Tennessee Valley Authority
Research and Technology Applications

TEXAQS-II 2005 Supporting Information for Deliverables

Topic: Audits

The original records are maintained at the address below:

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In addition, electronic copies of the audit data files have been transmitted to Ken Rozacky at TCEQ via TVA's password protected ozone FTP site.

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Notes on TCEQ Audits of TVA Twin Otter System - Summer 2005
Ralph J. Valente 1-31-06

The raw data files from the audits have been processed in the same manner as the regular flight data with two necessary exceptions. The altitude correction factors have been set to unity since the audits were performed at the same altitude (on the ground) as the calibrations and because no "in-flight" zeros are performed during the audit the zero baselines are all referenced to the zero air calibration with the TVA zero air source. (This zero air has relative humidity of about 20% and has been filtered with Hopcalite, Purafil, and activated charcoal.)

The workbook TX05AU2.xls containing the processed second audit mimics our flight workbook. The raw data sheet is "ALLDATA". This includes both 5 second (for some variables) and 1 second measurements then "5SEC" reduces all the data to a five second time base. Next "AB_ONLY_ZCORRECTED" shows zero adjusted data and finally "SPAN_CALIBRATED" shows the final data after the daily calibration factors, conversion efficiencies, etc. are applied. For the audit files I have added one more worksheet called "AUDIT_SORTED". In this file I have pulled out only the stable 5 sec readings from each of the audit test points and reduced them to a 60 sec average of twelve 5 sec readings. These records appear in columns BW through CF of the AUDIT_SORTED spreadsheet and the variable names end in "…sta" to indicate stabilization. These can be readily compared to the audit test concentrations. The gas data are all in ppb and the nephelometer data are in m^{-1}.

A variable called "stabilized" has been added at the end of the records from the processed 5 second audit data to indicate a one minute period for each audit test level when the readings have stabilized. That variable is blank except during that one minute period for each audit test gas level and during the stable period a number corresponding to the TCEQ audit L code given by Ken Rozacky has been placed in the "stabilized" variable. So when "stabilized" is 9, I have determined that the L9 mixture readings had stabilized. In general, I chose the 60 second period that ended 60 seconds before switching to the next level.

Notes pertinent to the first audit

At the beginning of the summer study (on July 20 when the first audit was performed) we were having newly developed flow control problems with our 146 calibrator (used for NOy, NOy*, NO2, NO and the SO2 systems so the results of the first audit are strictly as found tests of instruments with uncertain calibrations for these variables. Nevertheless, I think the results are still useful. I have tried to "back out" the instrument performance during the audit to the period a few days later after I had resolved the calibrator problems, but that is proving rather difficult since in the process of trying to pin down the trouble I did more than the usual amount of instrument tweaking. We resolved our calibrator problems within a few days after the audit so that at the time of the second audit we have a true comparison of the instrument system as calibrated with our repaired system versus the audit system.

During the first audit the NOy inlet heater was not yet installed. I got it in just before we moved up to Dallas to start the NETTS program so all the NETTS flights used the heated NOy inlet. I believe that the second audit (with the 60 C heated inlet) shows a much improved HNO3 response. (Assuming that the test concentrations were similar for both audits.)

The nephelometer was in rough shape at the beginning of the study. Thanks to Ken's observations during the first audit I decided to really dig into it to see what was wrong. It turned out that the neph had three problems (one major and two minor) going on July 20 - a chopper wheel that was developing pin holes in the finish causing unstable and unreliable calibration (major), two PM tubes that were somewhat loose in their bases causing some noise (minor), and an error in my datalogger program that was erroneously averaging the exponents in the scattering coefficients (minor), but only when the exponent was changing during a five second period. It took me a few days to sort out and fix these problems so I invalidated the neph data for the SETTS flights.

During the second audit L21 was an HNO_3 point combined with a nephelometer Freon test. Since the nephelometer test did not last as long as the HNO_3 test I have labeled the stable neph readings as L21 and the stable HNO_3 readings as L21.5. All other labels match Ken Rozacky's during the audit.

General notes on instrument performance throughout the study

Every study has seems to teach (and humble) me in a new way and this one was no exception. During this program Bill Hicks and I had an ongoing battle to keep the NOx suite of instruments balanced, that is to say, to precisely document and adjust for the day to day variation in spans of the four NOx boxes. This is very important to get a good speciation breakdown and especially so for the NO2 since it must be derived using both the NO and NO2 raw instrument readings combined with about a 63 percent photocell conversion efficiency factor. A quick back of the hand calc shows that a 10 percent high NO instrument with a ten percent low NO2 instrument can result in a very large error in NO2 when NO and NO2 are present in equal proportions. We noticed early on that the span levels just didn't seem to be quite as steady as we have usually experienced so we resolved to keep a close eye on their performance. As the study progressed we began doing several special tests and generally increasing the frequency of our span tests on the NOx systems, including several unplanned mid-day span checks between the morning and afternoon flights.

What we observed was that was the NO, NO2, and NOy* instruments, and to a lesser extent, the NOy system would sometimes change their span response by as much as 20 or even 30 percent on occasion. At first we could not discern any pattern to what would make a change occur. We were following the usual protocol for changing sample filters and ozonator drierite when needed, performing daily autocals with our repaired calibrator, which incidentally functioned very well. Of course, we verified early on in the study that there were no leaks in the entire sampling system (our total and individual inlet flows agreed with our instrument exhaust flows within 2 percent and all our MFM's dropped to zero when we closed the inlets), Marty Buhr's factory refurbished NO2 photocell lamp was exceptionally stable throughout the summer consistently converting about 63 percent of the NO2 to NO, and our handy new mass flowmeters installed on every gas inlet line showed rock steady flow throughout the study, a certain indication of stable pump operations! So we new we were definitely in uncharted waters as far as explaining and/or fixing this one. That's saying a lot because Bill and I have combined experience of about 50 years working hands on with these NOx instruments!

Of course we suspected calibrator trouble since we had resolved some at the beginning of the study, but we quickly ruled that out since the single tri-gas tank with our NO, SO2, and CO showed no such variability in the SO2 and CO spans, so we knew the calibrator was nice and stable at mixing the gases from day to day from our continuously recorded air and gas MFMs.

The first indication we had that we might be getting closer to a cause/effect type of answer was when we began to specifically change the ozonator drierite and then feed span gas to the system for a long time to see if we could make "it" happen whatever "it" was.