GGMT 2015 Presentation Notes

1. Title: Over the past 2.5 years, we’ve been working on an update and expansion of the WMO CH4 mole fraction scale. Here I will summarize our progress since the previous GGMT meeting. I thank my NOAA colleagues, especially Andy Crotwell who did most of the analysis of the scale and Brad Hall who made new primary standards using the gravimetric technique.

2. Outline:

The X2004A scale is based on the core set of standards used in the X2004 scale, which I will review in a moment, but it has been expanded at the high end to accommodate measurements on continents closer to sources by our lab and GAW partners. It also involves a fundamentally different, but more robust method of propagating the scale that accounts for non-linearity in our calibration system. After a review of the X2004 scale, I will discuss addition of new primary standards, show how the expanded scale is propagated to new secondary standards, show how we’ll propagate the scale to working standards, then discuss how you can get the new assigned values for your standards.

3. The key analyses of the X2004 scale are shown here: On the left, values assigned by the grav technique are plotted vs the original CMDL 1983 scale. The bottom panel shows residuals from a straight line fitted to the standards. These are typical of residuals from a gravimetric process. Standards were prepared using a variety of different methods for transferring gas from a high concentration cylinder into another cylinder for dilution indicated by different color symbols. All methods agreed within experimental uncertainty. We also found a small negative intercept (-5 ppb), which we interpreted as CH4 in the diluent air to make the standards. At the time, we tried to measure CH4 in the zero air, but we were limited by use of stand-alone HP integrators with relatively low-resolution A/D converters, and all were below our detection limit. Now, with 24 bit A/Ds and a lot of care in making the measurement, we believe we have a detection limit of ~1-2 ppb. Based on this intercept and other reasoning, the gravs were corrected for the zero air. Another view of this is shown on the rt. Here, grav values are plotted vs the response of each grav normalized to air at ambient CH4 for 2 cases: with and without correction for 5 ppb CH4 in the zero air. Without the correction, shown by diamonds, the normalized response/ppb changed dramatically at low CH4 values. With the correction, it remained about constant as expected with an FID. That is the scale; given the linearity of the FID, we propagated the scale using a single point cal extrapolated through zero.

4. Here is the tree that describes our CH4 standards starting at the top with pure CH4. In yellow are all the standards that make up the core of the scale. Others that are key to this analysis, but not part of the core range are at 5.8 ppm, 10.8 ppm and 20.5 ppm. Subsequent to these standards, mostly prepared in the late-1980s and early-1990s, Brad prepared additional gravs, one to overlap with the core range and others to expand the scale. All these were made with a single transfer method for the high-conc mixture, and CH4 in the diluent gas was measured and corrected in each one.

5. This roughly brings us up to GGMT-2013, where I showed this plot. We believed then that new standards made in 2013 did not agree with the previous ones from the early-1990s. Plotted here are differences between calibrated and gravimetrically assigned values for new standards intended to fill in the gap between 2600 and 5800 ppb. The measured values are based on a linear response curve fitted to the original standards, including the one at 5.8 ppm, which we have a good deal of confidence in. The source of this problem was unknown; we had no reason to question our 5.8 ppm standard, at least wrt the others. We felt the new standards were different from the previous set, but we also had to check to see if our 5.8 ppm stnd fortuitously falls in with the assumption of a linear FID response.

6. To do that, Brad ran a number of tests on the gravimetric method trying to determine a potential bias (e.g., leaky transfer tube), and none was found. Andy then ran a response curve that included new and old gravs, including the extended range up to 20 ppm. The result is shown here. The top panel shows grav-determined values as fn of normalized response. Over this range, you, of course, can not see any problems with either a linear or quadratic fit. But the residuals show that 1. the response is not linear and 2. that the 5.8 ppm standard is an outlier among all others. This realization was a major step forward.

