

Appendix G: Summary of Hydrogen Sulfide and Ammonia Precision and Accuracy Results

Quality control and assurance checks were done for both hydrogen sulfide and ammonia, by challenging the analyzers with gases of a known concentration. Precision checks are typically done at only one concentration, while accuracy audits can involve as many as five gaseous levels.

For hydrogen sulfide, the Sampling Manual (see Appendix E) specifies the following goals for these checks and audits: “As a goal, the 95% probability limits for precision should be less than $\pm 15\%$. At 95% probability limits, the accuracy for hydrogen sulfide should be less than $\pm 20\%$. Calculations of precision and accuracy for hydrogen sulfide will follow the procedures for gaseous pollutants in the United States Code of Federal Regulations (40 CFR Part 58, Appendix A).”

The following remarks pertain to the annual probability limits for hydrogen sulfide in tables G.1a and G.1b. The precision goal was met every year for hydrogen sulfide. The lowest level accuracy goal was only met in 17% of the years. As the concentrations increased, the accuracy results improved, and at the highest level the goal was attained in all years. Across all accuracy levels, 65% of the annual limits were within the goals. All annual probability limits for hydrogen sulfide, if rounded to the nearest integer, were within $\pm 30\%$.

Although the sampling manual only specifies goals for hydrogen sulfide, it is interesting to observe the results when the same precision and accuracy goals are applied to the annual confidence limits for ammonia (given in tables G.2a and G.2b). The probability limits for the first year of ammonia monitoring (2003) were barely outside the precision goal. The annual precision goal was met for ammonia in each of the following years. The lowest level accuracy goal was never met. At the next two levels, the accuracy goal was attained 40% of the time. Performance dropped off at the fourth level, with only 20% of the years meeting the goal. Level five ammonia audits were only done in the 4th quarter of 2003, and the annual goal was not met that year. With the exception of the level five ammonia audit, all annual probability limits for ammonia were within $\pm 30\%$.

Table G-1-a.

Hydrogen Sulfide Precision and Accuracy Statistics

| Year Quarter | No. of monitors | No. of checks | LCL | UCL | No. of Audits | L1 LCL | L1 UCL | L2 LCL | L2 UCL | L3 LCL | L3 UCL | L4 LCL | L4 UCL | L5 LCL | L5 UCL |
|-----------------|--------------------|------------------|-------|------|------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 2002 | Precision | | | | Accuracy | | | | | | | | | | |
| 1 | NA | NA | NA | NA | 0 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| 2 | 2 | 13 | -4.5 | 5.9 | 2 | -10.5 | 13.3 | 1.4 | 6.8 | NA | NA | NA | NA | NA | NA |
| 3 | 2 | 14 | -5.7 | 2.2 | 2 | -5.4 | 2.5 | -4.2 | 1.1 | NA | NA | NA | NA | NA | NA |
| 4 | 2 | 16 | -3.1 | 1.8 | 2 | -5.0 | 2.3 | -1.8 | -0.1 | NA | NA | NA | NA | NA | NA |
| Annual | 2 | 43 | -4.8 | 3.6 | 6 | -6.9 | 6.0 | -5.2 | 6.3 | NA | NA | NA | NA | NA | NA |
| 2003 | Precision | | | | Accuracy | | | | | | | | | | |
| 1 | 4 | 14 | -9.1 | 3.2 | 2 | -5.9 | -5.9 | -5.4 | 2.5 | -3.9 | 0.6 | -6.0 | 1.0 | NA | NA |
| 2 | 6 | 35 | -6.4 | 8.9 | 2 | -16.3 | 16.3 | -29.8 | 26.6 | -23.7 | 22.9 | -22.9 | 23.6 | NA | NA |
| 3 | 6 | 43 | -10.9 | 12.6 | 2 | -35.8 | -9.1 | -11.4 | -2.6 | -6.2 | -1.6 | -5.8 | -2.7 | NA | NA |
| 4 | 7 | 47 | -9.4 | 8.4 | 2 | 0.7 | 17.0 | 6.0 | 14.0 | 1.5 | 14.1 | 1.4 | 14.6 | -3.3 | 18.9 |
| Annual | 8 | 139 | -10.0 | 10.3 | 8 | -30.3 | 20.5 | -17.0 | 17.0 | -12.6 | 13.5 | -13.1 | 13.9 | -3.3 | 18.9 |
| 2004 | Precision | | | | Accuracy | | | | | | | | | | |
| 1 | 7 | 45 | -5.8 | 11.3 | 2 | 5.3 | 25.5 | 7.9 | 18.9 | 7.0 | 8.1 | 3.8 | 9.4 | 4.7 | 7.6 |
| 2 | 11 | 48 | -6.2 | 12.3 | 2 | -26.0 | 42.8 | -31.2 | 38.1 | -27.6 | 39.2 | -28.3 | 37.5 | -26.1 | 37.9 |
| 3 | 10 | 78 | -5.3 | 9.0 | 3 | -25.9 | 14.1 | -13.3 | 3.8 | -14.0 | 6.6 | -11.7 | 4.3 | -9.3 | 2.7 |
| 4 | 10 | 84 | -9.1 | 9.5 | 3 | -27.4 | 7.8 | -26.4 | 18.8 | -27.3 | 16.2 | -20.5 | 8.7 | -19.0 | 10.7 |
| Annual | 15 | 255 | -7.7 | 11.0 | 10 | -27.0 | 27.1 | -21.0 | 22.6 | -19.8 | 19.6 | -17.9 | 16.6 | -16.2 | 16.6 |

