AN EVALUATION OF THE DETERMINATION OF TOTAL ORGANIC CHLORINE (TOCl) IN WATER BY ADSORPTION ONTO GROUND GRANULAR ACTIVATED CARBON, PYROHYDROLYSIS, AND CHLORIDE-ION MEASUREMENT

by

Ronald C. Dressman
Earl F. McFarren
James M. Symons

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WATER SUPPLY RESESEARCH DIVISION
U.S. ENVIRONMENTAL PROTECTION AGENCY
26 W. ST. CLAIR STREET
CINCINNATI, OHIO 45268

An Evaluation of the Determination of Total Organic Chlorine (TOCl) In Water by Adsorption onto Ground Granular Activated Carbon, Pyrohydrolysis, and Chloride-Ion Measurement

Ronald C. Dressman, Earl F. McFarren, James M. Symons
Water Supply Research Division
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

INTRODUCTION

Total organic chlorine (TOCl) is a group parameter that is intended to be a measure of the chlorinated organics present in water. Because chlorinated organics are not naturally occurring, and because many chlorinated organics are known to be seriously detrimental to the health of the water consumer, a TOCl measurement has been suggested as an extremely useful indicator of water quality.

The first serious attempts to measure TOCl on a routine basis as an indication of water quality was done on the Rhine River. Kuhn, Fuchs, and Sontheimer[1,2] collaborated at the Engler-Bunte Institute in Karlsruhe, Federal Republic of Germany to develop a "pyrohydrolysis" technique for the determination of the total organic chlorine value of compounds adsorbed onto activated carbon.

Their initial work was directed at a method for determining the TOCl concentration adsorbed onto samples of granular activated carbon (GAC) taken from full-scale activated carbon beds or sampler units. The principal goal at that time was to evaluate or characterize the efficiency and life of the GAC beds being used in the water treatment process to remove organic contaminants, although the sampling system was used in an attempt to determine TOCl concentrations in water.

Later, the granular-activated-carbon-sample method was modified for the analysis of water samples for concentration of TOCl (unpublished). For this determination granular activated carbon ground to produce a finely divided activated carbon (GGAC) is used to adsorb organo-chlorine compounds from discrete water grab samples. The actual method of pyrohydrolysis of the carbon is the same for both procedures.

GENERAL METHOD DESCRIPTION

Concentration

The concentration of organochlorine compounds onto the ground granular activated carbon is accomplished by adding one gram of Filtrasorb 400* (or its equivalent), ground 90 seconds in a laboratory mill and wetted with Super-Q water for 30 min under vacuum, to 10 liters of water. The sample is stirred for one hour and then the carbon is flocculated by the addition of 50 mℓ of aluminum sulfate solution (conc. 1 gm Al/ℓ) and 20 mℓ of a polyacrylamide floc aide (magnifloc 985 N, Cyanamid - conc 200 mg/ℓ). Before the addition of the floc aide, pH is adjusted within the range of 6.5 to 7.5 with 5 N sodium hydroxide. After settling, the carbon sludge is recovered on a 47 mm diameter 8 μm pore size cellulose acetate membrane filter (Millipore) and transferred to a quartz boat for pyrohydrolysis. This procedure is performed twice on each sample.

Pyrohydrolysis

Pyrohydrolysis is accomplished by combusting the carbon and its charge of adsorbed compounds in the presence of steam and oxygen, and condensing the steam containing the combustion product, HCl, for later measurement of its chloride ion concentration.

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*Mention of trade names does not consititute endorsement by the U.S. Environmental Protection Agency.

The carbon sample is placed in a quartz boat and inserted into the first of a series of two pyrohydrolysis furnaces (Figure 1). The furnace into which the sample is placed has an initial temperature of less than 100°C. The second furnace is maintained at 1,000°C. They are served by a common, quartz pyrolysis tube that contains a plug of quartz wool in the zone of the 1,000°C furnace. A flow of oxygen and steam is passed through the pyrolysis tube at a rate of 200 mℓ/min O_2 and a condensation rate of about 0.8 mℓ water per minute. At the same time the first furnace is heated to reach 700°C within 15 to 20 minutes.

In the first furnace the organic compounds are volatilized and the carbon eventually reduced to an ash. As the volatilized organochlorine compounds pass through the second furnace, set at 1,000°C, they are combusted to HCl. This combustion in the presence of the steam is termed pyrohydrolysis. The process takes about one hour, in which time about 50 mℓ of pyrohydrolyzate is collected in a beaker.