7. In the end, we ended up with 22 primary standards, the 16 original from the core range of the scale prepared in the early-1990s and published in 2005, and 6 new ones prepared in 2013. These are tabulated here with their assigned CH4 mole fractions, which are the gravimetrically-determined values + CH4 in the diluent gas. The nominal range is 300 ppb to 5.9 ppm and uncertainties at 68% CI range from 2 to 3.5 ppb. In the original standards, a blanket correction for CH4 in diluent air of was applied; in the recent ones, CH4 in diluent gas was measured and the measurement used for the correction. These standards define the X2004A scale. The scale is propagated to secondary standards using a response curve as shown here.

8. In the top panel, CH4 mole fraction is plotted against the mean normalized response from 7 aliquots of primary bracketed by reference, i.e., the ratio of peak response of the grav-prepared primary to that of a cylinder of dry ambient air. As before, two fits are shown, linear in blue, and this time a power function of this form. You can see, the response of the analytical system is quite non-linear over this range. Uncertainties in both axes are included in the fitting process; for the y-axis, we use the uncertainties at 68% CI from the previous table, and for the x-axis, a SD of the 7 ratios. Response curves were generated from the primary standards 6 times from July, 2013 to early-2015. During that time, we saw the non-linearity change significantly, especially in October, 2013. Initially we were using a quadratic fn fitted to the data, but the residuals were not consistent over the changing linearity. Andy and Kirk Thoning investigated various types of curve fits, and they found this power function, gave somewhat consistent residuals over the full range. We are still left with significant scatter in the residuals near ambient.

9. To account for non-linearity in our analytical system while propagating the scale, especially outside the ambient background range, we prepared a set of secondary standards shown here. These were prepared by spiking evacuated cylinders with air enriched in CH4 or with zero air, then filling them at NWR with ambient background air. The nominal range is 390 ppb to 5 ppm. These were then calibrated against 6 different response curves prepared from our primary standards. Listed here are the cylinder IDs, the mean CH4 mole fraction calculated based on a response function fitted to our primaries, and an uncertainty based on the standard deviations of the six determinations.

10. Since July, 2013, we can use monthly response curves based on 11 aliquots of each of the 14 secondary standards to calibrate tertiary (working) standards. An example of a response curve is shown here in the top panel, with residuals, the difference between the curve fit and the assigned value, in the bottom panel. Residuals have a relatively small range compared to the primary standards.

9. Here are examples of possible response curves. In red is a linear fit to the normalized response of each secondary, and in blue, a quadratic fit. They are indistinguishable until you look at the residuals. Note the structure in the red residuals; we can capture that better by using a quadratic fit. The functions with their coefficients are shown. To calculate XCH4 in an unknown, we measure it against the same reference, identical to how the single point calibration was done, and use this function with the mean ratio of responses to calculate X. We used the same procedure to calculate XCH4 for the secondary stnds, but starting with the primaries. What is the impact on our calibrations of changing our approach from single-point standard to response curve?

10. This is shown here for all calibrations made in 2013. These are differences in XCH4 between the two methods, single-point cal extrapolated through zero and response curve. The two colors show 2 cases: linear response curves in red and quadratic response curve in blue. Remember, we will use the quadratic to propagate the scale. Differences over this range in XCH4, 750 to 2850 ppb are within ±0.5 ppb. In the ambient range, they are about 0.2 ppb different. A single response curve was used to calculate XCH4 for all standards calibrated in 2013; in practice, these will be re-run about monthly, which will add some variability to re-calibrations. In other words, to make the system more robust over a wider range of CH4 mole fraction, we may sacrifice reproducibility.

12. Summary and conclusions…

I believe we’ve been doing reasonable well at transferring the scale over the past 3 decades, especially in the ambient background range.

To improve robustness of our ability to transfer the scale, we are implementing a set of secondary standards covering the nominal range 400 to 4000 ppm CH4. These will be used to prepare approximately monthly instrument response curves for our cylinder calibration system. Based on comparisons of cylinders calibrated this year, differences between this new method and the earlier single point calibration are small.

Finally, we have an important unresolved issue: the new gravimetrically-prepared standards designed to fill a gap between 2600 and 5800 ppb do not agree with the previous set. The new gravimetric values move systematically below the response defined by our original grav standards, either 300 to 2600 ppb or 300 to 5800 ppb. The reasons are still being investigated.