, 2006

　　　　The purpose of this memo is to summarize an analysis that was done to address the impact of measurement error on ozone design values. The results suggest that instrument measurement error, as assessed by EPA's Quality Assurance audit program, or possible instrument bias, contribute very little to the uncertainty in 8-hour average ozone design value concentrations. As described in more detail below, a simple simulation study that incorporates site-specific precision calculated from over 900 ozone monitors during 2002 to 2004 indicates that measurement imprecision contributes less than 1 part per billion to design value uncertainty. An additional simulation was also performed to determine the impact of randomly occurring instrument bias. Those results indicate that measurement bias could contribute approximately 1 ppb to design value uncertainty.

　　　　The frequency distribution of daily 8-hour maximum ozone values was simulated by taking random samples from a two parameter Weibull distribution. The shape parameter used in the simulation was the median value obtained by fitting a Weibull distribution to ozone data from selected monitoring sites in the eastern U.S. for each year between 2002 and 2004. The scale parameter was chosen such that the expected value of the 4th highest value was approximately 85 parts per billion. A sample representing an ozone season (153 days) was then taken and used to calculate the 4th highest daily maximum 8-hour concentration. This was repeated three times and the three resulting 4th highest concentrations were averaged to simulate a "true" ozone design value, without the influence of measurement error.

　　　　To accurately assess the impact of instrument measurement error, a parallel stream of design values was generated, *which included the effect of instrument measurement error,* to compare with the true design values created above. As described by the EPA's Quality Assurance (QA) audit program, instrument measurement error

consists of variability (precision) and bias.   Precision is calculated at each site using CFR Equations 1 and 3 from biweekly precision checks (Part 58, Appendix A, section 5.1). The biweekly precision checks are made according to guidelines in CFR (Part 58, Appendix A, section 3.1). To convert the calculated CFR precision value to one that applies to an 8-hour average ozone concentration requires the following:

The precision of an 8-hour average ozone concentration was estimated by dividing the precision of 1-hour ozone concentration by the square root of 8. This assumes that there is no appreciable serial correlation in 1-hour "measurement error". This measurement error was then incorporated by multiplying each of the "true" daily ozone values by a random sample from a log-normal distribution with a geometric mean of 1.0 and a geometric standard deviation that corresponds to 8-hour ozone measurement precision. The result of one simulation is thus a "true" ozone design value as well as a paired design value that represents the "true" ozone *plus measurement error*.   The difference between the two design values is a measure of the impact of instrument measurement error.

This simulation was repeated 1000 times and the difference between the two design values was summarized. Results of these simulations are shown below for various levels of assumed precision. The percentiles associated with these precision values were taken from a summary prepared from a retrieval (March 2006) from AQS.   The R code used to perform these simulations is provided in Attachment I.

A second series of simulations was carried out assuming that each 8-hour measurement was subject to a randomly occurring bias. Values of daily bias were assumed to arise from a normal distribution with zero mean (no average bias) and standard deviation of ~4 parts per billion.   This value (see Attachment II) is believed to be a reasonable estimate of bias expected from instruments operating under routine conditions. Results of this second simulation suggest that a random bias of 4 ppb produces an uncertainty in the ozone design value of approximately 1.3 ppb.

Table 1. Simulated Impact of Instrument Error on 8-hour Ozone Design Values.

Precision of 1-hour ozone (Percent)	Percentile from National Audit Samples	Standard Deviation of Difference in Design Values (parts per billion)
1.63	25th	0.27
2.22	50th	0.34
2.97	75th	0.45
3.89	90th	0.57
4.52	95th	0.63

