Column

Task1a TOX Data

TOX recovery test on model compounds

The first portion of task 1 involves in the analysis of known solutions of chlorine, bromine and iodine containing HAAs, THMs and others (e.g., halogenated nitrogenous compounds). Table 1 summarized all of the work done on the TOX recovery test on the model compounds. This part of the work was done using the Euroglas analyzer and the standard carbon columns supplied by CPI.

The TOX of first column and the sum of the two columns of each compound are also shown in Figures1-8. From Table 1 and Figures 1-8, the recoveries of TOX of THMs are 84-87% for chloroform, 85-92% for dibromochloromethane and 95-100% for bromoform. The recoveries of HAAs are 41-60% for chloroacetic acid, 60-76% for bromoaceitc acid, 78-87% for dichloroacetic acid, 90-100% for dibromoacetic acid and 86-96% for trichloroacetic acid. The TOX recovery test of the model compounds shows a general trend that the recovery rate increases with decreasing concentrations, but the increases vary with different compounds. Another phenomenon that we observed from the TOX recovery test is that some HAAs, especially chloroacetic acid, bromoaceitc acid and dichloroacetic acid, can be washed out by nitrate washing solution. This can be seen by comparing the TOX of the first and second columns (Figures 4-8).

The procedure used in these TOX recovery tests is as following:
Pass 50 ml standard solutions through 2 carbon columns; Wash columns with 30 ml Euroglas nitrate washing solution, then measure TOX by Euroglas analyzer.

Preliminary test on IC analysis was done by collecting off-gas from combustion. 50 ml 300 μgCl/L chloroform standard was passed through 2 carbon columns and put into the combustion tube of Euroglas. Off-gas was collected by a beaker with 50 ml water. The sample was analyzed by IC after 10 min collection. The result of TOBr is 303.5 μgCl/L. So a 100 percent recovery can be obtained for chloroform by Euroglas TOX and IC analysis.

Table 1: TOX standards testing results by Euroglas analyzer

Name	Molecular Formula	Standard (μg Cl/L)	TOX (μg Cl/L)			
			1st Column	2nd Column	Concentration	Recovery
Trihalomethanes (THMs)						
Chloroform	$CHCl_3$	349.7	272.4	27.1	299.5	85.6%
		235.3	188.2	8.3	196.5	83.5%
		88.4	72.7	3.8	76.5	86.5%
Dibromochloromethane	$CHClBr_2$	500	414.2	9.5	423.7	84.7%
		300	272.7	4.1	276.8	92.3%
		100	84.7	4.9	89.6	89.6%
Bromoform	$CHBr_3$	500	465.8	7.1	472.9	94.6%
		300	283.1	3.0	286.1	95.4%
		100	98.3	2.3	100.6	100.6%
Monohaloacetic Acids (MHAA)						
Chloroacetic Acid	$CH_2ClCOOH$	500	72.2	132.3	204.5	40.9%
		300	46.6	95.8	142.4	47.5%
		100	26.0	34.2	60.2	60.2%
Bromoacetic Acid	$CH_2BrCOOH$	500	179.6	130.7	310.3	62.1%
		300	91.0	134.7	225.7	75.2%
		100	42.2	33.4	75.6	75.6%
Dihaloacetic Acids (DHAA)						
Dichloroacetic Acid	$CHCl_2COOH$	500	195.4	202.7	398.1	79.6%
		300	109.3	123.6	232.9	77.6%
		100	48.4	38.2	86.6	86.6%
Dibromoacetic Acid	$CHBr_2COOH$	500	423.7	44.9	468.6	93.7%
		300	251.4	19.8	271.2	90.4%
		100	100.2	3.3	103.5	103.5%
Trihaloacetic Acids (THAA)						
Trichloroacetic Acid	CCl_3COOH	500	386.5	43.3	429.8	86.0%
		300	266.8	20.7	287.5	95.8%
		100	86.6	5.1	91.8	91.8%

