Sampling and Analysis of Chlorinated Isocyanuric Acids

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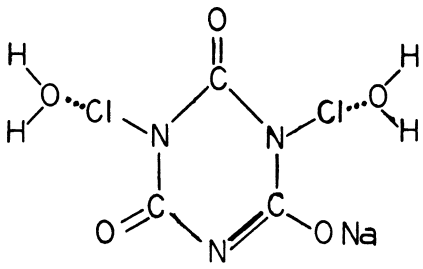
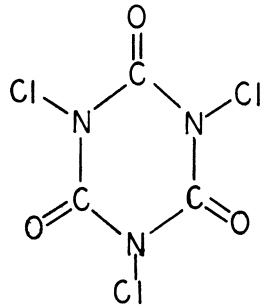
Chlorinated isocyanurates have applications for both swimming pools and as commercial sanitizers (1, 2, 3, 4). Sodium dichloroisocyanurate dihydrate (NaDCC) and trichloroisocyanuric acid (TCCA) are the most common derivatives of chlorinated isocyanurates. Generally they are used as bactericides, algicides, and sanitizers. They are also used as active ingredients in dry bleaches, dishwashing compounds, scouring powders, water and sewage treatment and generally as replacement of calcium hypochlorite.



Sodium Dichloroisocyanurate Dihydrate (NaDCC)



Trichloroisocyanuric Acid (TCCA)

Despite apparent widespread use, the toxicological data on these compounds are insufficient (5). Because of the strong oxidation properties, low concentrations of NaDCC and TCCA particulates are extremely irritating to the respiratory tract and mucous membranes of the eyes (6). They can also cause irritation

and erythema of exposed skin areas. The systemic toxicological characteristics are not known. Currently there is no TLV or Federal Standard on either compound. The National Institute for Occupational Safety and Health (NIOSH) conducted a Health Hazard Evaluation (HHE) at a chlorine dry bleach plant to determine the extent and effects of exposure to these chlorinated isocyanuric acids (6). The work reported in this paper is a result of the HHE request to develop a method for the analysis of air samples for NaDCC and TCCA.

The preferred method for analyzing chlorinated isocyanuric acids and their salts is the iodometric titration (7). The main limitation of the iodometric titration method is sample size; generally one would need a minimum of 100 milligrams for titrating either compound. For industrial hygiene samples, this is a problem because sample weights are usually smaller by a factor of 20, i.e. less than 5 milligrams. Therefore, modifications of the iodometric titration method were needed to make the method applicable to industrial hygiene samples.

Experimental

Air Sampling. Since NaDCC and TCCA were manufactured in different buildings, the compounds were collected separately, thus eliminating problems with interferences in analysis. Personal exposures to both total and respirable particulates of NaDCC and TCCA were determined. The total particulates were collected on a 37-mm diameter, 5.0 μm pore size polyvinyl chloride copolymer membrane filter (Gelman DM-5000) contained in a three-piece closed-face cassette. The respirable particulate fraction (<10 μm aero-dynamic equivalent diameter) was collected on the same type of filter contained in a two-piece cassette mounted in a 10-mm cyclonic separator. The one-and-two-stage samplers were attached to the worker's shirt lapel at the breathing zone; air was pulled through the sampler by means of a personal sampling pump operating at 1.7 L/min.

Apparatus. The titration assembly consisted of a pH meter with a millivolt display and capable of supplying 10 microamperes constant current to the electrodes, two platinum electrodes, a 5-mL microburette, nitrogen gas supply, a magnetic stirrer and bar, a 250-mL beaker for titration, and a 50-mL burette.

Reagents and Stock Solutions. Deoxygenated distilled water, prepared by bubbling nitrogen gas into distilled water for 10-15 minutes using flexible tubing connected to a glass Pasteur Pipette, was used.