Attachment I.   R-code used to perform ozone design values simulations.

```
##############################################################################
#  Simulate three years of 8-hour max summer data.  Create a parallel
#  data set that contains measurement error. Compute
#  the 4th highest value for each year and average across the three
#  years to simulate the ozone design concentration.  Replicate this
#  for a number of cases and generate a data set of true design values
#  and another data set of true design values with measurement error.
#  Calculate the precision associated with the difference between
#  the true design values and those that include
#  measrement error. The scale or location parameter
#  of the Weibull distribution is chosen so that the expected value of the
#  4th highest value is = to 85 ppb the assumed NAAQS for ozone.
#  Parameters are lam = the shape parameter of the Weibull distribution,
#  N = the number of ozone season days per year, ns = the number of
#  simulations, pr = precision of 1-hour ozone as a fraction,
#  bsd =standard deviation of random 8-hour bias.
#  Two measurement error structures are simulated (1) assumes that
#  measurement error for successive values in an 8-hour
#  period are statistically independent and (2) assumes that every
#  8-hour ozone average is subject to a random bias that averages zero
#  with a standard error of bsd (ie. 4 ppb).
##############################################################################


wsim2 <- function(lam,N,ns,pr,bsd)
{
pr8 = pr/sqrt(8)
p <-  (4 - 0.4) / (N + 0.4)
theta <-  85 / ((-log(p))^(1/lam))
 h4tlist <- list()
 h4elist <- list()
 h4blist <- list()
 tvect <- vector()
 tvece <- vector()
 tvecb <- vector()

 for (i in seq(1:ns))
 {
  for (ny in seq(1:3))
  {
   true <- rweibull(N,shape=lam,scale=theta)
   rlog <- rlnorm(N,sdlog=pr8)
   terr <- true*rlog
   tbia <- true + rnorm(N,0,bsd)
```

```
  tvect[ny]  <- rev(sort(true))[[4]]
  tvece[ny]  <- rev(sort(terr))[[4]]
  tvecb[ny]  <- rev(sort(tbia))[[4]]
  }

 h4tlist[[i]] <- mean(tvect)
 h4elist[[i]] <- mean(tvece)
 h4blist[[i]] <- mean(tvecb)
 }
 v4t <- as.vector(do.call("rbind",h4tlist))
 v4e <- as.vector(do.call("rbind",h4elist))
 v4b <- as.vector(do.call("rbind",h4blist))
 dele <- v4t - v4e
 delb <- v4t - v4b
out <- data.frame(v4t=v4t,v4e=v4e,v4b=v4b,dele=dele,delb=delb)
out
}

set.seed(673)
test2 <- wsim2(lam=3,N=153,ns=1000,pr=0.0163,bsd=4)
sqrt(diag(var(test2)))

test2 <- wsim2(lam=3,N=153,ns=1000,pr=0.0222,bsd=3)
sqrt(diag(var(test2)))

test2 <- wsim2(lam=3,N=153,ns=1000,pr=0.0297,bsd=3)
sqrt(diag(var(test2)))

test2 <- wsim2(lam=3,N=153,ns=1000,pr=0.0389,bsd=3)
sqrt(diag(var(test2)))

test2 <- wsim2(lam=3,N=153,ns=1000,pr=0.0452,bsd=3)
sqrt(diag(var(test2)))
```

Attachment II: MEMORANDUM

SUBJECT: Ambient Ozone Systematic Error

FROM: Dennis Mikel. EPA-OAQPS, Measurement Technology Group
TO: Louise Camalier, EPA-OAQPS, Air Quality Data Analysis Group
DATE: July 7, 2006

At your request, I have performed a literature search, analyzed current EPA instrument performance and gathered technical specifications for ambient ozone instruments that are currently available commercially and attempted to estimate the systematic error involved in the collection of ozone data.

The ozone reference measurement principle and calibration procedure, promulgated in 1971 and amended in 1979, is based on detection of chemiluminescence resulting from the reaction of ozone with ethylene gas. Later, Rhodamine B, an organic dye embedded in a disc, was approved for use in place of ethylene to detect chemiluminescence. But neither method was problem-free. The flammability of ethylene was a constant concern, especially when monitoring was conducted in or near a public facility. The Rhodamine B analytical system did not regain a stable baseline rapidly enough after exposure to ozone. Thus, when Ultraviolet (UV) analyzers were first approved as equivalent methods in 1977, they gained rapid, almost universal acceptance[1]. The first UV photometer instrument introduced was the Dasibi models 1003 AH, RS and PC. Within a few years, a number of other UV photometer manufacturers (Thermo Electron, Monitor Labs and Environics) had submitted their instruments to EPA for equivalency and were accepted.