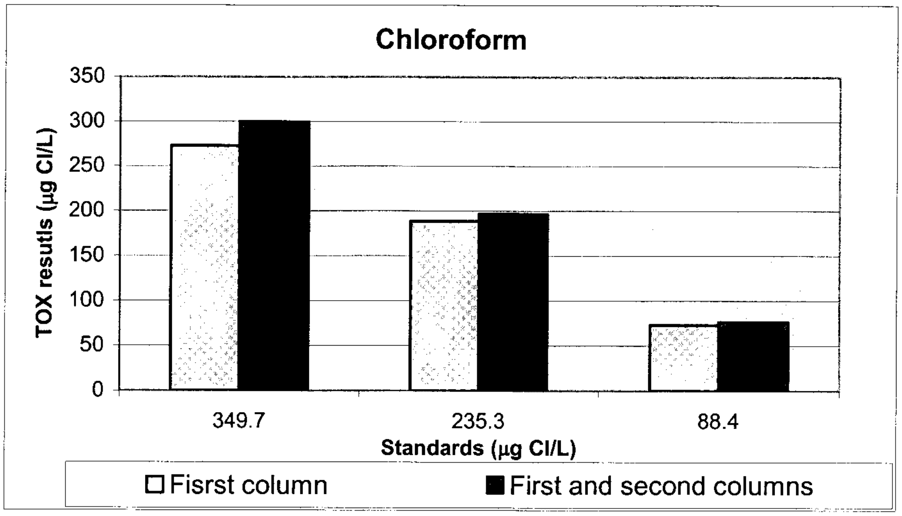


Figure 1: Chloroform standards testing results

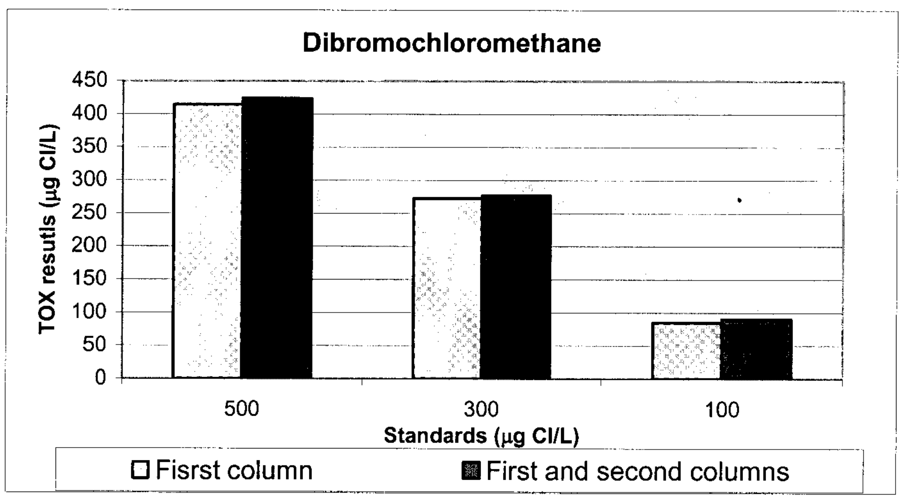


Figure 2: Dibromochloromethane standards testing results

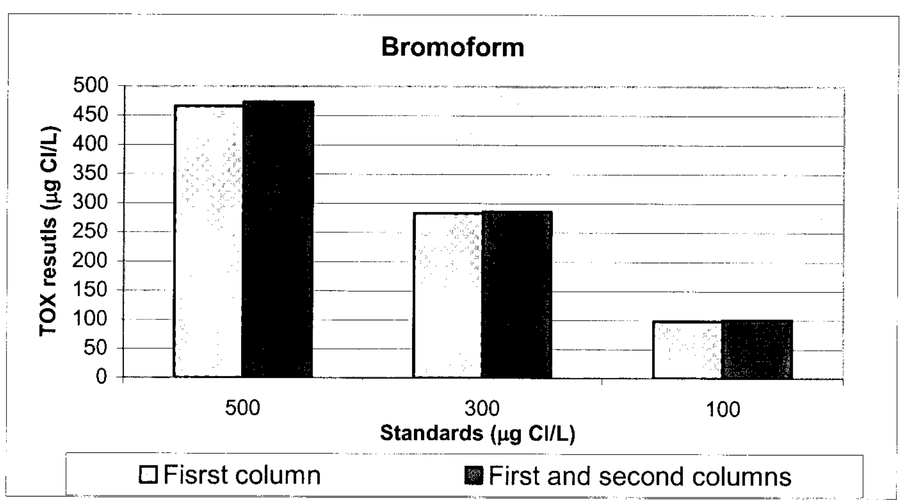


Figure 3: Bromoform standards testing results

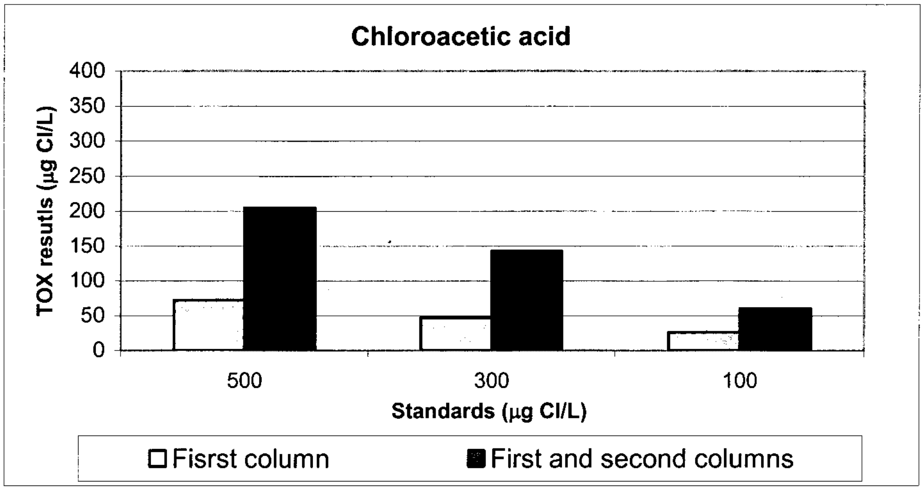


Figure 4: Chloroacetic acid standards testing results

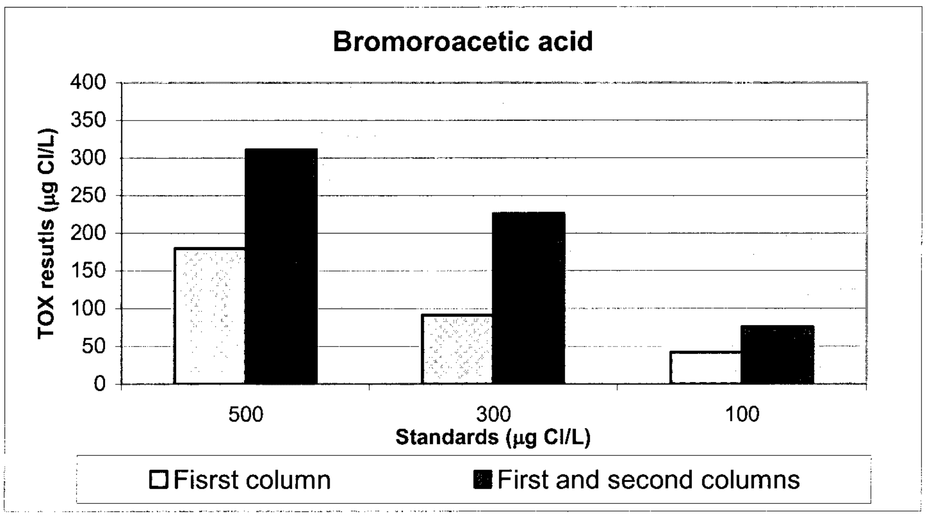


Figure 5: Bromoacetic acid standards testing results

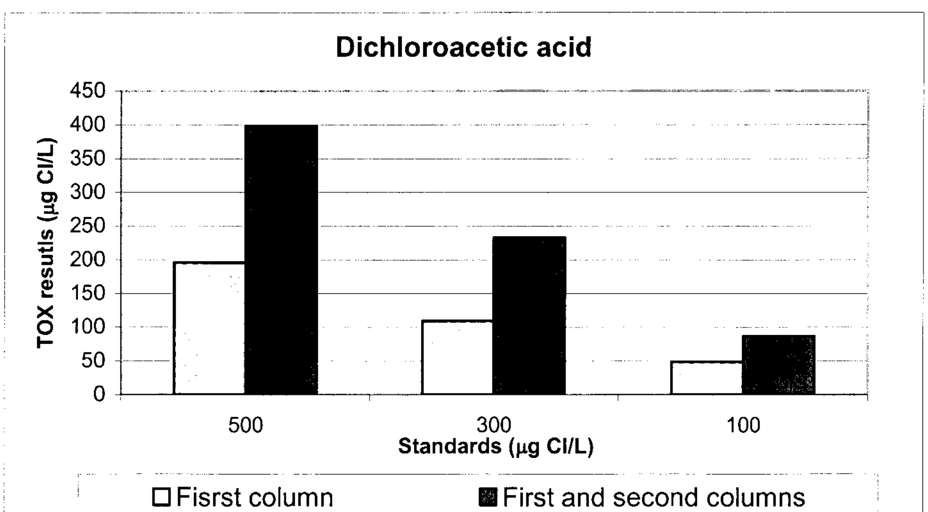


Figure 6: Dichloroacetic acid standards testing results

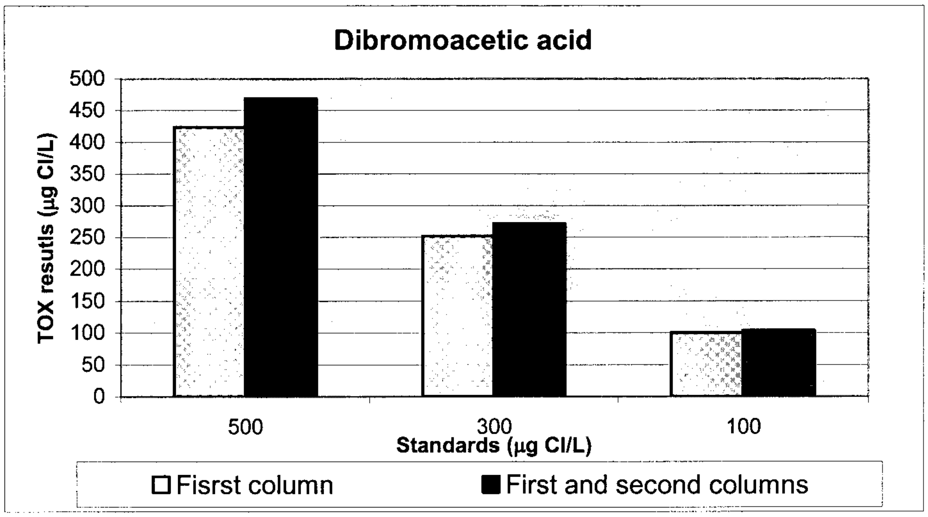


Figure 7: Dibromoacetic acid standards testing results

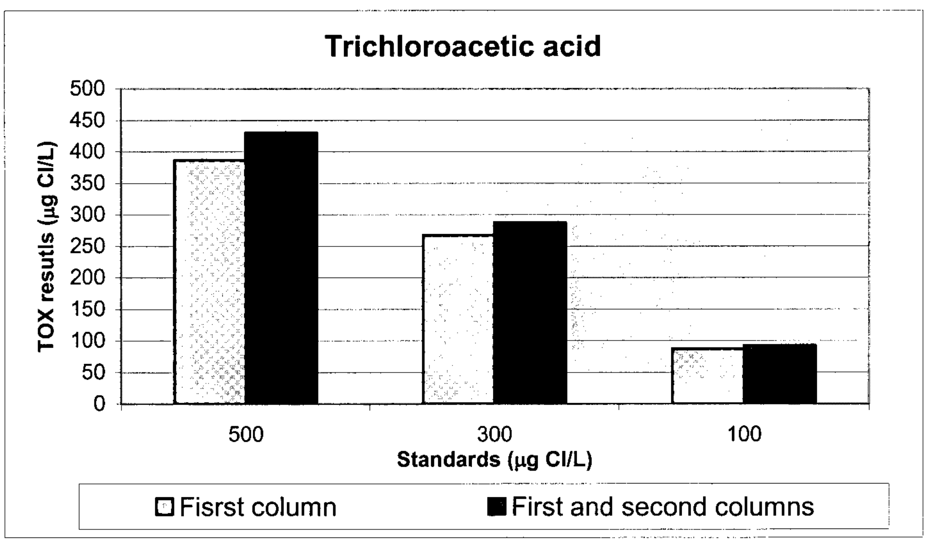


Figure 8: Tibromoacetic acid standards testing results

Some raw water and disinfected water results

Some raw waters and treated waters were collected for the analysis of TOX and other parameters. The results are shown in Tables 2 and 3.