The oxygen, of course, provides for the oxidative pyrolysis of the organic compounds to produce the HCl, and at the same time serves as a sweep gas. The steam aids in preventing Cl^- from being adsorbed on the walls of the system, and is also the solvent in which Cl^- is solubilized for subsequent detection and measurement. Measurement can be by bench titration, use of a select, chloride-ion probe, or microcoulometry, choice to be discussed later.

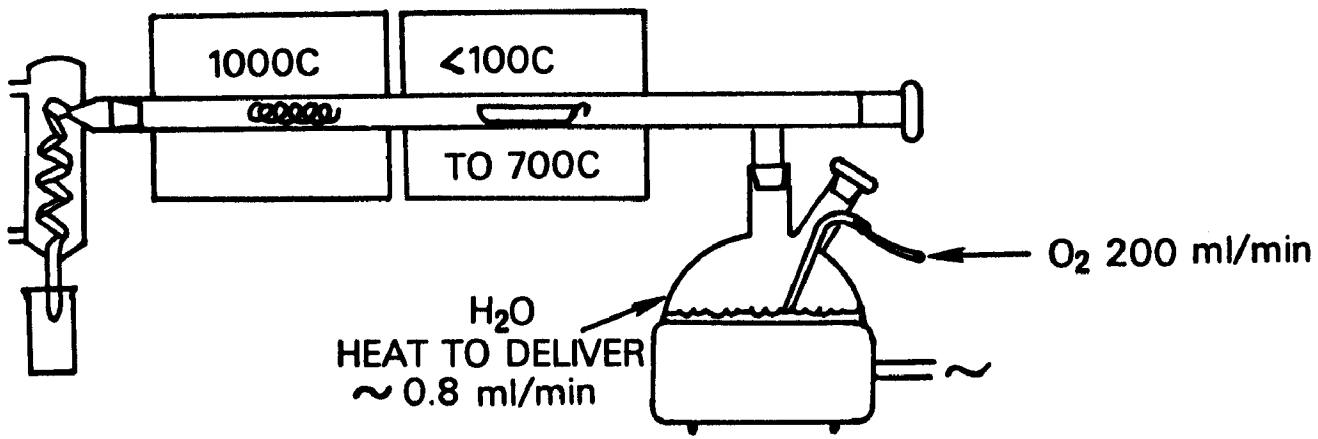


FIGURE 1: SCHEMATIC OF PYROHYDROLYSIS SYSTEM

Inorganic Chloride Interference

Whether the activated carbon has been taken from an operating filtration system or recovered from a water sample, inorganic Cl^- is adsorbed on the carbon. For water grab samples, the amount of inorganic ion adsorbed onto the carbon varies with the concentration of the ion in the water. According to data published by Kuhn et al.[1] at concentrations of 50, 100, 400 and 1,000 mg/ℓ, Filtrasorb 400 will adsorb the following amounts of Cl^- respectively in mg per gm of activated carbon: 0.65, 1.03, 1.69 and 1.85.

Accounting for this contribution of Cl^- from the inorganic source is very important, especially when the ratio of organic Cl^- to inorganic Cl^- does not overwhelmingly favor the organic contribution, as is usually the case. Kuhn et al. make this correction on water grab samples by extracting a duplicate water sample. Instead of pyrohydrolyzing the carbon sludge recovered from the duplicate sample, it is in turn extracted with 200 mℓ of 0.1 N $NaNO_3$ solution for at least 6 hours. Nitrate ion displaces the Cl^- adsorbed onto the carbon, and the displaced Cl^- is then measured in the nitrate solution and subtracted from the value obtained by the original pyrohydrolysis This procedure of measuring and subtracting the nitrate-displaced inorganic Cl^- is referred to as the "difference" method. A second procedure that involves the pyrohydrolysis of the carbon from which the inorganic Cl^- has been displaced or excluded will be discussed as an alternative to the "difference" measurement, and is referred to as the "direct" measurement of TOCl.

For carbon taken from operating filter beds or sampler units containing carbon, it is necessary to dry and split the carbon sample to provide equal portions for a pyrohydrolysis determination and a nitrate wash determination.