Sodium Dichloroisocyanurate Dihydrate (NaDCC). A 10^{-3} M solution was prepared by dissolving 25.59 mg into a 100-mL volumetric flask with distilled water.

Trichloroisocyanuric Acid (TCCA). A 10^{-3} M solution was prepared by dissolving 23.24 mg into a 100-mL volumetric flask with distilled water.

Potassium Iodide (KI). A 1 M solution was prepared by dissolving 16.60 g into a 100-mL volumetric flask with distilled water.

Potassium Iodate (KIO_3). A 0.1000 N solution was prepared by weighing 3.567 g and dissolving into a 1000-mL volumetric flask with distilled water.

Sodium Thiosulfate ($Na_2S_2O_3$). 0.005 N and 0.001 N solutions were prepared by dissolving 1.25 g and 0.250 g, respectively, into 1000-mL volumetric flasks with distilled water. These solutions were standardized against potassium iodate (see standardization section).

Sulfuric Acid. A 6 N solution was prepared by slowly adding 84 mL of 95% concentrated sulfuric acid into 400 mL distilled water in a 500 mL volumetric flask and bringing up the volume to the mark with distilled water.

Hydrochloric Acid. A 1 N solution was prepared by slowly adding 43.1 mL of concentrated (11.6 M) hydrochloric acid into a 500-mL volumetric flask containing 400 mL distilled water. The total volume was brought to the mark with distilled water.

Standardization. A 50-mL aliquot of deoxygenated distilled water was measured with a graduated cylinder and placed in the titrating beaker. When the 0.005 N sodium thiosulfate solution was standardized, 2 mL of 0.1000 N potassium iodate was placed in the titrating beaker; for the standardization of 0.001 N sodium thiosulfate solution only 0.2 mL of 0.1000 N potassium iodate solution were placed in the titrating beaker. A 6-mL aliquot of the 1 M potassium iodide solution, plus a 15-mL aliquot of the 1 N hydrochloric acid solution, were added into the titrating beaker. The solution in the beaker was stirred and the nitrogen purge was over the surface in the beaker during titration. The potassium iodate was then titrated with proper sodium thiosulfate solution. For each new addition of sodium thiosulfate, a stabilized millivolt reading was recorded. The titration was continued well beyond the end-point until no change in the millivolts was observed when excess sodium thiosulfate was added. A plot of millivolts versus volume of sodium thiosulfate used was made and the end-point was determined from the plot. The normality, N_S, of sodium thiosulfate was calculated from the equation:

$$N_S = \frac{M_p \cdot N_p}{M_S}$$

where M_p= milliliters of potassium iodate titrated (2 or 0.2 mL)
N_p= normality of potassium iodate
M_S= milliliters of sodium thiosulfate at the end point.

Preparation of Standards. To account for the errors which may be introduced in the presence of residual oxygen in the titration, particularly at low analyte concentrations, greater accuracy was obtained by using a calibration curve.

Sodium Dichloroisocyanurate Standards. Using the 10^{-3} M solution, each volume of 0.5, 1, 2, 4, and 8 mL yielded, respectively, 0.128, 0.256, 0.512, 1.02, and 2.05 mg of sodium dichloroisocyanurate dihydrate.

Trichloroisocyanuric Acid Standards. Using the 10^{-3} M solution, each volume of 0.5, 1, 2, 4, and 9 mL yielded, respectively, 0.116, 0.232, 0.464, 0.928 and 2.09 mg of trichloroisocyanuric acid.

Replicates of six samples per each level of concentration were prepared for each compound. Each standard was prepared and titrated immediately. The data sets of end-point volumes and milligrams of the standards were treated statistically, where the standard deviations and regression analysis were performed.

