NMR procedure for determining concentrations of methanol and formic acid in solutions from a chlorine dioxide generating plant

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Chlorine dioxide is produced commercially by reacting sodium chlorate in sulfuric acid solution with a reducing agent such as sodium chloride or methanol (*1-4*). When sodium chloride is used, chlorine is a major by-product. Methanol has increased in importance as a reducing agent for environmental reasons, since the methanol-chlorate process produces not chlorine but, rather, oxidation products of methanol, as seen in Eq. 1. Complete oxidation of methanol to carbon dioxide, for example, leads to the most efficient utilization of methanol and the following stoichiometry.

$$6NaClO_3 + CH_3OH + 4H_2SO_4 \rightarrow 6ClO_2 + CO_2 + 5H_2O + 2Na_3H(SO_4)_2 \quad (1)$$

One widely used process involves continuously feeding methanol and sodium chlorate and sulfuric acid solutions to a single vessel (generator) that serves as a reactor, evaporator, and crystallizer. Steam and product gases exit through a vapor pipe at the top of the generator. The gases flow through a condenser, where the steam is condensed, and pass into a packed column where chlorine dioxide is absorbed in water. Carbon dioxide is vented to the atmosphere. A slurry of sodium sesquisulfate crystals is continuously pumped from the bottom of the generator to a filter, where the crystals are removed from the process. Filtrate is returned to the generator.

Because methanol is volatile, some methanol vapor leaves the generator in the steam and product-gas stream. A recent patent (*4*) shows that methanol utility is highly dependent upon the location of the methanol feed point in the generator. This reference also suggests that formaldehyde and formic acid can form in the generator if there is incomplete oxidation of methanol. Equations 2 and 3 are stoichiometries of the methanol-chlorate reactions with incomplete oxidation of methanol.

$$6NaClO_3 + 1.5CH_3OH + 4H_2SO_4 \rightarrow 6ClO_2 + 1.5HCOOH + 4.5H_2O + 2Na_3H(SO_4)_2 \quad (2)$$

$$6NaClO_3 + 3CH_3OH + 4H_2SO_4 \rightarrow 6ClO_2 + 3HCHO + 6H_2O + 2Na_3H(SO_4)_2 \quad (3)$$

Based on this information, we suspected that methanol, formaldehyde, and formic acid might be present in solutions from both generators and absorbers in chlorine dioxide generating plants.

We recently analyzed generator and absorber solutions from several chlorine dioxide plants using the procedure described in the following Experimental section. Results are presented in **Table I**. The generator solutions contained formic acid in the amount of 0.2-0.3 moles/L but no measurable concentrations of methanol or formaldehyde. (We estimate that the lower limit of detectability for each of the organic species is less than $10^{-6}M$.) The absorber solutions contained formic acid (0.01-0.04 moles/L), methanol (0.01-0.05 moles/L), and no measurable concentrations of formaldehyde.

For the purposes of quality control, production efficiency, and cleanliness of the environment, there is a need for an accurate method of measuring residual concentrations of methanol and formic acid in process solutions from chlorine dioxide generating plants. Any analytical method involving ion exchange, chromatography, and mass spectrometry is likely to encounter difficulties because of the presence of sulfuric acid, sodium chlorate, and sodium sesquisulfate in very high concentrations. On the other hand, proton nuclear magnetic resonance (^1H NMR) facilitates the quantitative analysis of organic species in admixture with these species, since chlorates and sulfates do not affect NMR signals. In addition, NMR signals for HOD, H_3O^+, etc. are widely separated from those of the organics of interest. This work is the outcome of our efforts to develop a procedure to detect methanol and formic acid in process solutions from chlorine dioxide generating plants.