Calculation of TOCl

For water grab samples, TOCl is calculated using the following equation:

$$(1)\quad \left(\frac{C\ mg}{\ell} \cdot \frac{1000\ \mu g}{mg}\right)\left(\frac{V_2\ m\ell}{1000\ m\ell}\right)\left(\frac{\ell}{V_1\ \ell}\right) = \frac{C\ V_2\ \mu g}{V_1\ \ell} = \mu g/\ell TOCl$$

where C = concentration of Cl^- in pyrohydrolyzate (mg/ℓ)

V_1 = volume of water sample (ℓ)

V_2 = volume of pyrohydrolyzate (mℓ)

METHOD EVALUATION

An evaluation of the method has been undertaken to determine if it can indeed produce a valid measure of total organic chlorine. This paper will describe the specific details of that evaluation as it concerns itself with four main points, namely:

1. The completeness of the adsorption of organochlorine compounds.
2. The qualitative and quantitative accuracy of chloride ion measurement in the pyrohydrolyzate.
3. The influence of inorganic chloride ion on the measurement.
4. The limits of precision, accuracy and sensitivity of the method.

Because the validity of the total organic chlorine measurements taken on clarified river water during the evaluation was undefined during this study, all measurements are referred to as apparent total organic chlorine ("TOCl"). All raw water was flocculated and settled

because the question remains unresolved at present whether or not the presence of suspended solids will bias the results by the combustion of those solids recovered with the activated carbon sludge. Certain modifications in the procedure will also be discussed.

Completeness of Adsorption of Organics

Information acquired to define the extent to which organics are adsorbed during the extraction process included Total Organic Carbon (TOC) measurements taken on two water samples before, between, and after two successive extractions. The extractions were performed with one gram of carbon on 10 liters of river water that had first been flocculated and settled to remove suspended solids. In this case no organic floc aide was used in any of the flocculation steps. 250 mℓ of supernatant liquor from each extraction step was passed through a separate 8 μm Millipore cellulose acetate filter. 70-mℓ aliquots of the 250 mℓ of filtered supernate liquor were taken in septa-sealed bottles for TOC analysis. The three results were then averaged.

The filter membranes were washed before and after with three successive washings of 250 mℓ of Super-Q water which was analyzed for TOC in the same manner. The TOC concentration value for the Super-Q water was determined and subtracted from the filter wash- water value, which was in turn subtracted from the sample value to obtain the TOC concentration remaining after each extraction. For the first extraction, 88 and 82 percent removal of TOC was accomplished on the duplicate samples, and 62 percent of the remainder was removed by the second extraction. For the two extractions combined, 95 and 93 percent of TOC was adsorbed from the two samples of raw water.

Detector Selection

Two methods of detecting and measuring chloride ion were tried. The first was a select chloride-ion probe(SIP), which is being used routinely by Kuhn et al.[1], and the second was the Dohrmann microcoulometric titration (MCT) system. The SIP appeared to be working well on distilled-water controls, but when raw water samples were analyzed, results were affected by a large and erratic positive bias that rendered the results meaningless.

Table 1 presents tabulated data obtained by difference and direct measurements using both the SIP and MCT system on four clarified river water samples. Results of attempts to remove the interference encountered in the use of the SIP, by treatment with hydrogen peroxide (H_2O_2) and copper sulfate ($CuSO_4$), are also given.

Table 1. "TOCl" in µg/ℓ for Clarified Ohio River Water[a]--Select-Ion Probe Interference

Method	by "Difference"				"Direct"			
Detector	MCT	SIP			MCT	SIP		
Treatment	H_2O_2	None	H_2O_2	$CuSO_4$	H_2O_2	None	H_2O_2	$CuSO_4$
1	25	108	120	26	13	58	42	26
2	27	120	137	53	10	58	44	22
3[b]	36	170	144	46	9	95	72	37
4[b]	32	192	163	52	9	95	71	40

a. Cl^- concentration = 35 mg/ℓ; suspended solids removed by flocculation and sedimentation.
b. 20 µg/ℓ TOCl dosed as PCP subtracted

Two drops of H_2O_2 were added to each 50-mℓ pyrohydrolyzate to remove interference from sulfur[5] by oxidizing it to sulfur dioxide (SO_2). The pyrohydrolyzate was then boiled to drive off excess H_2O_2 that also interferes with the probe. A few grains of $CuSO_4$ were added to eliminate hydrogen sulfide (H_2S) as an interference by precipitating copper sulfide (CuS). As can be seen in Table 1, neither treatment brought the final result down to that obtained by "direct" measurement using the MCT system.

Evidence that interferences were present is borne out by the fact that values can be diminished by chemical treatment designed to eliminate those interferences, and by the fact that they are considerably higher than the MCT measurements both before and after chemical treatment. Because these interferences could not be completely eliminated however, use of the SIP was discontinued and the MCT system was designated as the detector of choice, in spite of the considerable difference in cost. Data presented below to define blank or background levels, precision, accuracy and sensitivity limits, pertain to the method using the MCT system for detection and measurement.

