EMISSION MEASUREMENT CENTER
GUIDELINE DOCUMENT

SULFUR DIOXIDE INTERFERENCE IN METHODS 7 AND 7A

INTRODUCTION

At high levels of sulfur dioxide (SO_2) concentrations, Method 7 and 7A have been reported to yield low nitrogen (NO_x) results. It was believed that SO_2 depletes the hydrogen peroxide (H_2O_2) in the absorbing solution, which then causes incomplete absorption of the NO_x. The concentration of H_2O_2 in the absorbing solution has therefore been increased. For example, the American Society of Testing and Materials Method D-1608 [Test Method for Oxides of Nitrogen in Gaseous Combustion Products (Phenol-disulfonic Acid)] uses an absorbing solution containing H_2O_2 that is equivalent to five times the concentration currently specified in EPA Method 7.

A laboratory study was conducted to (1) determine whether SO_2 is an interferent and (2) correct the problem if one exists.

TESTING AND DISCUSSION

To determine whether SO_2 interferes, several sets of samples with varied amounts of SO_2 were collected and analyzed according to Method 7A using the same absorbing solution as Method 7. The results are shown in Table 1. The NO_x results indicate that SO_2 begins to interfere at about 2100 ppm SO_2.

The concentration of H_2O_2 in the absorbent was then increased. Samples were taken with at least 2000 ppm SO_2 and with an absorbing solution having a H_2O_2 concentration four times the original strength. The results of this series of tests are reported in Table 2. Overall, the increased H_2O_2 solution showed some improvement compared to the regular Method 7 solution; however, the precision and accuracy were still poor. A second set of samples was taken with the increased H_2O_2 and analyzed by both Methods 7 and 7A to determine if the increased H_2O_2 interferred with the ion chromatograph (IC). The results in Table 3 indicate there is variability with both methods; therefore, it does not appear that H_2O_2 is an interferent to the IC.

The H_2O_2 level was then increased to five times the Method 7 level to conform with the ASTM method. Five additional sets of samples were taken containing NO_x and SO_2, and six sets of samples were taken containing only NO_x. Table 4 shows the results of the samples analyzed by Methods 7 and 7A, and Table 5 shows the results of the remaining sets of data analyzed by Method 7A. the results in Tables 4 and 5 indicate better absorption with increased H_2O_2 solution when SO_2 is present. The results in Tables 4 and 5 show that the sets with only NO_x are consistently lower than the sets containing NO_x and SO_2. The analyses also indicate that both methods did not yield acceptable results.

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TABLE 1. Determination of SO_2 Interference

SO_2 conc., ppm	M-7A NO_x conc., ppm	Actual NO_x conc., ppm	Percent diff. from act. NO_x conc.
664	326	360	- 9
823	305	319	- 5
1033	225	223	+ 0.5
1050	279	303	- 8
1112	237	261	- 9
1142	256	268	- 5
1527	255	245	+ 4
1712	207	192	± 8
1735	212	233	- 9
2059	192	200	- 4
2082	180	165	+ 9
4436	27.4	26.3	+ 4
2659	113	118	- 3
3135	38.4	120	- 68
3389	77.8	93.6	- 17
3611	67.5	105	- 36
4769	63.4	81.9	- 23
4769	42.3	82.9	- 49
2132	94.9	190	- 50
2312	63.7	194	- 52
2836	92.2	128	- 50
3080	129	141	- 8
4682	68	121	- 44
5366	31	88.4	- 65
2631	112	148	- 35
3044	86.6	129	- 33

TABLE 2. Methods 7A Samples with Four Times H_2O_2

SO_2 conc., ppm	M-7A NO_x conc., ppm	Actual NO_x conc., ppm	Percent diff. from act. NO_x conc.
2953	132	163	- 19
2853	170	131	- 29
2249	139	145	+ 5
3649	145	125	- 16

TABLE 3. Methods 7 and 7A Samples with Four Times H_2O_2

SO_2 conc., ppm	M-7A NO_x conc., ppm	Actual NO_x conc., ppm	Percent diff. from act. NO_x conc.	M-7 NO_x conc., ppm	Percent diff. from act. NO_x conc.
2447	189	179	+ 6	202	+ 13
2341	193	173	+ 12	119	- 31
3464	111	95.4	+ 16	60.7	- 36
2992	138	135	+ 2	160	+ 18
2877	158	147	+ 7	151	+ 3
2663	128	171	- 25	129	- 24

TABLE 4. Methods 7 and 7A Samples with Five Times H_2O_2

SO_2 conc., ppm	M-7A NO_x conc., ppm	Actual NO_x conc., ppm	Percent diff. from act. NO_x conc. (M-7A)	M-7 NO_x conc., ppm	Percent diff. from act. NO_x conc. (M7)
2761	142	154	- 8	132	- 14
2807	134	144	- 7	lost	
2387	145	165	- 12	168	+ 1.7
2414	180	189	- 4.6	143	- 24
2376	168	191	- 12	162	- 15
0*	157	179	- 13	113	- 37
0	148	185	- 20	97.6	- 47
0	150	186	- 19	164	- 12
0	149	186	- 20	144	- 22
0	154	182	- 16	168	- 7

* A colorimetric analysis for nitrite indicated no nitrite was present.

TABLE 5. Method 7A Samples with Five Times H_2O_2

SO_2 conc., ppm	M-7A NO_x conc., ppm	Actua NO_x conc., ppm	Percent diff. from act. NO_x conc.
2657	175	159	+ 10
2532	143	153	- 7
2771	138	138	- 0.5
2766	118	124	- 5
2979	145	148	- 2
2553	197	194	+ 1
2446	157	148	+ 6
2848	138	125	+ 9
3288	119	110	+ 9
3046	116	109	+ 6
3322	106	97.7	+ 8
2355	206	201	+ 2
0	377	403	- 7
0	341	345	- 1
0	363	401	- 9
0	343	400	- 14
0	401	419	- 4
0	382	418	- 9
0	335	361	- 7
0	381	397	- 4
0	366	391	- 7
0	367	394	- 7
0	385	412	- 7
0	401	417	- 4
2784	170	160	+ 7
2655	173	156	+ 11
2663	162	131	+ 24
2010	198	192	+ 3
0	345	379	- 10
0	289	371	- 22
0	282	351	- 20
0	320	347	- 8
0	326	400	- 19
0	203	186	+ 10
0	162	161	+ 0.3
0	186	134	+ 39
0	161	172	+ 6
0	198	182	+ 9

The problem with precision and accuracy may be due to the formation of nitrous oxide (N_2O). A study performed by the Air and Energy Engineering Research Laboratory indicates that NO may be converted to N_2O when in the presence of SO_2 and moisture. The N_2O would not be absorbed into the solution nor detected. However, the problem with the five times H_2O_2 solution occurs when no SO_2 is present.

CONCLUSION

In conclusion, this laboratory evaluation indicates that SO_2 begins to interfere with Method 7A at SO_2 levels about 2100 ppm. The Method 7A (and Method 7) absorbing solution with a H_2O_2 concentration five times its current strength appears to compensate for the SO_2 interference. However, a consistently low bias occurs when only NO_x is sampled and is apparently due to the increased H_2O_2 concentration.

RECOMMENDATIONS

Since N_2O will not be absorbed into solution, then increasing the H_2O_2 in the absorbing solution will not be effective. If conversion to N_2O is a problem, an instrumental method may be needed. It is recommended that further testing should be performed in order to establish the exact level of SO_2 that causes interference and when the regular Method 7 solution should be used, and to determine if there is conversion to N_2O.