Experimental

All NMR spectra were obtained using a broad-band switchable probe in a Varian XL-400 Fourier transform spectrometer operating at 399.915 MHz. A measured volume of sample to be analyzed was diluted with an

equal volume of D_2O (99.9 D atom %, Aldrich). To avoid significant H-D exchange on the organic molecules, spectra were taken within 15 min after diluting the aqueous sample with D_2O. One mL of the diluted sample was placed into a 5-mm NMR tube. The intensities of the ^1H NMR signals for the organic species were measured relative to *t*-butanol (0.1*M* solution in D_2O) sealed inside a 1.0-mm-ID capillary tube and placed concentrically within the 5-mm NMR tube.

To ensure good signal-to-noise ratio and sufficient relaxation time, multiple scans (64 for most samples) were obtained using a pulse angle of 25° and a 4-s pulse cycle. The large water peak was suppressed by selective saturation during a 2-s delay time prior to acquisition. Calibration samples were prepared by diluting standard solutions of formic acid (neutralized with sodium hydroxide) and methanol. ACS-certified grade methanol (99.9%) and formic acid (90%) were obtained from Fisher Scientific. These samples were buffered at pH 7 by addition of Na_2HPO_4 at a concentration of 0.025*M*.

Two sets of samples were prepared to simulate commercial solutions from a generator and an absorber at a chlorine dioxide generating plant. The simulated generator samples were prepared by combining equal volumes of two solutions. One solution contained 0.94*M* $NaClO_3$, 0.7*M* Na_2SO_4, and 0.056*M* Na_2HPO_4 and was saturated with ClO_2. The other solution contained 0.2*M* NaOH and desired concentrations of methanol and formic acid. Simulated absorber samples were prepared by combining equal volumes of two solutions, one containing 0.0567*M* Na_2HPO_4 and saturated with ClO_2 and the other containing 0.2*M* NaOH and desired concentrations of methanol and formic acid. NaOH and Na_2HPO_4 were included in these samples for neutralization and approximate pH adjustment. All samples had a strong yellow color, characteristic of the high chlorine dioxide content.

The two sets of samples were used to develop a method to stabilize methanol and formic acid concentrations in samples from a commercial chlorine dioxide process. Stabilization is especially important if there is an extended period of time between sampling and analysis. For example, companies that do not have convenient access to a Fourier-transform NMR spectrometer may require several days for delivery and analysis of samples at an analytical laboratory. In this regard, we explored two possible methods of stabilizing the samples: (a) nitrogen purging to remove chlorine dioxide and (b) pH adjustment.

I. Analyses of samples obtained from chlorine dioxide generating plants

Plant	Sample no.	Source of solution	Concentration, M	
			Methanol	Formic acid
A	1	Generator	0.000	0.204
A	2	Generator	0.000	0.252
A	3	Generator	0.000	0.300
A	4	Absorber	0.036	0.043
A	5	Absorber	0.034	0.028
B	6	Generator	0.000	0.340
B	7	Absorber	0.010	0.039
C	8	Absorber	0.022	0.034
D	9	Absorber	0.048	0.035
E	10	Absorber	0.013	0.013