Efficiency of the Pyrohydrolysis System

The efficiency of the condenser is considered to be excellent in view of the quantitative recovery of TOCl dosed into the controls in the form of pentachlorophenol (PCP). Also no chloride ion could be detected in condensate collected after a pyrohydrolysis run, indicating that there was no residual chloride ion left in the system. This was

also borne out by the quantitative recovery of the TOCl dosed into controls in the absence of inorganic chloride ion. Thus, the operation of the pyrohydrolysis system, in particular the condenser section, was not found to measurably affect the precision or accuracy of the method.

Inorganic Chloride-Ion Correction

The accuracy of the method of correcting the final result for inorganic chloride ion by subtracting out the contribution of inorganic chloride ion adsorbed onto the activated carbon, as determined by extracting a duplicate sample and measuring the amount of chloride ion washed off the carbon into a 0.1 N sodium nitrate solution, was carefully investigated.

In a test similar to that performed by Kuhn et al. to verify the displacement of chloride ion by nitrate ion, 200-mℓ aliquots of Super-Q water previously dosed with sodium chloride to contain a chloride ion concentration of 50 mg/ℓ were extracted 24 hours with 2 gms of activated carbon. The carbon was recovered by filtration and stirred for 24 hours in 200 mℓ of a 0.1 N sodium nitrate solution. The carbon was again recovered by filtration and then pyrohydrolyzed to determine if all chloride ion had been eliminated by the nitrate wash.

The chloride ion concentration in the pyrohydrolyzate of the nitrate washed carbon was at approximately the same level as experimentally determined for blank carbon (see below). Under the conditions of the test, therefore, the displacement of chloride ion by nitrate ion was essentially complete.

A second series of tests were run to determine if the displacement of chloride ion was sufficiently reproducible to prove a precise and accurate correction under the conditions of analysis. On two separate occasions six ten-liter Super-Q water samples were dosed to a concentration of 50 mg/ℓ using sodium chloride, and to 20 µg/ℓ total organic chlorine using pentachlorophenol (PCP). Three such samples on each occasion were used to make a pyrohydrolysis determination on the activated carbon, and three were used to obtain an inorganic chloride ion correction by washing the carbon with the nitrate solution. As a check on the value determined by this "difference" method, the nitrate washed carbon was also analyzed to provide what is referred to as a "direct" measurement.

What is reported in Table 2 are the results of obtaining the difference measurement for each set of samples by subtracting the chloride ion contribution determined for each of the three nitrate wash test samples, from each of the three pyrohydrolysis samples. Nine pieces of data were thus generated for each set of three pyrohydrolysis samples analyzed by the "difference" method. The range of values, from -9.5 to 38 in one set and 39 to 54 in the other set, illustrate the variation that can be expected by the difference measurement.

Table 2. TOCl[a] in µg/ℓ by "Difference" Measurement[b] Using Super-Q Distilled Water

Sample Set	Number of Samples	Number of Determinations	Mean µg/ℓ	σ µg/ℓ	Range Limits µg/ℓ
1	3	9	20.5	± 17.09	-95 to 38
2	3	9	47.1	± 4.90	39 to 54

a. 20 µg/ℓ TOCl dosed as PCP
b. 50 mg/ℓ Cl^- dosed as NaCl

As can be seen in Table 2, the "difference" method results exhibit quite poor precision and accuracy, while the direct measurement exhibits (Table 3) excellent precision and accuracy under the conditions of this test. The data for direct measurement also includes four determinations made independently of the above study.

Table 3. TOCl[a] in µg/ℓ by "Direct" Measurement Using Super Q Distilled Water[b]

Sample Set	Number of Determinations	Mean µg/ℓ	σ µg/ℓ	Range Limits µg/ℓ
1	3	19.5	± 0.50	19 to 20
2	3	18.5	± 1.50	17 to 20
3	4	22.6	± 1.18	21 to 23.5
1, 2 & 3	10	20.5	± 2.17	17 to 23.5

a. 20 µg/ℓ TOCl dosed as PCP
b. 50 mg/ℓ Cl^- dosed as NaCl

As expected, the explantion for the lack of precision and accuracy for measurement by difference (Table 2), at least at the low levels of TOCl tested, appears to be that the adsorption of inorganic chloride ion is not sufficiently consistent or reproducible to avoid introducing significant error of a random nature when substracted out by the analysis of a "duplicate" sample. The inconsistency may in part, at least, be due to the fact that duplicates are difficult to obtain with certainty. On the other hand, as shown in Table 3, the displacement of inorganic chloride ion by nitrate ion during washing apparently is essentially complete every time, and at least for the case of PCP, does not remove organic chlorine, thus accounting for the excellent precision and accuracy by direct measurement.

