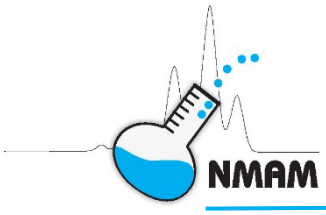
NIOSH Manual of Analytical Methods (NMAM) 5th Edition



BACKUP DATA REPORT
NIOSH Method No. 6011

Title: Bromine and Chlorine

Analytes: Bromine and Chlorine

Author/developer: Mary Ellen Cassinelli (Issues 1 & 2), Method revised by Dawn Farwick (Issue 3)

Date: February 18, 2022

Table 8. Method validation for bromine at low humidity (~20%)

Concentration Level (x PEL)	n	Concentration taken[a] (mg/m^3)	Concentration found (mg/m^3)	s_r	Recovery (%)
0.1	6	0.076	0.077	0.039	101
0.5	6	0.351	0.358	0.033	102
1	6	0.696	0.673	0.026	96.7
2	6	1.42	1.50	0.028	106

Mean recovery = 102%; Precision (pooled s_r) = 0.032

[a]Concentration determined from generator source and dilution flows where sampling rate=0.3 L/min and sampling time=4 hr.

All data were within the accuracy criterion of ±25% at the 95% confidence level and coefficient of variation (precision) recommended for a valid NIOSH method [10]. Bartlett's test for homogeneity was applied to the data before pooling. The mean recovery for the overall method (Cl_2 and Br_2) was 98.7% (-1.3% bias) with a sampling and analytical precision of 5.2%, and a total coefficient of variation estimate (CV_T) of 7.2%.

Instrument LOD/LOQ and linear range

The limit of detection (LOD), the smallest amount of analyte that can be distinguished from background, was defined in this study as three times the standard error of the calibration graph divided by its slope. The limit of quantitation (LOQ) was defined as ten times the standard error of the calibration graph divided by its slope [9]. The LOD of Cl^- in the thiosulfate matrix was 0.06 µg/mL with a limit of quantitation (LOQ) of 0.19 µg/mL. For Br^-, the LOD and LOQ were 0.16 and 0.54 µg/mL, respectively. The linear range for Cl^- at the sensitivity setting used in this work (10 µS) was 0.05 to 5 µg/mL, and for Br^-, 0.20 to 15 µg/mL. The LOD and LOQ may be reduced and linear range proportionally extended at the lower end by using a more sensitive instrumental setting, e.g., 3 µS or 1 µS full scale. Similarly, the linear range can be extended at the upper end by using a less sensitive instrumental setting or by diluting the sample.

The lower limit for the working range of air concentrations for a given sampling volume can be calculated based on the limit of quantitation (LOQ) of the analytical method and the liquid sample volume. The lower limit for the working range of air concentrations (mg/m^3) for a given sampling volume = LOQ (µg/mL) x liquid sample volume (mL) ÷ air sample volume (L):

For Cl_2: Lower limit of the working range for 45 L sampling volume = 0.19 µg/mL x 10 mL ÷ 45 L = 0.04 mg/m^3.

For Br_2: Lower limit of the working range for 360 L sampling volume = 0.54 µg/mL x 10 mL ÷ 360 L = 0.015 mg/m^3.

Cl_2 field study

Field samples for Cl_2 were collected at a plant that produces trichloroisocyanuric acid. The compound is prepared by treating cyanuric acid with Cl_2. Paired silver filter samples and sulfamic acid bubblers (OSHA Method ID-101) [12] were collected at rates of 0.5 and 1.0 L/min, respectively. The results are presented in Table 9.

Table 9. Chlorine field study results using paired silver filters and bubbler[a] samples

Pair number	Sampler numbers	Air volume (L)	Mass Cl_2 (µg)	Concentration (mg/m^3)	Difference[b] (mg/m^3)
1	Filter – 1	189	134	0.71	0.10
1	Bubbler – 1	377	230	0.61	
2	Filter – 3	211	122	0.578	0.12
2	Bubbler – 4	305	140	0.459	
3	Filter – 13	167	368	2.20	-0.02
3	Bubbler – 11	239	530	2.22	
4	Filter – 11	157	257	1.64	-0.10
4	Bubbler – 13	270	470	1.74	
5	Filter – 10	152	41.4	0.272	0.14
5	Bubbler – 12	313	43.0	0.137	
6	Filter – 4	218	460	2.11[c]	
6	Bubbler – 2	361	1700	4.71	
7[d]	Filter – 2	185	11.5	0.062	
7[d]	Bubbler – 3	342	4.8	0.014	
8[d]	Filter – 12	158	ND[e]	ND[e]	
8[d]	Bubbler - 14	293	1.6	0.006	

[a]OSHA Method ID-101
[b]Differences not statistically significant at 95% confidence level
[c]Probable breakthrough of silver filter
[d]Background levels in plant
[e] None detected, detection limit = 0.6 µg/sample

Pairs 1 through 6 were area samples collected at the production site. Pairs 7 and 8 were collected in the plant but away from the chlorination operation to ascertain background levels of Cl_2. In pair 6, possible breakthrough of the silver filter occurred, as evidenced by the large mass of Cl_2 found in the bubbler. The mean difference for pairs 1 to 5 was 0.048 mg/m^3. When a paired t-test for determining differences in paired observations [19] was applied to these data, the results showed that the difference between the two monitoring methods was not statistically significant at the 95% confidence level. However, since the number of samples taken at this field site was limited, more field studies must be done to verify the soundness of the significance statement.

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