Discussion

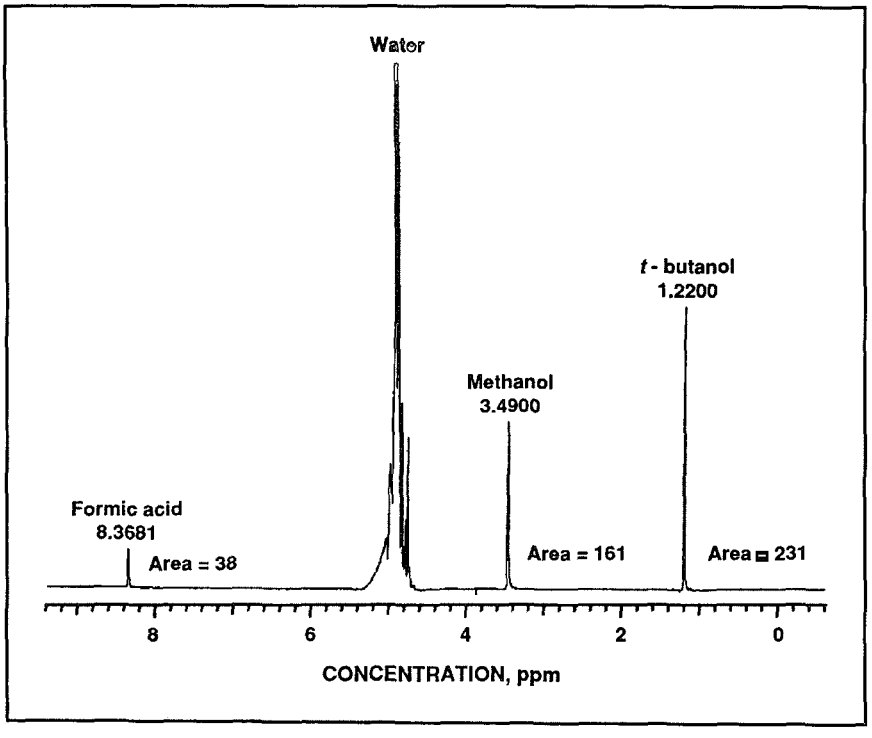
Figure 1 shows the result of 64 ^1H NMR scans of a sample solution from the absorber at a chlorine dioxide plant (Table I, Sample 10). The figure illustrates the effectiveness of this technique in suppressing the peak attributed to water, which is present at a concentration more than 1000 times greater than that of any other species.

Figure 2 shows calibration graphs of relative peak area vs. concentration for methanol and formic acid. Relative area was determined by dividing the peak area for a species by that of *t*-butanol. The concentrations of the methanol and formic acid solutions used in developing the graphs ranged from 0 to 0.2*M*. The data for both species produced good, straight lines that pass through the origin. The slopes are 49.87±0.35 for methanol and 13.58±0.15 for formic acid. To determine concentrations of organic species in a sample, one divides the relative area by the appropriate slope. The standard deviation in these slopes is equivalent to an uncertainty of about 1% in the concentrations.

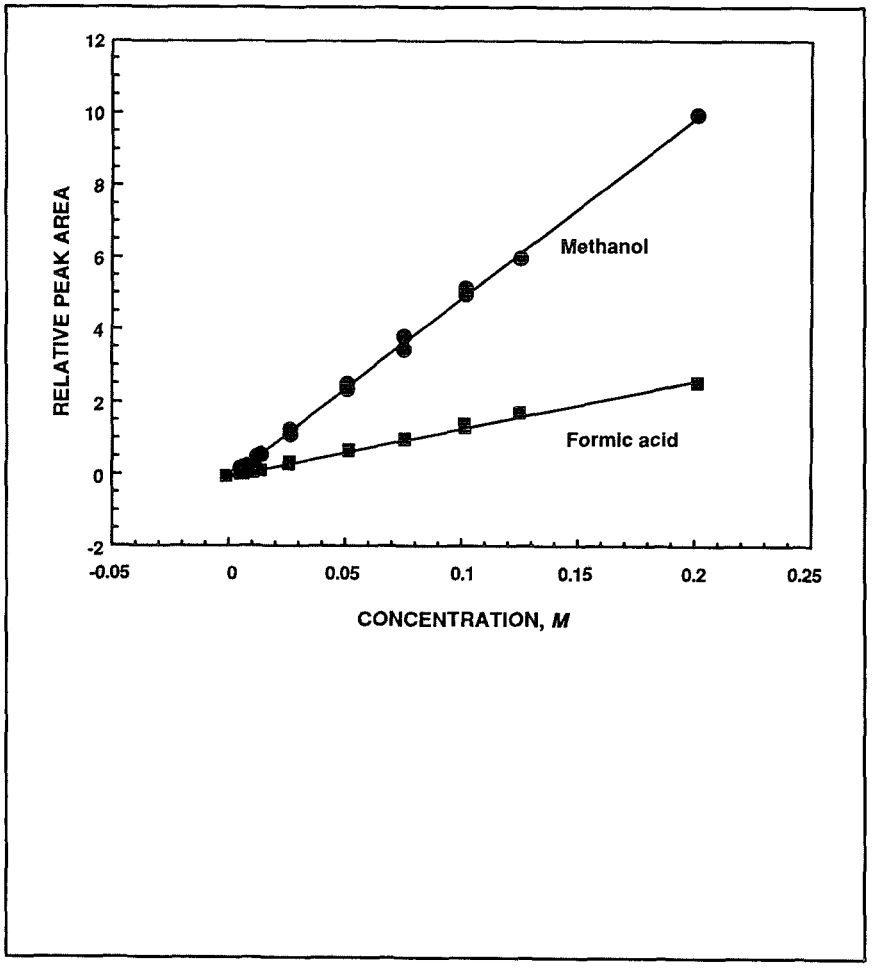
We analyzed samples containing very low concentrations ($5 \times 10^{-4}M$) of both methanol and formic acid. After replicate analyses, we found the standard deviation to be $0.1 \times 10^{-4}M$ and $0.4 \times 10^{-4}M$ for methanol and formic acid, respectively. We considered a concentration of $5 \times 10^{-4}M$ to be a lower practical limit for solutions from commercial plants.