A third series of tests was conducted on raw Ohio river water that was flocculated and settled to remove suspended solids. All of these samples were extracted one time with one gram of activated carbon rather than the recommended two-extraction procedure to save time.

A comparison of data (Table 4) obtained by difference and direct measurements on all 13 samples (including six dosed with 20 to 60 µg/ℓ

Table 4. "TOCl"[a] in µg/ℓ for Ohio River Water[b]
Suspended Solids Removed by Flocculation and Sedimentation

Sample Numbers	By Difference	Direct
1	25	13
2	27	10
3	36[c]	9[c]
4	32[c]	9[c]
5	-1	12
6	2	17
7	2[c]	6[c]
8	17[d]	7[d]
9	4	19
10	-4	13
11	6	12
12	3[c]	10[c]
13	4[d]	15[d]

a - See Table 5 for summary of precision and accuracy
b - Cl^- concentration 35 mg/ℓ
c - 20 µg/ℓ TOCl dosed as PCP subtracted
d - 60 µg/ℓ TOCl dosed as PCP subtracted

TOCl as PCP) shows that, as it had been for distilled water controls, direct measurement provided superior precision and accuracy on these raw water samples. Those samples that were dosed and the dosages are indicated by the footnotes c and d.

Table 5 presents the mean, standard deviation, and range limits of the values for dosed and undosed samples in Table 4 taken separately, and for all samples combined, for both the difference and direct measurements. Although the combined average values are quite similar for the samples by both measurements, the precision of the results by direct measurement is by far the better.

Table 5. Precision and Accuracy by Difference vs. Direct "TOCl" Measurement on Raw Ohio River Water[a]

Number and Type of Samples	Range Limits, µg/ℓ by Diff.	Direct	Mean µg/ℓ by Diff.	Direct	σ, µg/ℓ by Diff.	Direct
4 Dosed[b]	2 to 17	6 to 15	6.5	9.5	± 7.05	± 4.04
5 Undosed	-4 to 6	12 to 19	1.4	14.6	± 3.97	± 3.21
9 Combined[c]	-4 to 17	6 to 19	4.1	12.3	± 5.90	± 4.30
13 Combined[d]	-4 to 36	6 to 19	11.8	11.7	±13.74	± 3.77

a - Cl^- concentration 35 mg/ℓ
b - 20 to 60 µg/ℓ TOCl dosed as PCP subtracted
c - pyrohydrolyzate untreated chemically
d - includes pyrohydrolyzates chemically treated

The values for "TOCl" by direct measurement after subtracting the dose are for all practical purposes the same as those obtained on undosed samples. Thus for PCP at least, TOCl remains undiminished by the nitrate wash, and adsorption onto the activated carbon was essentially complete, even for one extraction, rather than the recommended two.

Aside from providing better precision and accuracy, direct measurement provides another benefit. In terms of sample treatment, the net effect of making a direct measurement of TOCl on nitrate-washed carbon is to halve the amount of work that needs to be done. Two successive extractions on one ten-liter sample would be all that is required. The duplicate sample to obtain the inorganic chloride-ion correction is eliminated. This not only represents a great savings in time, but also eases the logistics of sampling.

Background Values.

The activated carbon used for extraction was pyrohydrolyzed in 2 gm amounts to simulate the quantity required for a two step extraction, and the pyrohydrolyzate analyzed for its Cl concentration by direct injection of 5 µℓ of the pyrohydrolyzate into a microcoulometric titration cell. The blank contribution could not be lowered by washing the carbon for 5 days with "Super-Q" water in a continuous extractor.