Abbreviations:

L1, L2, L3, L4, L5 - five different concentration levels used during audits

LCL - Lower 95% confidence limit

NA - Not Applicable

No. - Number

UCL - Upper 95% confidence limit

Table G-1-b.

Hydrogen Sulfide Precision and Accuracy Statistics

| Year Quarter | No. of monitors | No. of checks | LCL | UCL | No. of Audits | L1 LCL | L1 UCL | L2 LCL | L2 UCL | L3 LCL | L3 UCL | L4 LCL | L4 UCL | L5 LCL | L5 UCL | |
|--------------|------------------|---------------|-------|------|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| 2005 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 10 | 83 | -9.7 | 7.0 | 3 | -16.5 | -3.1 | -25.3 | 19.5 | -17.9 | 8.3 | -19.3 | 6.4 | -14.4 | 6.1 | |
| 2 | 10 | 79 | -5.6 | 6.8 | 2 | -11.8 | 5.5 | -18.2 | 12.6 | -19.9 | 18.7 | -20.1 | 21.1 | -19.2 | 21.4 | |
| 3 | 10 | 79 | -4.3 | 7.3 | 3 | -25.5 | 27.9 | -10.2 | 6.5 | -3.1 | 6.8 | -4.2 | 11.8 | -4.2 | 21.6 | |
| 4 | 10 | 74 | -9.2 | 9.2 | 2 | -25.8 | 34.7 | -12.3 | 18 | -12.8 | 23.8 | -13.8 | 24.7 | -8.6 | 25.9 | |
| Annual | 10 | 315 | -8.1 | 8.4 | 10 | -22.5 | 17.8 | -15.5 | 12.7 | -13.4 | 13.6 | -14.9 | 15.8 | -13.3 | 19.9 | |
| 2006 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 10 | 78 | -7.1 | 11.1 | 3 | 11.8 | 11.8 | 3.6 | 23.8 | 12.5 | 19.0 | 7.7 | 27.9 | NA | NA | |
| 2 | 10 | 81 | -6.5 | 12.1 | 3 | -3.5 | 23.1 | 3.3 | 19.0 | 3.9 | 19.4 | 4.7 | 20.9 | NA | NA | |
| 3 | 10 | 77 | -5.8 | 9.2 | 3 | -4.7 | 8.6 | -9.1 | 13.5 | -12.8 | 18.6 | -5.8 | 17.4 | NA | NA | |
| 4 | 10 | 83 | -7.5 | 5.9 | 3 | -9.8 | 25.5 | -8.8 | 19.2 | -7.4 | 16.9 | -10.5 | 18.3 | NA | NA | |
| Annual | 10 | 319 | -7.9 | 10.7 | 12 | -4.5 | 20.2 | -5.2 | 21.3 | -5.2 | 22.8 | -4.8 | 25.0 | NA | NA | |
| 2007 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 10 | 80 | -12.4 | 11.5 | 3 | -27.3 | 46.9 | -10.8 | 28.0 | -6.3 | 18.9 | -3.1 | 15.9 | -5.4 | 15.4 | |
| 2 | 10 | 75 | -6.2 | 8.5 | 3 | -2.7 | 10.6 | -2.7 | 10.3 | -6.2 | 9.1 | -7.8 | 11.0 | -9.5 | 9.0 | |
| 3 | 10 | 75 | -7.0 | 6.0 | 3 | -9.8 | 25.5 | -9.3 | 18.9 | -9.8 | 15.7 | -8.5 | 13.2 | -8.7 | 11.2 | |
| 4 | 10 | 69 | -8.3 | 9.0 | 3 | -17.2 | 9.4 | -13.1 | 15.0 | -8.7 | 16.8 | -8.0 | 18.1 | -5.2 | 16.8 | |
| Annual | 10 | 299 | -9.5 | 9.7 | 12 | -17.1 | 25.9 | -8.9 | 17.9 | -6.9 | 14.3 | -6.2 | 13.9 | -7.1 | 13.0 | |