Below is a basic description of how an ozone UV photometer instrument operates. Ozone photometry is based on the Beers Law; if you measure the absorption of a compound at a wavelength that it absorbs maximally then measure in the absence of the compound, you can calculate the concentration. Initially, air is drawn into the inlet by a downstream pump.
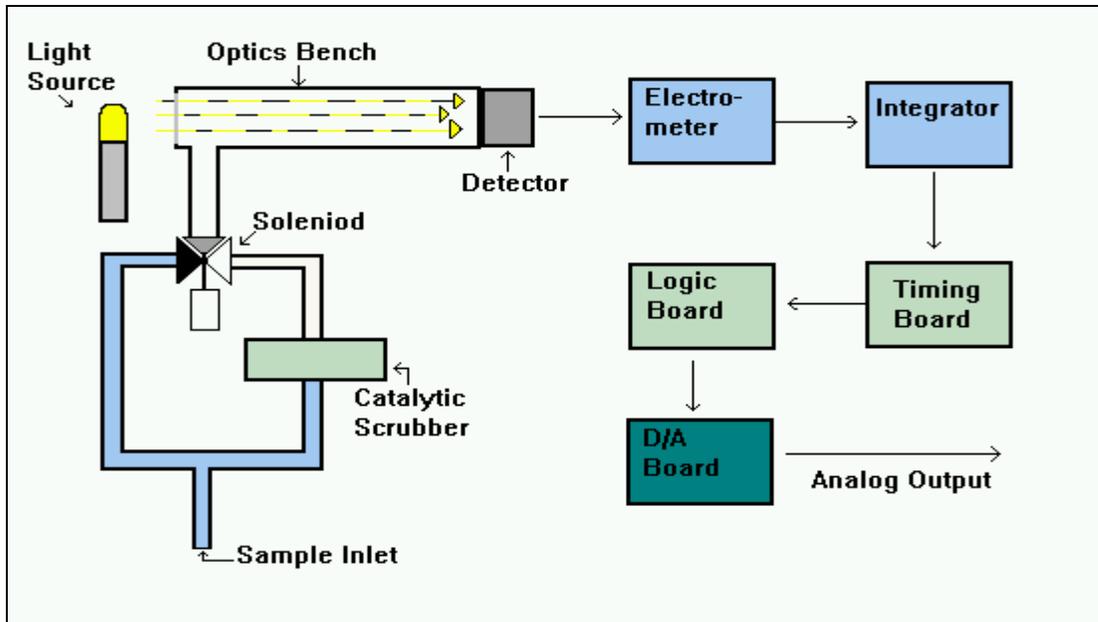
Figure 1. Ozone UV Photometry Schematic

The air is directed using a solenoid switch that is controlled by the timing board. There are two possible path configurations: one through the scrubber and the other around the scrubber. If the solenoid directs the flow through the catalytic scrubber, the material in the scrubber will reduce all ozone into oxygen (O_2). The air enters the optics bench and the detector accurately measures the light intensity in the absence of ozone (I_o). Then the solenoid switches so that air is directed around the scrubber. With ozone in the sample, the detector measures the light intensity (I). The ratio of I/ I_o can then be used to calculate the concentration using the Beers Law:

$$I/Io = e^{(-axC)}$$

where:

I = light intensity after absorption by ozone
Io = light intensity in the absence of ozone
a = specific ozone molar absorption coefficient
x = path length
C = concentration (ppb or ppm)

Over the years, the ozone instruments have evolved. Namely, the electronic components that interpret the signal from the detector have undergone major changes. However, the analytical components, the detector, optics bench and sample delivery system, have not changed. In older models, the signal output would be an amperage or analog voltage signal that would be measured and converted to a digital signal. The digital signal would then be stored and coordinated in the logic board. After the mathematics are generated, the digital/analog board converts the signal to an analog output, which can be directed to strip chart recorders or Data Acquisition Systems (DAS).

In 1997, EPA requested a contractor to look at systematic error in ozone instrumentation. The paper contents that error in ozone analyzers can generally be calculated using a systematic bias error equation[2] (Deuel and Cohen, 1997). This paper categorizes the systematic bias error using the following equation:

Systematic Bias Error = [(error due to drift)[2] + (error due to detector non-linearity)[2] + (precision error)[2] + (instrument calibration error)[2] + (NIST standard calibration error)[2] + (cross section uncertainty)[2]]$^{\frac{1}{2}}$.

The authors gave a conservation estimate of the error for 1995 and 1996 ozone data to be 4 ppb. In my opinion, there are several issues with this definition of systematic error:

1. The error due to drift and detector non-linearity should probably not be separated out. It should be noted that when manufacturers design instrumentation, they attempt to maximize the components. When manufacturers begin to produce instruments, there is variability in the components that are put into the instrument on the production line. Different lots of components can be a cause of variability; therefore the drift and non-linearity should be combined into "instrument drift error", which will change from instrument to instrument and manufacturer to manufacturer.