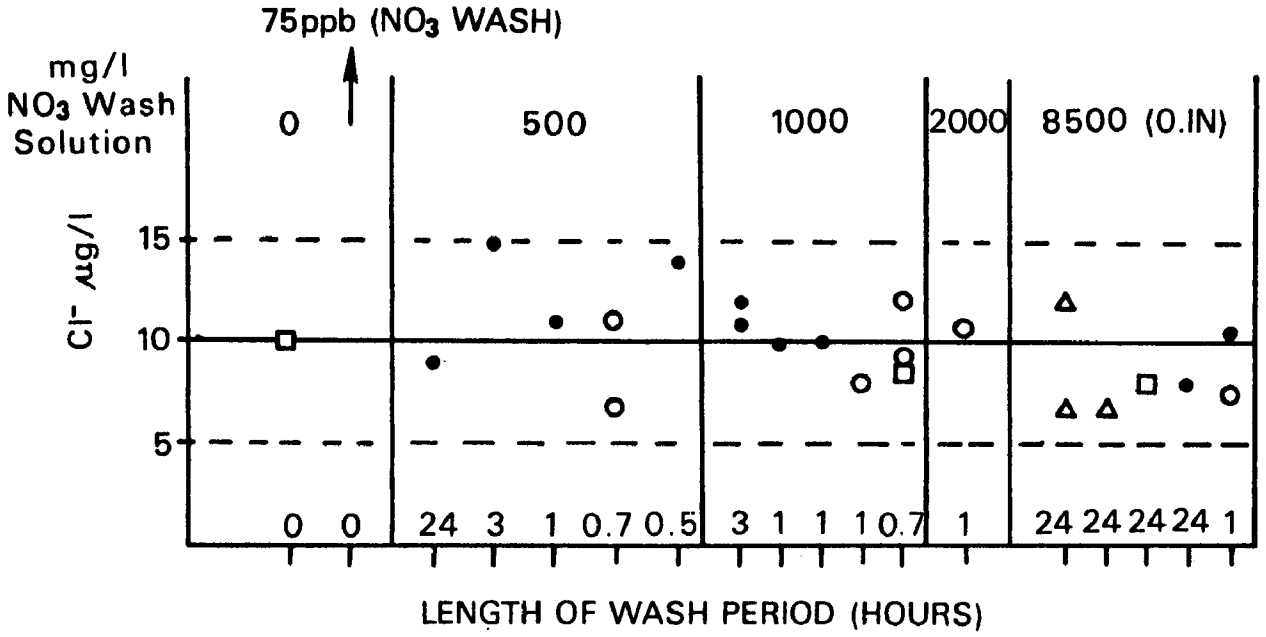
A second background value, termed the method blank, was established by extracting 10 liters of Super-Q distilled water with two grams of activated carbon and recovering the carbon by the usual procedure of flocculation, settling and filtration. When working with distilled water, samples are permitted to settle overnight. Pyrohydrolysis of the carbon sludge and subsequent measurement of chloride ion by MCT revealed the method-blank "TOCl" value to range from 8 to 10 µg/ℓ for five determinations. The increase over the carbon blank is not unexpected in view of the amount of sample handling involved, the size of the glassware employed, and the addition of various reagents to the sample, Thus 10 µg/ℓ was routinely deducted as the background correction for each analysis for total organic chlorine.

Chloride Ion Exclusion

Before proceeding with an evaluation of the method, a modification was studied. In an effort to simplify the direct method further by reducing the 6 hour nitrate wash time, investigation of the addition of nitrate ion to the sample before extraction was carried out, the purpose being to exclude or reduce the adsorption of inorganic chloride ion without interferring with TOCl adsorption. By preventing chloride ion from being adsorbed, only that chloride ion in the pore water of the carbon sludge would remain to be washed out. This wash should be able to be accomplished with a much more dilute nitrate solution than the recommended 0.1 N, and in much less time, with the advantage being that a more dilute solution of nitrate ion and the shorter time would not be as likely to displace (desorb) adsorbed organochlorine compounds during this step.

Sodium nitrate was added to the Super-Q water test samples to a concentration of 500 mg/ℓ nitrate ion, and sodium chloride was added to a concentration of 100 mg/ℓ chloride ion as a severe test. The samples were extracted once with 2 grams of activated carbon in a simplified test to establish a background equivalent for the amount of carbon sludge that would be recovered in two successive extractions. Several blanks containing no sodium chloride were also run.

Figure 2 presents data for four different concentrations of nitrate wash solutions, various sludge wash times, and various numbers of washes. Also included is the data for blanks and several samples dosed with PCP.



□ = BLANK, NO Cl^- IN SAMPLE; • = 1 WASH, 50ppm Cl^- IN SAMPLE
○ = 2 WASHES, 50ppm Cl^-; △ = DOSED 20-60ppb TO Cl(PCP), 50ppm Cl^-

FIGURE 2: EFFECTS OF VARYING STRENGTH OF WASH SOLUTION AND LENGTH OF WASH TIME.