Abbreviations:

L1, L2, L3, L4, L5 - five different concentration levels used during audits

LCL - Lower 95% confidence limit

NA - Not Applicable

No. - Number

UCL - Upper 95% confidence limit

Table G-2-a.

Ammonia Precision and Accuracy Statistics

| Year Quarter | No. of monitors | No. of checks | LCL | UCL | No. of Audits | L1 LCL | L1 UCL | L2 LCL | L2 UCL | L3 LCL | L3 UCL | L4 LCL | L4 UCL | L5 LCL | L5 UCL | |
|--------------|------------------|---------------|-------|-----|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| 2003 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 3 | 4 | -19.3 | 4.7 | 0 | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | |
| 2 | 6 | 36 | -17.5 | 8.3 | 2 | -2.9 | -0.1 | -6.1 | 4.2 | -11.4 | 12.1 | -11.2 | 8.4 | NA | NA | |
| 3 | 7 | 41 | -14.9 | 1.8 | 2 | -27.0 | 0.9 | -15.7 | -2.1 | -15.9 | 7.8 | -11.0 | 13.5 | NA | NA | |
| 4 | 8 | 49 | -12.2 | 9.1 | 2 | -24.9 | 28.0 | -22.5 | 23.7 | -31.6 | 30.3 | -22.4 | 36.4 | -14.3 | 33.6 | |
| Annual | 9 | 130 | -15.9 | 7.6 | 6 | -23.4 | 14.7 | -17.2 | 11.0 | -17.7 | 14.8 | -14.4 | 19.0 | -14.3 | 33.6 | |
| 2004 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 8 | 51 | -15.4 | 5.6 | 2 | -35.6 | 22.6 | -34.3 | 16.5 | -36.8 | 16.9 | -37.3 | 16.9 | NA | NA | |
| 2 | 12 | 57 | -13.7 | 2.7 | 3 | -24.1 | 13.0 | -20.0 | 1.3 | -18.6 | 1.3 | -16.7 | 2.5 | NA | NA | |
| 3 | 11 | 86 | -13.5 | 6.7 | 3 | -36.1 | 11.9 | -28.2 | -1.9 | -24.1 | 5.8 | -22.9 | 13.4 | NA | NA | |
| 4 | 11 | 93 | -10.8 | 9.7 | 3 | -30.3 | 18.1 | -32.6 | 22.3 | -30.2 | 25.0 | -27.9 | 26.5 | NA | NA | |
| Annual | 16 | 287 | -14.4 | 8.1 | 11 | -28.1 | 12.8 | -27.8 | 8.5 | -25.4 | 10.7 | -24.1 | 13.5 | NA | NA | |

Abbreviations:

L1, L2, L3, L4 - four different concentration levels used during audits

LCL - Lower 95% confidence limit

NA - Not Applicable

No. - Number

UCL - Upper 95% confidence limit

Table G-2-b.