Titration. Each standard or extract solution along with a 50-mL aliquot of distilled deoxygenated water were added into the titrating beaker. Three milliliters of 1 M potassium iodide followed by 5 mL of 6 N sulfuric acid solution were also added in the titrating beaker. The two platinum electrodes were lowered into the sample solution and the nitrogen purge started over the solution. The sample solution was stirred vigorously. For samples with filter loading of more than 0.5 milligram, the 0.005 N sodium thiosulfate solution was used for titration. For samples with filter loading of less than 0.5 milligram, the 0.001 N sodium thiosulfate solution was used for titration. For each addition of sodium thiosulfate, a new stabilized millivolt reading was taken. The titration was continued beyond the end-point until no change in the millivolts was observed when excess of sodium thiosulfate was added. The end-point was determined from a plot of millivolts versus the volume of sodium thiosulfate used for titrating that sample.

For consistency, all the 0.001 N sodium thiosulfate end-point volumes were converted to 0.005 N end-point volumes as follows:

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$$M_1 = M_2 \cdot \frac{N_2}{N_1}$$

where M_1= end-point volume of 0.005 N solution
M_2= end-point volume of 0.001 N solution
N_1= 0.005
N_2= 0.001

Filter Extraction. Each spiked or field filter sample was placed in the titration beaker containing 25 mL deoxygenated distilled water at room temperature. After five minutes, the filter was lifted with tweezers above the water level and was rinsed slowly on both sides with 25 mL of deoxygenated distilled water. Then the filter was rolled with the tweezers and squeezed against the inside wall of the beaker to remove excess water. Then the filter was discarded. The procedure described in the "Titration" section was followed to analyze the extract.

Recovery Study. Spiking solution. A 10 mg/mL spiking solution was prepared by dissolving 0.500 g of sodium dichloroisocyanurate dihydrate in 50 mL distilled water. (It may take up to 2 hours to dissolve all the material.)

Six filters for each level of concentration were spiked using variable volume pipettes. The following volumes 13, 25, 50, 100, and 200 µL of the 10 mg/mL solution yielded 0.13, 0.25, 0.50, 1.00 and 2.00 mg of sodium dichloroisocyanurate dihydrate on a filter, respectively. When the filter was dry, the "filter extraction" section was followed. The end-point volumes were converted to milligrams from the calibration curve and the percent recoveries were calculated.

Filter extraction efficiency study could not be performed for trichloroisocyanuric acid. When trichloroisocyanuric acid was dissolved in water or methanol and then was spiked on a filter and dried, it was not recovered as trichloroisocyanuric acid because it had reacted with the solvent and its chemical structure had changed. It is recommended that aerosol generating equipment be used in this case that generate known concentrations of dry trichloroisocyanuric acid aerosols which are deposited on filters.

Results and Discussion

A computer literature search revealed no direct analytical method specific for sodium dichloroisocyanurate dihydrate (NaDCC) or trichloroisocyanuric acid (TCCA). Each compound dissolved in water released chlorine in the positive oxidation state and formed complex equilibria reactions dependent on the pH of the solutions. NaDCC and TCCA are very strong oxidants and very reactive compounds, therefore, incompatible for chromatographic analysis. The only method that is used for analysis of compounds containing

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chlorine in the positive oxidation state is the classical iodometric titration. The two drawbacks of this method are, first, that one cannot distinguish two compounds in the same solution because titration is not a separating technique. Second, the iodometric method is recommended for samples of 100 milligrams or more; thus, it is incompatible for small samples (less than 5 mg).

Sampling Test. This experiment was conducted before any other experiments or titrations were conducted. The reason for doing this test was to determine if chlorine may be released and lost during air sampling of these two compounds.