These data show that neither the increased concentration of nitrate ion in the wash solution beyond 500 mg/ℓ, nor the length of time the carbon sludge is washed, nor whether it is washed once or twice produces any significant difference in results. All of the results are randomly scattered throughout the range of 7 to 15 μg/ℓ "TOCl" and represent a sample background value. Since the values for the blanks (samples containing no chloride ion) fall in the same range, the average of all of the results can be taken as a reasonable measure of the background level of chloride ion that will be measured in all samples containing 0 to 100 mg/ℓ Cl^-. That background calculates to be 9.9 μg/ℓ $\pm$ 2.24 μg/ℓ for a "2-gram", activated-carbon-sludge, pyrohydrolysis sample. This value is essentially the same as the 10 μg/ℓ determined for the method blank described previously.

Adsorption Efficiency

Recovery of TOCl dosed as PCP under conditions of the above test is essentially the same as that previously reported for direct measurement. This essentially complete recovery indicates that for compounds as amenable to adsorption on activated carbon such as PCP, at least, adding nitrate ion to the sample does not exclude those compounds from being adsorbed.

TOC measurements on clarified river water to which sodium nitrate had been added to a concentration of 500 mg/ℓ nitrate ion after extraction with carbon, indicate that the presence of the nitrate ion has no adverse influence on the completeness of adsorption of organics.

Precision, Accuracy and Sensitivity

All of the tests to date indicate that the reliable lower limit of sensitivity of this method should be set at no less than 10 µg/ℓ above the background value of 10 µg/ℓ. The reliability of the number, of course, increases with increasing TOCl. Further, the data on recovery of TOCl dosed as PCP show that, at least to 100 mg/ℓ Cl^-, results are just as reliable throughout the entire range of inorganic Cl^- concentrations. An examination of 113 cities for chloride ion concentration revealed that 96 percent of them had concentrations below 101 mg/ℓ. Thus the method should have wide applicability in this country.

LIMITATIONS OF THE METHOD

Several critical aspects of this method still must be evaluated before its validity as a measure of TOCl can be established. First of all, more information must be obtained to define the efficiency of the adsorption of compounds onto activated carbon from the lowest to the highest molecular weight compounds. The method must be demonstrated to be all inclusive before it can be considered to be a true measure of total organic chlorine.

Secondly, the contribution of other halides to the "TOCl" measurement must be delineated. Under the conditions of pyrohydrolysis it has been established, for example, that 70 to 80 per cent of the bromine in bromoform and dibromochloromethane can be converted to hydrogen bromide. Hydrogen bromide is a titratable species and is measured by the MCT system along with hydrogen chloride. Br^- also interferes with

measurements made with the chloride ion probe. It is estimated that when using the MCT system to make a "TOCl" measurement on finished drinking water containing various trihalomethanes, as much as 25 percent of the measured value can be attributed to the presence of organo bromine from the trihalomethanes. In those circumstances it would be desirable to isolate the measurement of each halogen. An ion chromatograph is a promising tool and should be investigated.

Finally, if the method is to be applied to water containing significant suspended solids, it must be determined to what extent both chloride ion and organochlorine compounds occluded in the solids will influence the "TOCl" measurement.

Until the above limitations and uncertanties are resolved, the method can most accurately be described as a semiquantitative measurement of carbon adsorbable organohalides measured as chloride (CAOX as Cl).

SUMMARY OF METHOD

A summary of the procedures now being employed in this method for carbon adsorbable organohalides measured as chloride (CAOX as Cl) is as follows:

1) Extract 10 liters of water, treated to be free of suspended solids and to which has been added 685 mg of sodium nitrate per liter of sample, for 1 hr with 1 gram of granular activated carbon previously powdered to 90 sec. in a lab mill, and wetted with Super-Q water for 30 min under vacuum. Stir at 200-500 rpm.

2) Settle the carbon by adding 50 mℓ of aluminum sulfate solution (1 gm of aluminum/ℓ) and sufficient 5 N sodium hydroxide to maintain pH in the range of 6.5 to 7.5, and then add 20 mℓ of polyacrylamide floc aide (200 mg/ℓ). Stirring rate should be reduced below 100 ppm during floc formation (about 10 min).

3) Allow to stand until floc has settled completely. (Time required will depend on the nature of the sample. Anywhere from 30 min. to overnight may be required). Siphon off supernatant liquor to leave about 200 mℓ behind with the sludge. Quantitatively transfer sludge to beaker. Return the supernatant liquor to the extraction vessel and repeat steps 1 through 3.

