

The Measurement of Total Organic Carbon and Total Organohalogenes as Parameters for Water Quality Evaluation*

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Abstract

The relationship between the biological oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) methods for water quality assessment is briefly reviewed. In addition, analytical techniques are briefly described for the determination of TOC and total organic halogens (TOH) in potable waters. Application of these techniques on three water purification plants in the Pretoria area illustrated that chlorination of these waters resulted in the formation of appreciable amounts of halogenated organic compounds ($> 100 \mu\text{g}/\text{dm}^3$ as Cl) and that in these plants, treatment with activated carbon was the only effective method for their removal.

Introduction

The impact of organic constituents on the aquatic environment as a result of man's activities is of growing concern for ecological and hygienic reasons. The number of identified organic chemicals in drinking-water alone have increased from ten in 1970 to over seven hundred in 1978 out of approximately two million organic compounds that are known to be in circulation (Trussel and Umphres, 1978; Junk, *et al.*, 1976; Cotruvo and Wu, 1978). Synthetically manufactured chlorinated hydrocarbon compounds such as pesticides, herbicides, fungicides, etc., are extensively utilised in agriculture, industry and in the home for pest control. These compounds inevitably find their way into surface and groundwaters either unchanged or as some degradation product and there they are often extremely persistent. Modern water treatment plants are ineffective in removing traces of many dissolved organic chemicals from the water and even activated carbon filters become ineffective after relatively short times (Ott, 1975). Chloroform and other trihalogenated methane compounds are present in many municipal water supplies and it has been established that they are formed during the chlorination of water containing algae, humic substances, and other chemicals (Bellar *et al.*, 1974; Stevens *et al.*, 1976; Cotruvo and Wu, 1978).

A national survey in the USA during 1971 showed that many potentially harmful compounds present in water supplies were well below the limits regarded as safe (Heusden, 1971; Robeck, 1971). However, considerable controversy exists concerning the possible long-term ill-effects of these compounds on humans (Pendygraft *et al.*, 1979).

Reasons for Development of Instrumentation

The results of a national survey carried out in the USA on the occurrence of organohalogen compounds in chlorinated drinking-waters are summarised in Table 1 (Symons *et al.*, 1975).

TABLE 1
THE OCCURRENCE OF ORGANOHALOGEN
COMPOUNDS IN CHLORINATED WATERS OF
80 CITIES OF THE USA DURING 1974

Range of trihalomethane compounds ($\mu\text{g}/\text{dm}^3$)					
$\text{C}_2\text{H}_4\text{Cl}_2^*$	CCl_4^{**}	CHCl_3^+	CHCl_2Br^+	CHBr_2Cl^+	CHBr_3^+
0 - 6	0 - 3	<1-311	0 - 116	0 - 100	0 - 92

* Not found in 65,5 per cent of waters tested

**Not found in 87,5 per cent of waters tested

+ Widespread throughout the final chlorinated waters

The Environmental Protection Agency (EPA) has subsequently proposed a limit of $100 \mu\text{g}/\text{dm}^3$ for total trihalomethane compounds in drinking-waters (US Federal Register, 1978). A survey of Dutch surface waters during 1974 showed the extractable organic halogen concentration (expressed as chlorine) to generally range between $<1,0$ and $55,0 \mu\text{g}/\text{dm}^3$ although outliers in the region of $1 \text{ mg}/\text{dm}^3$ were also recorded (Wegman and Greve, 1977). Since the majority of the Republic's water treatment plants utilise chlorination as a disinfectant, similar products and concentrations should be encountered here.

Besides the need to gain an insight into the extent and concentrations of these compounds in drinking-waters, suitable measuring techniques would also find wide application in advanced water purification plant technology, i.e. wastewater reclamation, where activated carbon is used as a final polishing step to the water purification system. Optimization of the latter unit process for a particular water is presently receiving serious attention at the National Institute for Water Research (NIWR).

Though many literature references indicate the existence of potentially suitable instruments for total organic carbon (TOC) and to a lesser extent total organohalogen (TOH) deter-

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minations, reasons for our own instrument development stemmed largely from economic considerations; lack of spares and maintenance; the doubt cast on manufacturer's specifications; and the absence of a more sensitive TOC analyser system and the lack of a more rapid and/or confirmatory TOH analysing system.

Group Determinands Presently Used for Water Quality Assessment

Biological oxygen demand (BOD)

The BOD test was established as the standard measure of organic pollution as early as 1911 (Grady, 1971) and was defined as the oxygen utilised by bacteria during a fixed period of time (usually 5 days) of incubation with an aqueous solution or suspension of organic material. The BOD test is today still a basis for regulatory actions and is used routinely in almost all control and research studies on sewage and industrial waste treatment. Besides being used for treatment efficiency and regulatory action it is also used for plant design, plant operation, pollution surveys and the prediction of the dissolved oxygen content in receiving streams. In spite of all the uses to which the BOD test has been put or *because of them*, few people have been fully satisfied with the test (Davis, 1971).