The methyl-orange test for free chlorine in air from NIOSH method P&CAM 209 was performed. The lower limit of detection of chlorine by this method was 0.05 μg/mL and, for 20 mL that were used, it was 1 μg. Normally, the orange color of the solution turns clear with chlorine. An amount of 3.55 mg of TCCA was placed on a DM-5000 filter in a three-piece cassette. The humidity of the room was checked with a Bendix Psychron (wet and dry bulb) hygrometer that indicated 50% humidity. The air was drawn through the cassette to a bubbler containing 20 mL of methyl orange reagent solution and through a sampling pump operating at 1.7 L/min. The flowrate of the pump was checked every 10 minutes. After four hours and thirty-five minutes, the test was stopped. No color change was observed in the solution; therefore, chlorine was not detected in less than 0.028%, concluding that no sample loss occurred in that sampling interval. To check the validity of the solution, a small particle was taken from the filter, introduced in the bubbler, and the color immediately turned clear.

The sampling test was repeated with NaDCC. A 4.26 mg amount was tested with a fresh reagent. After four hours and forty-five minutes of sampling no color change was noted. The reagent did turn color after a small particle was introduced in the bubbler. Again, the conclusion was that no sample loss occurred during the sampling period.

Method Development. Solid state specific ion electrodes for chlorine and chloride were investigated and both showed interferences from iodide ions. Since no other techniques were available, we decided to modify the iodometric method for smaller samples. Samples of 2 mg were titrated using the visible end-point change from very faint blue to clear. The detection of the visible end-point was very difficult to determine, and precision results of replicate standards were very poor. A 5-mL microburette was used for small additions, but that did not really improve the precision of end-point detection. It was decided to determine the end-point potentiometrically; and thus we employed two platinum electrodes connected to a digital pH meter with millivolt readout, providing 10 microamperes constant current to the electrodes. The precision of detecting the end-point for titrated standards did improve. The starch indicating solution

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that gave the faint blue color was eliminated from that point on, since the visible end-point was not needed. Without the starch indicator, the samples had a faint yellow color (from the iodine) which turned clear at the end-point. The problem of poor precision at the levels - less than one milligram - still existed. Also, potassium iodide in different amounts may have contributed in the imprecision, but standards prepared purposely with different amounts of potassium iodide and then titrated did not show any significant difference in the precision.

The solution to the problem was discovered when a titrated sample (clear solution) was left on the bench and, after a period, it started changing back to a faint yellow color. We hypothesized that air oxidation may have caused that effect and, consequently, air may have interfered with analysis. Standard samples prepared and purposely delayed during the analysis showed that end-point volumes were larger, indicating that some of the iodide ions turned into free-iodine by air oxidation which, in turn, required more thiosulfate for titration and, therefore, larger end-point volume. The following chemical equations obtained from the literature (8) show what happens before, during, and after titration. The reaction of a chlorinated isocyanuric acid compound with potassium iodide in acidic pH is:

$$OCl^- + 2I^- + 2H^+ \longrightarrow Cl^- + I_2 + H_2O$$

Because of excess potassium iodide in solution, the iodine turns into the triiodide form:

$$I_2 + I^- \rightleftharpoons I_3^-$$

During titration, still in acidic pH, the triiodide ion is reacted with sodium thiosulfate to form iodide ion:

$$I_3^- + 2S_2O_3^{=} \rightleftharpoons 3I^- + S_4O_6^{=}$$

After titration is completed or even during a titration without a nitrogen purge oxidation does occur and the iodide ion goes back to form free iodine (I_3^-):

$$6I^- + O_2 + 4H^+ \rightleftharpoons 2I_3^- + 2H_2O$$

Therefore, it was decided that a nitrogen purge be used during titration and the distilled water to be deoxygenated before use. Consequent experiments that were performed with either NaDCC and TCCA indicated that precision did improve at all levels of concentration.

Calibration Curves. After many experiments the procedure was optimized and the final version is described in (9) and in the "experimental" section in this paper. The NaDCC calibration curve

was determined from 34 standards ranging from 0.128 to 2.05 mg, indicating a pooled relative standard deviation of 4.5%. Table I contains the statistical analysis of the calibration curve data for NaDCC. Figure 1 depicts the calibration curve graph for NaDCC. A typical end-point titration graph at the 2.05 mg NaDCC level using constant current amperometry is shown in Figure 2.