Table 2: Water samples from Binghampton, NY

Sample	pH	UV_{254}(Filtered)	TOC (mg/L)	DOC (mg/L)	TOX (µg Cl/L)
Raw water	6.96	7.15E-2	2.94	2.42	12.5
Filtered water	6.57	2.96E-2	1.79	1.42	12.4
Finished water (Clearwell)	6.51	2.43E-2	2.20	1.64	146.7
Distribution system water (Espail Reservoir)	6.79	3.19E-2	2.29	1.98	267.6
Finished water (Clearwell) Quenched	6.45	2.15E-2	1.74	1.52	70.4
Distribution system water (Espail Reservoir) Quenched	6.44	2.49E-2	1.68	1.44	179.0

Table 3: Water samples from Gardner and North Brookfield, MA

Sample	TTHM (µg/L)	HAA6 (µg/L)	TOX (µg Cl/L)
Gardner treated water	44	32	284.8
North Brookfield treated water	38	30	162.1

Impact of nitrate washing volume and Cl^- concentrations on TOX measurement

From the TOX recovery test of model compounds, it is observed that some HAAs can be washed out by nitrate solution. Further tests were conducted to evaluate the possibility of improving the recovery of TOX by reducing the nitrate washing volume. The impact of the inorganic chloride on TOX measurement was also studied.

The nitrate washing solutions of different methods are shown as below. It can be seen that the three methods are quite different as far as nitrate washing solution is concerned.

Euroglas

(1) Stock Nitrate Solution: Weigh out 17 g of $NaNO_3$, Transfer it to a 1000 ml measuring flask and add 1.4 ml nitric acid (HNO_3) 65%, top up the solution to 1000 ml.
(2) Nitrate Washing Solution: Pour 100 ml of the stock nitrate solution into a 1000 ml measuring flask and fill to 1000 ml.
(3) Wash microcolumns with 25 ml nitrate washing solution at a rate of 3 ml/min for 100 ml sample. This equals to 31.0 mg NO_3^-/sample.

Dohrmann

(1) A 5000 ppm nitrate solution is prepared by dissolving 8.2 gm of reagent grade KNO_3 in 1 liter of reagent water.
(2) Washing microcolumns with 2 ml nitrate washing solution at a rate of 0.5 ml/min for 100 ml sample. This equals to 10 mg NO_3^-/sample.

Standard Method

(1) Dilute 8.2 g KNO_3 to 1000 ml with reagent water. Adjust to pH 2 with HNO_3. 1L = 5000 mg NO_3^-.
(2) Pass 2 to 5 mL NO_3^- solution through columns at a rate of approximately 1 mL/min. This equals to 10 mg to 25 mg NO_3^-/sample.

Test on dichloroacetic acid recovery with different Euroglas nitrate washing volumes was conducted and the results are shown in Table 2. From Table 2, the recovery of DCAA increases form 78% to 95% when reducing the nitrate washing volume from 30 ml to 13 ml. By comparing the TOX of the first and second columns, it is clear that the problem of washing out is greatly improved by reducing the nitrate washing volume.