4) Allow the sludge in the beaker to settle for 5 or 10 minutes. Pour supernatant liquor from beaker through 8-μm pore diameter cellulose acetate filter and wash sludge onto filter paper for vacuum filtration. Return filtered sludge cake to same beaker, now containing 200 mℓ of 685 mg/ℓ sodium nitrate (500 mg/ℓ NO_3^-) wash solution, by washing sludge from filter membrane with small amount of Super-Q water. Add a stirring bar and stir moderately for 1 hour on stir jack (be sure sludge cake has been dispersed). Settle and refilter sludge as before. Repeat step four on sludge recovered from second extraction.

5) Combine sludge cakes from filter membrane into quartz boat and pyrohydrolyze as outlined above.

6) Analyze pyrohydrolyzate by MCT by injecting one to 20 μℓ directly into the titration cell. The size of the injection for

quantitation will be determined by the approximate concentration of titratable halide ion in the pyrohydrolyzate as estimated by screening injections. Three injections of sample should be made to determine an average value for nanograms of halide ion titrated. If a Dohrmann C-300 microcoulometer is used, nanograms of halide ion titrated as Cl^- will be displayed as a net integrated signal. If a C-200 is used, a strip chart recorder must be employed and peak areas calculated. In either case, a corrected value for nanograms of halide ion injected and titrated as Cl^- must be obtained from a standard curve constructed by plotting known amounts of Cl^- injected into the cell vs response.

Nanograms injected divided by µℓ injected is equivalent to mg/ℓ of halide ion as Cl^- in the pyrohydrolyzate. Use this value and equation (1) to calculate CAOX as Cl in µg/ℓ, and then subtract 10 µg/ℓ background value to obtain final result. Note that when using equation (1) to calculate µg/ℓ CAOX as Cl, C = the concentration of titratable halide ion in the pyrohydrolyzate.

Appendix

Equipment and Supplies*

1. Furnace, Split tube Lindberg 55035 (2)
   (Fisher Scientific pp 384)

2. Wool, Quartz, Coleman ∿ 20 gms
   (Curtin-Matheson)

3. Combustion Tube, Quartz, 74 cm long (Joint to Joint
   x 18 mm I.D. min. x 25 mm O.D. max ℔ 24/40

4. Boat, Quartz, 15 mm O.D. x 14 mm I.D. x 12 cm long (2) ea.

5. Adapter, T-joint ℔ 24/40 (cut back)
   items 3, 4, 5 Paxton Woods Glass Shop - James Leue
   7500 Brill Road
   Cincinnati, Ohio 45243
   (513) 561-8199

6. Condenser ℔ 24/40

7. Heating Mantle

8. Flask, round bottom, 1 liter, two neck ℔ 24/40

9. Adapter ℔ 24/40 with hose connection

10. Stopper ℔ 24/40 (2)

11. Flask, vacuum, 100 mℓ (4)

12. Filtering Apparatus, all glass, Millipore, xx1504700

13. Filters, Millipore, 8 mm, 47 mm dia., SCWRP04700

14. Mill, Analytical, Tekmar model A-105

15. Balance, Analytical

16. Stirring motor and blade

17. Jars, Cylindrical, Pyrex No. 6945, 13.2 liters (case of 4)
    (Sargent-Welch Scientific Co.) - cover plates recommended

18. Titration Cell, Dohrman T-300S (w. cell enclosure)

19. Microcoulometer, Dohrman C-300 digital; or C-200B with strip-chart recorder

20. Meter, pH

21. Sample Bottles, 5 gal carboy, (SCIENTIFIC PRODUCTS, B7570-5A)

22. Sample Bottles, 1 gal

23. Stir Jacks

Reagents and Chemicals

1. Oxygen, extra dry

2. Carbon, granular, activated, Calgon Corporation, Filtrasorb 400

3. Flocculant, granular, ultra high molecular weight, non-ionic polymer, Magnifloc 985N - 200 mg/ℓ
(Cyanamid-Industrial Chem & Plastics Div., Wayne, NJ 07470)

4. Water, Millipore "Super-Q" or equivalent

5. Aluminum Sulfate - 1 gm of aluminum/ℓ

6. Sodium nitrate

7. Sodium Hydroxide - 5N

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*Mention of brand name does not imply endoresement by the U.S. Environmental Protection Agency.

REFERENCES

1. Kuhn, W., Sontheimer, H., Several Investigations on Activated Charcoal for the Determination of Organic Chloro-Compounds. Vom Wasser, 15, 65 (1973).

2. Kuhn, W., Sontheimer, H., Analytic Determination of Chlorinated Organic Compounds with Temperature - Programmed Pyrohydrolysis. Vom Wasser, 41 1 (1975).

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