TABLE I

Statistical Analysis of NaDCC Calibration Curve Data

Number of Samples	Concentration Level (mg)	Relative Standard Deviation (%)
9	2.05	4.56
7	1.02	2.90
6	0.51	4.72
6	0.256	2.22
6	0.128	6.70

Y-Intercept = -0.024 ± 0.08 at 95% Confidence Limits
Slope = 2.62 ± 0.07 at 95% Confidence Limits
Linear Correlation Coefficient = 0.9992

Since all the method development was performed with NaDCC, the established procedure was applied to TCCA. The calibration curve was determined from 19 TCCA standards ranging from 0.116 to 2.09 mg, indicating a pooled relative standard deviation of 3.9%. Table II shows the statistical analysis of the calibration curve data for TCCA. Figure 3 depicts the calibration curve graph for TCCA.

TABLE II

Statistical Analysis of TCCA Calibration Curve Data

Number of Samples	Concentration Level (mg)	Relative Standard Deviation (%)
6	2.09	1.25
6	0.93	2.22
7	0.116	5.10

Y-Intercept = 0.234 ± 0.072 at 95% Confidence Limits
Slope = 4.62 ± 0.05
Linear Correlation Coefficient = 0.9997

Recovery Study. Recovery of NaDCC from DM-5000 filters was performed according to the "recovery" procedure described in this paper. Table III contains the recovery data and variance results for each NaDCC concentration level.

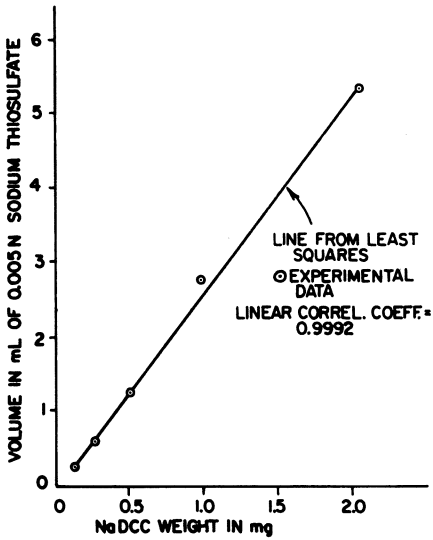

Figure 1. Sodium dichloroisocyanurate dihydrate calibration curve

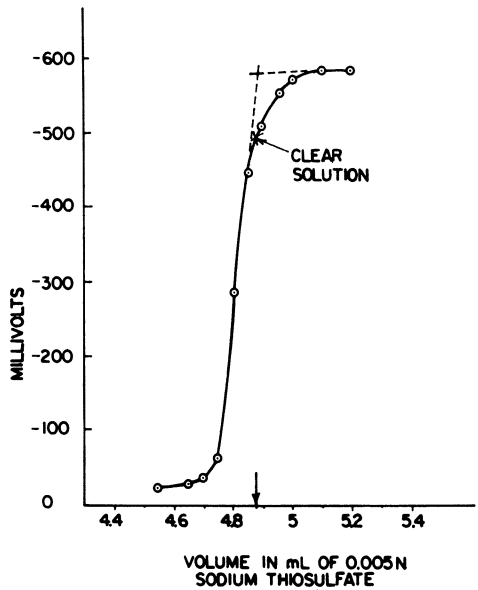

Figure 2. A typical constant-current amperometric titration of 2.05 mg sodium dichloroisocyanurate dihydrate