Table II contains results of NMR analyses of simulated absorber samples (A-1 through A-6) and simulated generator samples (G-1 through G-10). The initial concentrations were calculated, based on preparation. The pH was adjusted to either 7 or 11 within minutes after preparing the samples. In some cases, nitrogen was sparged through the solution to remove chlorine dioxide. About 5 min of sparging was required to remove all observable yellow color from the solutions. Each sample was subsequently analyzed for methanol and

1. ^1H NMR spectrum (based on 64 scans) of solution from absorber in chlorine dioxide plant (Table I, Sample 10)



2. ^1H NMR calibration graph for methanol and formic acid



formic acid by NMR after either 3 h or 5 days of storage in closed containers.

Table II shows the percent deviation between the initial and final concentrations of each sample. The results indicate that pH and the nitrogen purge had a greater influence on the stability of the methanol analysis than on formic acid analysis, as evidenced by the percent deviation between initial and final concentrations. The formic acid analysis for both sets of samples was relatively stable regardless of treatment conditions and length of storage. The maximum deviation, 3.2%, is probably acceptable for most practical purposes. The methanol analysis is most stable for samples that have been adjusted to pH 11 and have not been purged with nitrogen. Such samples can be stored for at least 5 days without much decline in methanol stability. Methanol stability declines for samples that have been adjusted to pH 7 and for those that have been purged with nitrogen. It is evident that even a 5-min purge causes significant loss of methanol by evaporation.

Neutralization and pH adjustment would be extremely important in stabilizing generator samples from a commercial process, since these adjustments greatly slow down reactions that depend on acidity. A generator typically operates at 3-4*M* H_2SO_4. It has been well established that the rate of chlorine dioxide is highly dependent upon sulfuric acid concentration (13th-14th order) in a process based on the chloride-chlorate reaction (*5*). Our laboratory studies indicate that sulfuric acid order is also high for a process based on the methanol-chlorate reaction.

Neutralization and pH adjustment also would be important for the stability of absorber solutions, which are somewhat acidic because of the presence of formic acid. Absorber solutions typically contain ca. 0.12*M* chlorine dioxide and variable concentrations of decomposition products of chlorine dioxide that form in storage (*6*). Oxidation of methanol by some of the ingredients, particularly chlorine dioxide (*7*) and chlorite ions (*8*, *9*),

[1]Chlorite is decomposed to chlorine dioxide in acidic solutions. The resulting chlorine dioxide reacts with methanol.