Ammonia Precision and Accuracy Statistics

| Year Quarter | No. of monitors | No. of checks | LCL | UCL | No. of Audits | L1 LCL | L1 UCL | L2 LCL | L2 UCL | L3 LCL | L3 UCL | L4 LCL | L4 UCL | L5 LCL | L5 UCL | |
|--------------|------------------|---------------|-------|-----|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| 2005 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 11 | 92 | -9.5 | 7.0 | 3 | -17.0 | 6.2 | -15.1 | 10.6 | -14.6 | 10.2 | -15.6 | 12.0 | NA | NA | |
| 2 | 11 | 88 | -8.9 | 8.3 | 3 | -36.6 | 40.0 | -29.3 | 34.6 | -28.3 | 37.2 | -27.1 | 39.7 | NA | NA | |
| 3 | 11 | 90 | -11.8 | 9.2 | 3 | -13.1 | 16.8 | -12.5 | 9.6 | -8.2 | 5.5 | -4.5 | 5.2 | NA | NA | |
| 4 | 11 | 87 | -10.3 | 7.8 | 2 | -4.2 | 12.0 | -5.6 | 10.2 | -2.3 | 13.6 | 0.6 | 15.0 | NA | NA | |
| Annual | 11 | 357 | -11.4 | 9.3 | 11 | -20.4 | 20.8 | -16.8 | 17.1 | -16.3 | 18.9 | -15.6 | 21.1 | NA | NA | |

| | | | | | | | | | | | | | | | | |
|--------|------------------|-----|-------|-----|-----------------|-------|------|-------|------|-------|------|-------|------|----|----|--|
| 2006 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 11 | 84 | -9.9 | 6.7 | 3 | -3.8 | 11.8 | -14.8 | 29.6 | -15.7 | 36.3 | -20.8 | 47.7 | NA | NA | |
| 2 | 11 | 91 | -9.2 | 6.2 | 3 | -9.7 | 21.7 | -4.0 | 15.1 | -6.2 | 17.2 | -4.9 | 17.9 | NA | NA | |
| 3 | 11 | 84 | -9.3 | 7.6 | 3 | -0.1 | 23.5 | -3.9 | 17.3 | -3.2 | 10.5 | -2.6 | 10.9 | NA | NA | |
| 4 | 11 | 90 | -10.0 | 8.6 | 3 | -21.0 | 38.3 | -19.6 | 32.4 | -13.7 | 18.1 | -9.8 | 6.7 | NA | NA | |
| Annual | 11 | 349 | -10.6 | 8.3 | 12 | -9.0 | 24.2 | -9.4 | 22.3 | -10.1 | 20.9 | -13.8 | 25.1 | NA | NA | |

| | | | | | | | | | | | | | | | | |
|--------|------------------|-----|-------|------|-----------------|-------|------|-------|------|-------|------|-------|------|----|----|--|
| 2007 | Precision | | | | Accuracy | | | | | | | | | | | |
| 1 | 11 | 87 | -9.2 | 11.0 | 3 | -11.1 | 23.1 | -24.2 | 19.2 | -30.4 | 23.1 | -35.9 | 23.0 | NA | NA | |
| 2 | 11 | 83 | -9.4 | 6.6 | 3 | -1.2 | 9.2 | -11.4 | 8.2 | -9.3 | 3.7 | -9.5 | -1.8 | NA | NA | |
| 3 | 11 | 90 | -10.5 | 4.2 | 3 | 5.4 | 28.0 | -5.6 | 27.1 | -2.2 | 20.7 | -9.5 | 12.9 | NA | NA | |
| 4 | 11 | 79 | -11.9 | 5.5 | 3 | -29.8 | 43.1 | -25.4 | 44.0 | -26.2 | 49.7 | -25.1 | 55.6 | NA | NA | |
| Annual | 11 | 339 | -13.2 | 9.8 | 12 | -12.2 | 28.9 | -18.9 | 26.9 | -21.4 | 28.7 | -27.0 | 29.4 | NA | NA | |

Abbreviations:

L1, L2, L3, L4 - four different concentration levels used during audits

LCL - Lower 95% confidence limit

NA - Not Applicable

No. - Number

UCL - Upper 95% confidence limit