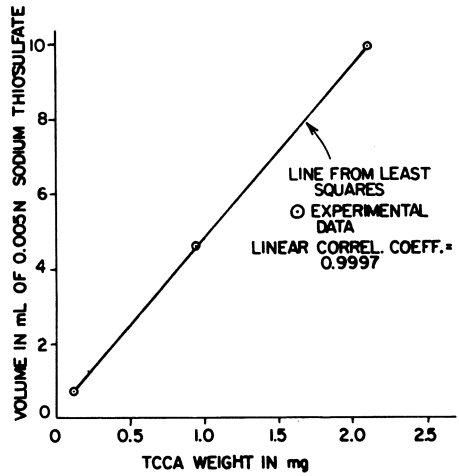

Figure 3. Trichloroisocyanuric acid calibration curve

TABLE III

NaDCC Recovery Efficiency From DM-5000 Filters

Number of Samples	Amount Spiked (mg)	Average Amount Recovered (mg)	Average Recovery (%)	Relative Standard Deviation
5	2.00	1.96	98.0	1.89
6	1.00	1.06	106.0	1.97
5	0.50	0.49	98.0	3.44
6	0.25	0.232	92.8	5.34
6	0.13	0.131	100.8	4.01

Average Recovery = 99.1%
Pooled Relative Standard Deviation = 3.63%

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TABLE IV

Sodium Dichloroisocyanurate Dihydrate Field Sample Results

Sample Number	Job Classification	Air Volume Liters	NaDCC Respirable Dust mg/Filter	NaDCC Respirable Dust mg/m^3	NaDCC Total Dust mg/Filter	NaDCC Total Dust mg/m^3
01, 02	Patrol Operator	433	28.3	65.4	288.8	528.4
03, 04	Patrol Operator	448	0.02	0.04	92.5	206.5
05, 06	Patrol Operator	51	5.81	113.9	68.6	1345.1
07, 08	Patrol Operator	544	0.02	0.04	0.54	0.99
09, 10	Patrol Operator	680	0.20	0.29	14.2	20.9
11, 12	Maintenance	340	0.02	0.06	1.04	3.06
13, 14	Maintenance	340	0.02	0.06	0.88	2.60
15, 16	Maintenance	76	0.02	0.26	1.90	24.8

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Field Samples. Field samples were collected using DM-5000 filters. The two producing plants for NaDCC and TCCA were located in two different areas of the same manufacturing facility; therefore, we anticipated no interferences from either process. Results showing the respirable fraction and total dust for different employees in the two processes are included in Tables IV and V. Extracts of samples with filter loadings higher than 2 mg were diluted and then were titrated.

TABLE V

Trichloroisocyanuric Acid Field Sample Results

Sample Number	Job Classification	Air Volume Liters	TCCA Respirable Dust mg/Filter	TCCA Respirable Dust mg/m^3	TCCA Total Dust mg/Filter	TCCA Total Dust mg/m^3
20,21	Patrol Operator	656	0.02	0.03	0.02	0.03
22,23	Patrol Operator	471	0.02	0.04	0.02	0.04
24,25	Patrol Operator	34	0.02	0.59	14.51	426.8

Conclusions. A sampling and analytical method for two chlorinated isocyanuric acids, NaDCC and TCCA, in air has been described. Briefly, these acids can be collected from air with DM-5000 (PVC copolymer) filters. The filter samples are extracted with water and titrated against sodium thiosulfate using constant-current potentiometry. The titration method will neither separate or distinguish NaDCC in the presence of TCCA or the reverse. The identity of either compound must be known in the workplace environment along with the identities of any other interfering

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substances, i.e., compounds containing chlorine in a positive oxidation state. Concentration results for a compound will be valid only when there are no interferences; otherwise the results will be a combined result of the concentrations of all the compounds containing positive chlorine. Calibration curves in the range of 0.1 to 2 mg of NaDCC or TCCA indicated good linearity (r = 0.999 minimum). Recovery study of NaDCC from filters indicated that NaDCC can be extracted with 99.1% efficiency and 3.6% precision. Experimental results indicate that this method may be used for the analysis of other compounds containing halogens in a positive oxidation state, i.e., hypochlorites, chloramines and chlorinated isocyanuric acids and their salts.

Acknowledgements

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