Chemical oxygen demand (COD)

Like the BOD test the COD test is used for pollution assessment to express the organic content of a wastewater in mol/dm³ oxygen. While the BOD test relies on biological activity to convert the oxidisable matter (largely carbonaceous matter) to stable compounds, the COD test depends on oxidation by a powerful chemical oxidising agent. The COD test can be performed within two hours and was considered a good substitute or supplement to the BOD test due to its more rapid determination. Because of the vastly different method of oxidation the COD test does not yield the same results as the BOD test and is in addition subject to chloride interference. Although a chloride correction factor is taken into account, the COD method is still questionable when chloride is present in high concentrations (Davis, 1971).

Total organic carbon (TOC)

The instrumental technique of TOC analysis is a relatively new concept initiated by Van Hall *et al.*, (1963) and unlike the indirect oxygen-based measurements for determining the presence of organic contamination such as the BOD and COD methods, this technique determines organic carbon directly. Many of the carbonaceous compounds of particular interest in water pollution control as well as many organic chemical compounds have been tested with the method but no selectivity was detected (Chapman, 1965). Irrespective of the type of TOC analyser used (Table 2) analysis time is considerably faster than the COD or BOD test and eliminates many of the variables such as temperature, time and dilution factors that confound oxygen-based tests, particularly the BOD test. In research, processing a large number of samples quickly and economically is desirable. Also rapid feedback of results permits adjustments to optimize performance of a process within a reasonable time. The method of TOC analysis consists basically of the combustion of organic compounds contained in a syringe-injected water sample follow-

ed by measurement of the carbon dioxide produced. The infrared photometer and flame ionization detectors are the two main types of detectors used. The latter detector requires the CO₂ to be further reduced to methane. It should further be stressed that most TOC analysers are designed to determine dissolved organic carbon (DOC) which places a question mark on the often liberally used term TOC. The latter term includes suspended material.

One would expect the stoichiometric $\frac{\text{COD}}{\text{TOC}}$ and $\frac{\text{BOD}}{\text{TOC}}$ ratios of a wastewater to approximate the molecular ratio of oxygen to carbon, i.e. 2.66. However, that the ratios obtained between these three determinands could be highly variable is illustrated in Table 3 (Hill, 1969).

Analytical Instrumentation Development for the Micro-Analysis of Organopollutants in Water

A complete characterization of organic materials present in drinking-water does not yet exist. The small organic residual, usually <10 mg/dm³ carbon, retained in drinking-water after chemical treatment is a very complex mixture containing hundreds of different compounds, some of them of natural and some of synthetic origin. The principal approach to their determination has until now been accomplished by gas chromatography with or without coupling to a mass spectrometer. The latter technique is only capable of accounting for a fraction of these organic compounds (Rosen 1976; Giger *et al.*, 1976; Garrison *et al.*, 1976), which leaves the majority of the organic contents unaccounted for and for which there are no simple methods of identification or quantification.

In South Africa very little has been done on the determination of the *total* amount of a specific group of organic compounds in potable water supplies simply because no instrumentation was available or the instruments were unable to cope with the low detection limits required. Manufacturer's specifications are numerous and often difficult to interpret which makes the correct choice of an appropriate instrument so much more difficult. Furthermore, the practical detection limits of most modern commercial TOC analysers are usually close to the actual concentrations found in potable waters which therefore raises an analytical problem. One of the major problems encountered by users of TOC analysers is the amount of time required for equipment maintenance and repair.

The consensus from experience over many years (Westlake and Gunther, 1967) is that new models of most instruments are rushed onto the market before they have been tested properly both for engineering and for component performance and that manufacturer's inspection and testing procedures in general are distressingly inadequate. The fact that a variety of trihalomethane compounds are formed at water purification plants as a result of chlorination practice, and that these compounds are suspect regarding their long-term ill effects on man and the environment, required the development of methodology to establish the occurrence and fate of these compounds in potable waters. Few practical methods exist for the determination of TOH in water with the possible exception of the microcoulometric technique initiated by Coulson *et al.* (1960).