Table 4: Test on DCAA recovery with different Euroglas nitrate washing volumes

Standards	Washing Volume	Nitrate	First Column (μg Cl/L)	Second Column (μg Cl/L)	Concentration (μg Cl/L)	Recovery
DCAA 300μg Cl/L	30 mL	37.3 mg NO_3^- /sample	107.5	125.4	232.9	77.6%
DCAA 300μg Cl/L	25 mL	31.0 mg NO_3^- /sample	141.4	112.2	253.6	84.5 %
DCAA 300μg Cl/L	13 mL	16.1 mg NO_3^- /sample	207.6	76.9	284.5	94.8%

The purpose of the nitrate wash is to remove the inorganic chloride from the carbon columns thus remove the interference of inorganic chloride on TOX measurement. From the test mentioned above, reducing the nitrate washing volume can improve the DCAA recovery. But the reduced nitrate washing volume must satisfy the requirement of the removal of inorganic chloride to guarantee the proper TOX measurement. Tests were conducted to evaluate the impact of varying chloride concentrations and nitrate volumes on TOX measurement.

Protocol: Make chloride solutions with different concentrations, pass 100 ml of each solution through 2 carbon columns, then wash the columns with different nitrate washing volumes, measure TOX of columns by Euroglas analyzer.

Solutions:

(1) Nitrate washing solution: Dissolve 1.63g KNO_3 into 1000 ml deionized water, adjust pH to 2 by HNO_3 acid. 1L = 1000 mg NO_3.

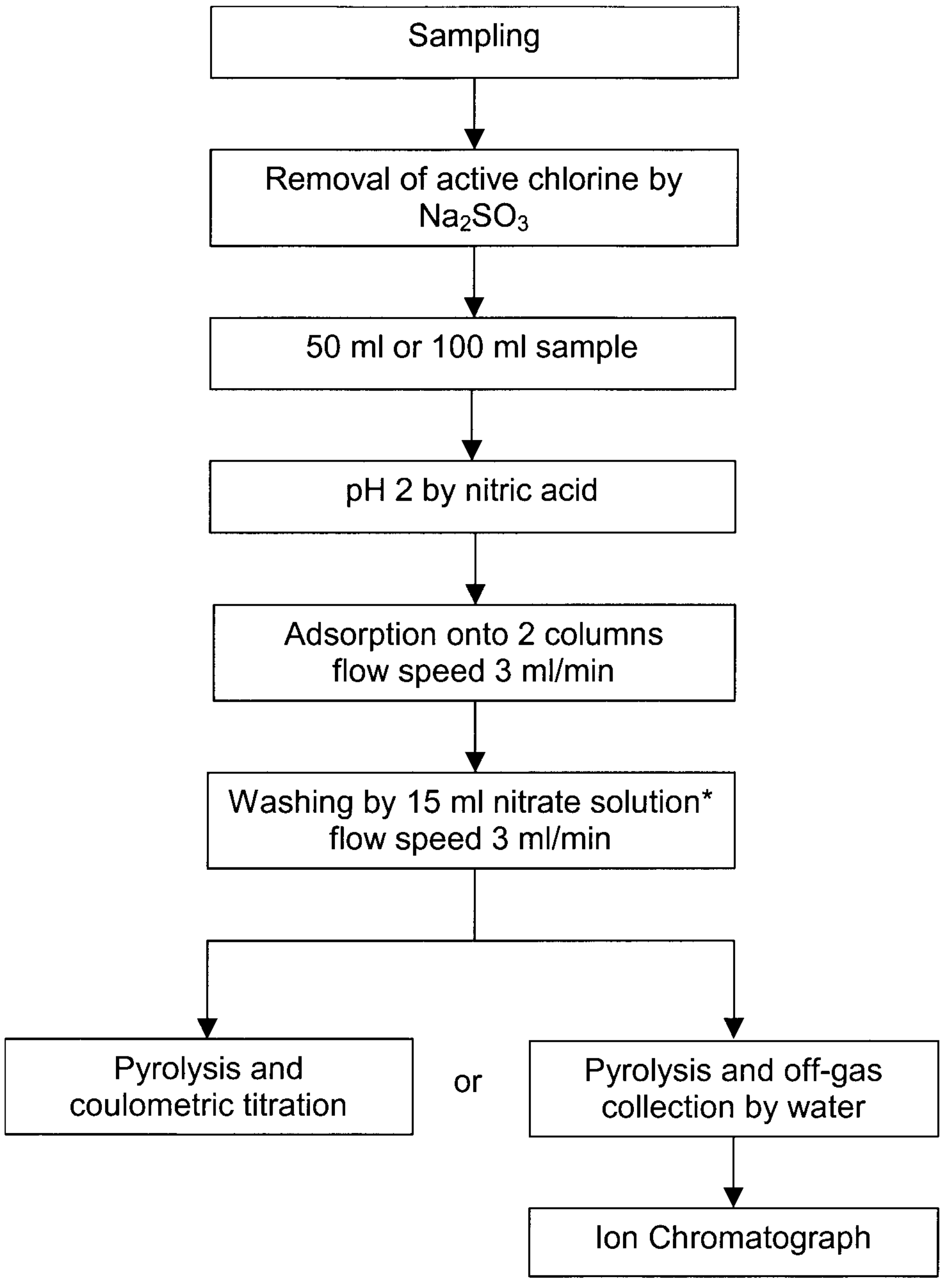
(2) Chloride solutions: 0.5, 1.0 and 2.0 g Cl/L, adjust pH to 2 by HNO_3 acid