2. The equation included cross section error. This is a function of the uncertainty of the molecular absorption as a function of the cross section of the ozone optic bench and eventual losses of O_3 within the instrument, i.e., when air flows through the optics bench, ozone next to or adhering the to walls of the optic bench do not absorb light, therefore, the estimate of the intensity, I, is slightly lower. Cross section loss has been estimated to be 1.5%[3] (Proffitt and McLaughlin, 1983). The issues with this estimate is that the larger the bore of the optic bench, the greater the loss, as this is a function of diameter. It is my opinion that cross section loss should be included in "instrument drift error" since this would be difficult to estimate due to there being many manufacturers of ozone instruments.

3. The authors in Reference #2 state "Note that the noise term from Table 1 is explicitly excluded from the calculation." The authors continue to state, "In an actual field application, signal noise will provide an additional source of experimental error." Almost all ambient ozone data collected and reported to AQS is done so in actual field situations. Signal noise error should be included in the systematic error equation. Therefore ignoring the signal noise error is erroneous and should be a factor in the systematic error equation.

It is my opinion that the systematic equation be expressed in the following manner:

Systematic Bias Error = [(instrument drift error)[2] + (error due to noise)[2] + (precision error)[2] + (instrument calibration error)[2] + (NIST standard calibration error)[2]]$^{\frac{1}{2}}$

The following sections outline data gathered from different sources that will allow us to estimate the errors in this new equation. In order to understand the errors for the

instrument drift, precision and noise, I performed an Internet search of some of the manufacturers of ozone instruments that are Equivalent Methods[4].

Instrument Drift, Noise and Precision Error Estimates

Table 1 lists the instrument specifications of instruments that are widely utilized today.

Make/Model	EPA Equivalency	Noise (ppb)	Zero Drift (ppb) for 24 hrs	Precision (ppb)
Dasibi 1008[5]	EQOA-0383-056	1.00 ppb	NA	1.0 ppb
Thermo 49c[6]	EQOA-0880-047	0.50 ppb	1.0 ppb	1.0 ppb
Monitor Labs 9810[7]	EQOA-0193-091	0.25 ppb	1.0 ppb	1.0 ppb
Teledyne 400E[8]	EQOA-0992-087	0.30 ppb	1.0 ppb	0.5 ppb at 100 ppb
Average		**0.50 ppb**	**1.0 ppb**	**0.9 ppb**

Table 1. Reported Ozone Performance

I have averaged the zero drift (i.e., instrument drift error) noise and precision reported from 4 manufacturers of ozone instruments. Their technical specifications can be obtained from References 5 – 8. From these technical specifications, the average noise is 0.5 ppb and the instrument drift, which is estimated from the zero drift, is 1.0 ppb. The reported precision of these instruments averages 0.9 ppb.

NIST Standard Calibration Error

EPA performed research into NIST standard calibration error in the early 1980s[9] (Smith, et.al 1986). This research paper compared the national network of regionally located Standard Reference Photometers (SRPs) that are utilized for the assay of ozone concentrations. The SRP program was developed by the National Bureau of Standards (now known as the National Institute of Standards and Technology, NIST) and the EPA. The SRPs are highly stable, highly precise, computer-controlled instrument for the assay of ozone concentration. EPA's lab in Research Triangle Park (RTP), North Carolina operates and helps maintain a SRP network in cooperation with EPA Regional Office or State Agencies. Each network SRP was fabricated and certified by the NBS/NIST before deployment and is recertified annually by EPA. The results of the research found that 86 comparisons of local ozone standards had been performed within the network. Of the 55 verifications of local ozone primary standards conducted, 46 comparison results (84%) were within the acceptable range (+/-3% throughout the range) Of the 31 verifications of local ozone transfer standards conducted, all 31 comparison results (100%) were within the acceptable range (+/- 5%) with 94% within +/- 3%.   If this information is extrapolated to the NIST standards calibration error, then 3% of 100 ppb would be 3 ppb.

Instrument Calibration Error

In order to understand the calibration error, I polled data from the EPA's Burden's Creek ambient air monitoring station located on the RTP campus. An ozone instrument (Teledyne –API Model 400E) has been operated there for ~ 6 months. The instrument is challenged with ozone generated by the on-site calibrator that is traceable to an SRP. The daily checks include a zero air point, a precision level (~ 90 ppb) and upper level point (180 ppb to 450 ppb).