II. ^{1}H NMR analyses of laboratory-prepared solutions

Sample no.	pH	N_2 purge, min	Storage time	Methanol Concentration, M Initial	Methanol Concentration, M Final	Methanol Deviation, %	Formic acid Concentration, M Initial	Formic acid Concentration, M Final	Formic acid Deviation, %
A-1	11	...	3 h	0.033	0.033	0.0	0.033	0.032	3.0
A-2	11	...	5 days	0.033	0.031	6.1	0.033	0.034	-3.0
A-3	7	...	3 h	0.031	0.029	6.5	0.031	0.031	0.0
A-4	7	...	5 days	0.031	0.026	16.1	0.031	0.031	0.0
A-5	7	5	3 h	0.031	0.027	12.9	0.031	0.030	3.2
A-6	7	5	5 days	0.031	0.027	12.9	0.031	0.031	0.0
G-1	11	...	3 h	0.033	0.034	-3.0	0.167	0.171	-2.4
G-2	11	...	5 days	0.033	0.034	-3.0	0.167	0.172	-3.0
G-3	7	...	3 h	0.033	0.031	6.1	0.167	0.172	-3.0
G-4	7	...	5 days	0.033	0.030	9.1	0.167	0.170	-1.8
G-5	7	5	3 h	0.033	0.029	12.1	0.167	0.166	0.6
G-6	7	5	3 h	0.033	0.029	12.1	0.167	0.167	0.0
G-7	7	5	5 days	0.033	0.028	15.2	0.167	0.168	-0.6
G-8	11	...	3 h	0.025	0.024	4.0	0.125	0.126	-0.8
G-9	7	...	3 h	0.025	0.022	12.0	0.125	0.125	0.0
G-10	7	5	3 h	0.025	0.021	16.0	0.125	0.127	-1.6

increases with acidity.[1]

We anticipated that H-D exchange would cause low NMR analyses of the samples adjusted to pH 11, since numerous examples of base-catalyzed hydrogen isotope exchange have been reported (*10, 11*). However, in the present study, we found that if NMR analyses of freshly prepared samples were completed within 15 min after adding D_2O, there was excellent agreement between the concentrations determined by NMR analysis and those calculated based upon preparation.

This work does not rule out the possibility that formaldehyde is produced in the methanol-chlorate process by the reaction depicted in Eq. 3. However, we suspect that any formaldehyde that is formed will rapidly react with other species in the mixture. In a strong oxidizing environment, at highly acidic conditions, formaldehyde reacts much faster than formic acid. For example, in related studies that used chlorine as an oxidizing agent, we showed that formaldehyde is converted to formic acid in 4*M* sulfuric acid solution about 20 times faster than formic acid is converted to carbon dioxide (*12, 13*). If formaldehyde were present in the commercial chlorine dioxide solutions we analyzed, it would have been at concentrations below the detection limit (ca. $10^{-6}M$) of the NMR technique.

Sample preparation

We recommend the following procedures when preparing plant samples for NMR determination:

A 100-mL sample (either drawn from generator or absorber) should be added slowly to 50 mL of sodium hydroxide solution containing about 4 $\times 10^{-3}$ moles of Na_2HPO_4.[2] The solution should be cooled in an ice bath and stirred while the acidic sample is added. The amount of sodium hydroxide should be such that the mixture has a final pH of 11. Based upon the results of this laboratory study, the concentrations of methanol and formate in these alkaline samples should remain unchanged for at least five days.

The volume of the mixture should be recorded before making the NMR measurement. The NMR spectra should be taken within 15 min after the sample is mixed with D_2O. Because of the possibility of significant H-D exchange in the *t*-butanol reference solution over an extended period of time, the calibration should be checked at least once a week with standards of at least three different concentrations.□

[2]The sample should be collected and handled only by experienced personnel who have been properly trained in the safety procedures for handling such solutions. Personnel should use the recommended protective clothing, face and eye protection, and respiratory devices.

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