Table 5: Impact of varying chloride concentrations and nitrate volumes on TOX

Cl^- (g/L)	Nitrate washing volume (ml)	First column (μg Cl/L)	Second column (μg Cl/L)	Total (μg Cl/L)
blank	15	5.3	5.7	11.0
0.5	10	6.0	4.8	10.8
0.5	15	5.4	5.6	11.0
1.0	10	7.6	5.8	13.4
1.0	15	6.4	5.3	11.7
1.0	20	6.7	4.6	11.3
2.0	15	8.9	8.3	17.2
2.0	20	6.1	8.0	14.0

Table 3 summarized the results of the test on the impact of varying chloride concentrations and nitrate washing volumes on TOX. For 0.5 g Cl/L solution, The TOX of both 10 and 15 ml nitrate washing volumes are nearly equal to blank value. For 1.0 g Cl/L solution, The TOX increases by 2.4 μg Cl/L compared to blank value when 10 ml nitrate washing volume is used. However, the TOX is very close to blank value when 15 or 20 ml nitrate washing volume are used. For 2.0 g Cl/L solution, TOX increases by 3 μg Cl/L and 6.2 μg Cl/L for 20 and 15 ml nitrate washing volume respectively. From this test, it is concluded that 15 ml of 1000 mg NO_3^-/L washing solution is enough to remove the inorganic chloride from the carbon columns for 1 g Cl/L solution. It is determined to use 15 ml of 1000 mg NO_3^-/L washing solution for TOX analysis. In case water samples contain more than 1 g Cl/L inorganic chloride, dilution is recommended.

TOX Analysis Procedure



* Nitrate washing solution: Dissolve 1.63g KNO_3 into 1000 ml deionized water, adjust pH to 2 by HNO_3 acid. 1L = 1000 mg NO_3.

To: <reckhow@ecs.umass.edu>
Subject: TOX Task1a data
Date: Mon, 21 Apr 2003 16:53:20 -0000
From: <ghua@ecs.umass.edu>
X-Mailer: TWIG 2.7.4
X-Client-IP: 128.119.87.252
X-Scanned-By: MIMEDefang 2.1 (www dot roaringpenguin dot com slash mimedefang)

Dr. Reckhow:

This is my final version of Task1a data. I suppose the Gardner and North Brookfield waters are from MA. If not, please change the title of Table 3.

Please write to me, if any questions.

Guanghui

Task1a Data(column)1.doc

To: <reckhow@ecs.umass.edu>
Subject: TOX report
Date: Mon, 14 Apr 2003 16:57:33 -0000
From: <ghua@ecs.umass.edu>
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Dr. Reckhow:

I just found an error in my Task1a TOX report. In page #8, third line: 20 and 10 ml nitrate washing solution. 10 should be 15. If you haven't submited it, please make the correction. I am sorry about this. I have the data for Bringhamton water anb the waters you collected several weeks ago. If you think we can add them into this report, I will email you.

Guanghui