The following table and graphs illustrate the instrument calibration error for the ozone instrument at the EPA's Burden's Creek station.
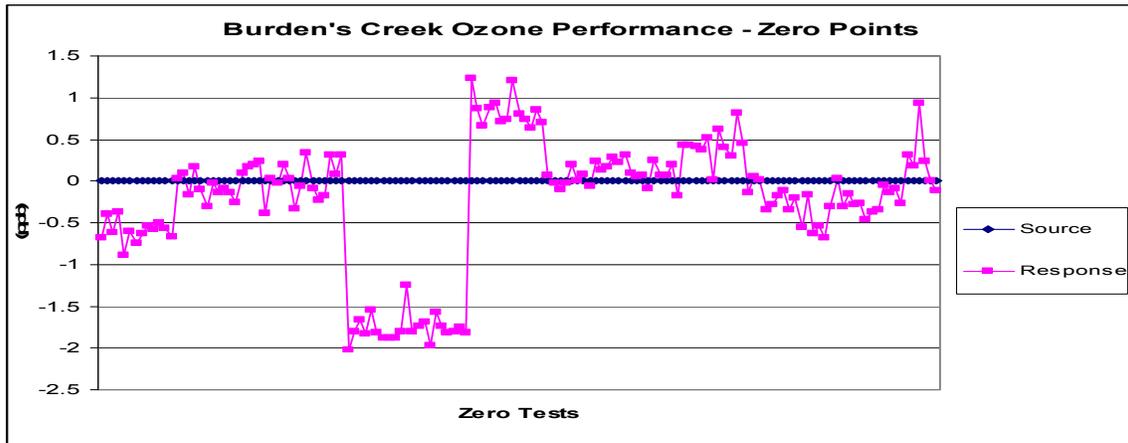

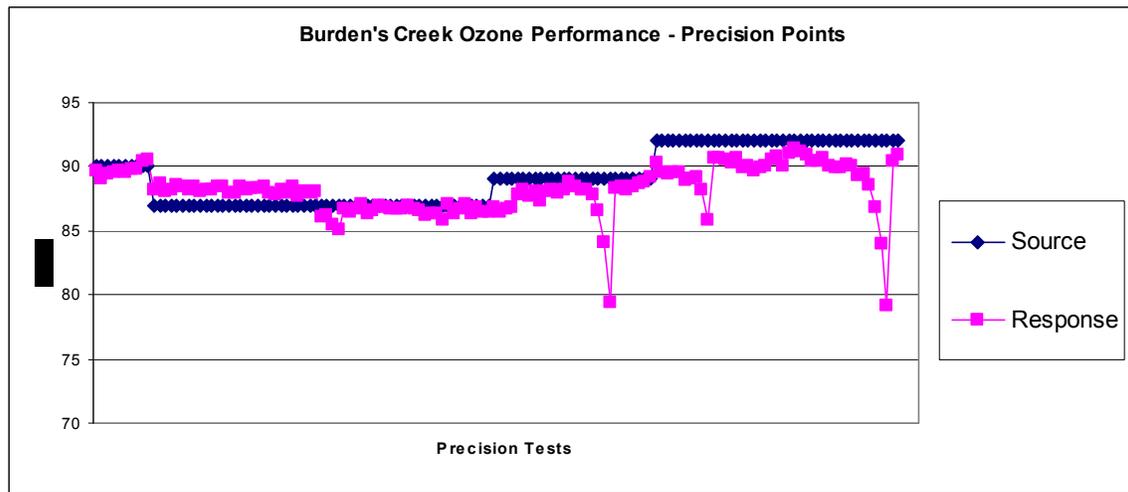**Figure 2. Zero Point Response 01/01/06 to 07/05/06**

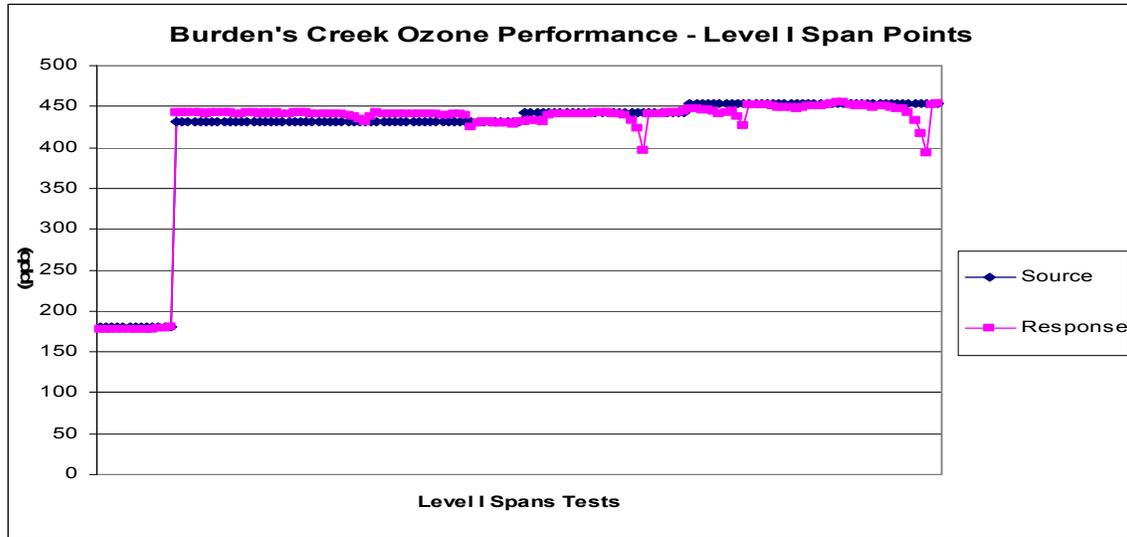**Figure 3. Precision Level Response 01/01/06 to 07/05/06**

Figure 4. Level I Span Responses 01/01/06 to 07/05/06

Table 2 summarizes the performance of the ozone instrument at the Burden's Creek Station. The overall averages at these three levels are very similar, 0.2, 0.3 and 0.9 ppb, respectively. However, if you notice the standard deviation (or standard error) at these levels you can see that these increase as the span concentration increases. Since it is important to understand the calibration error of ozone near the National Ambient Air Quality Standard (NAAQS), I believe the best estimate is 2.0 ppb.

Check Level	Average Difference	Standard Deviation	Coefficient of Variance	Bias
Zero	0.2 ppb	0.8 ppb	NA	NA
Precision Test	0.3 ppb	**2.0 ppb**	2.4%	1.9%
Level I Span	0.9 ppb	10.6 ppb	2.5%	1.8%
Average	**0.3 ppb**	**4.4 ppb**	**2.5%**	**1.9%**

Table 2. Summary of the Burden's Creek Performance

Summary

This exercise was performed to look at the performance of ozone instruments, look at theoretical values and consider what the overall systematic error should be. As mentioned earlier, the systematic error is the sum of errors that are based on information gathered in this memorandum and other sources. Below is a summation of these errors:

Systematic Bias Error = [(instrument drift error)^2 + (error due to noise)^2 + (precision error)^2 + (instrument calibration error)^2 + (NIST standard calibration error)^2]$^{\frac{1}{2}}$

Error Type	Estimate of Error	Source
Instrument Drift Error	1.0 ppb	Table 1
Noise Error	0.5 ppb	Table 1
Precision Error	0.9 ppb	Table 1
Calibration Error	2.0 ppb (at ~ 90 ppb)	Table 2
NIST Standards Error	3.0 ppb (3% at 100 ppb)	Reference 9

Table 3. Summary of Systematic Errors

Using these estimates, the systematic error is estimated to be:

Systematic Bias Error = $[(1.0\ ppb)^2 + (0.5\ ppb)^2 + (0.9\ ppb)^2 + (2.0\ ppb)^2 + (3.0\ ppb)^2]^{\frac{1}{2}}$

Systematic Bias Error = 3.9 ppb

Reference:

1. McElroy, F., Mikel, D., Nees, M, Determination of Ozone by Ultraviolet Analysis, A New Method for Volume II, Ambient Air Specific Methods, Quality Assurance Handbook for Air Pollution Measurement Systems, Final Draft, May 1, 1997

2. ICF Kaiser Consulting Group Memorandum to Warren Freas, EPA, EPA 68D30101, Work Assignment 3-01, "Determination of a reasonable systematic error estimate for ozone monitors," 02 May 1997.

3. Proffitt, M.H., and R.J. McLaughlin, Fast response dual-beam UV-absorption photometer suitable for use on stratospheric balloons*, Rev. Sci. Instrum., 54,* 1719-1728, 1983.

4. List of Designated Reference & Equivalent Methods -- May 3, 2006, EPA document, at: http://www.epa.gov/ttn/amtic/criteria.html

5. AMKO Systems Website: http://www.amkosystems.com/prodserv/amblevel/1008.htm

6. Thermo Instruments Website: http://www.thermo.com/com/cda/resources/resources_detail/1,2166,13042,00.html

7. Monitor Labs Website: http://www.teledyne-ml.com/9800main.asp

8. Teledyne – API Website. http://www.teledyne-api.com/manuals/index.asp

9. Smith, C., and K. Rehme. Standard Reference Photometer Network for Verification and Certification of Ozone Standards. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/D-86/107 (NTIS PB86205465).

.