Improvements to TOC instrumentation

The major difficulties arising with the micro-analysis of TOC are background interference, small sample volume and operator technique. According to Goulden (1972) the detection limit for

TABLE 2: Commercial instruments available for TOC analyses

Instrument Type	Manufacturer	Sample Introduction	Catalyst used	Response time (min)	Detector	Concentration range ($\mu\text{g C/dm}^3$)	Utilities required
TOC/TC	Astro Ecology Corp. P.O. Box 98159, Houston, Texas, 77058	Metered into system	Fixed bed, non precious metal catalyst 900 °C	10	NDIR	0-15000 0-5000	Water, HCl
TOC/TC	Beckman Instruments, Fullerton, California 92634	Syringe	Cobalt Oxide 900 °C Phosphoric acid 150 °C	2-4	NDIR	0-5 0-4000	Air or Oxygen
TOC	Carle Instruments Inc., Fullerton, California	Syringe	Volitilization into FID	20	FID	Function volitilization time	Nitrogen, Hydrogen
TOC/TC	Dohrmann Div. Envirotech. Corp., Santa Clara California 95050	Syringe	Cobalt Oxide 900 °C Ni reducing agent	6	FID	DC50 0-2000 DC52 0-20 DC54 0-10	Air, Nitrogen, Hydrogen
TOC/TC	Enviro Control (Rockville, Md)	Metered into system	Fixed bed CuO 920 °C	4½	FID	0-1000	Air, Nitrogen, Hydrogen
TOC/TC	Ionics, Inc. 65 Grove Street, Watertown, Massachusetts 02172	Syringe	Palladium 900 °C Acid salt 170 °C	2-4	NDIR	-	Nitrogen
TOC/TC	Ionics, Inc. 65 Grove Street, Watertown, Massachusetts 02172	Slide plate valve	Palladium fixed bed 900 °C Acid salt 170 °C	5	FID	0-5000	Air, Nitrogen, Hydrogen
TOC/TC	Ionics, Inc. 65 Grove Street, Watertown, Massachusetts 02172	Slide plate valve	Palladium catalyst 900 °C Pre-carbonate removal	5	NDIR	0-3000	Air, HCl, Nitrogen
TC	Ionics, Inc. 65 Grove Street, Watertown, Massachusetts 02172	Slide plate valve	Palladium catalyst 900 °C	5	NDIR	0-3000	Air, Nitrogen
TOC/TC	Oceanography International Corp., 512 West Loop, College Station, Texas 77840	Ampule 10 cm ³	Sample heated in ampule with Oxidizing agent	2-5	NDIR	0,2 and >	Oxygen, Propane, Nitrogen
TOC/TC	Delta Scientific Corp. 120E Hoffmann Ave., Lindenhurst, N.Y. 11757	Samples metered	Fixed bed CuO 900 °C	5	Nephelometer	0-5000	HCl, Ba(OH) ₂
TOC	Phase Separation Ltd. Desside Industrial Est., Queensferry Clwyd, Gt. Britain	Automatic	-	-	FID	0,1-1000	Air, Hydrogen
TOC	Arro Laboratories Inc.						
TOC	Bendix Corporation						
TOC	Coulometrics Inc. Wheat Ridge, Colorado 80033	Syringe	BaCrO ₄ at 900 °C	5-10	Coulometric	μg range	Oxygen
TOC	Ratheon Co. P.O. Box 360, Portsmouth, Rhode Island 02871						
TOC	Union Carbide Corp. (White plains, New York)				FID		
TOC	Precision Scientific Co. "Equator"California			15	NDIR	0,2-300	
TOC	Carlo Erba Instruments, P.O. Box 4342 - 20100 Milan, Italy	Automatic	CuO, Nickel	5	FID	0-25 0-250 0-2500	Air, Nitrogen, Hydrogen
TOC	Dyne Rocket Organic Carbon Analyser, Canoga Park, California 91304	Manual		1	FID	0-3000	Nitrogen, Hydrogen
TOC	Kontron Instr. Ltd. UK.. Agents: Oceanography Int. Co. Texas			2½	NDIR	< 1	Oxygen
TOC	Trace Organic Carbon Monitor, Allegheny Equipment Co. Box 461, Carnegie, Pa 15206	Continuous Flow			UV	> 10	
TOC	Aug. Schnackenberg & Co. 56 Wuppertal 2	Automatic			NDIR	50-2000	
TOC	UNOR. H. Mahak AG. Sempertstrasse 38, 2000 Hamburg 60, W. Germany	on-line	ultraviolet radiation	30	NDIR	0 - 3,0	
TOC	Mess Und Regelabteilung der Badischen Anilin- & Sodafabrik Ag, Ludwigshafen RL	Automatic	Wet Oxidation		NDIR	0-100	

TOC = Total Organic Carbon
TC = Total Carbon

any commercial TOC analyser was approximately 100 $\mu\text{g/dm}^3$ C. Because of the small sample volumes which must be used on these instruments (20 to 200 mm³) entailing thereby limited sensitivity and possible automated sample introduction, the trend is towards instrumentation that can handle large sample volumes incorporating wet chemical oxidation techniques. Automation of a Beckman 915 TOC analyser was previously accomplished for carbon concentrations in excess of 10 mg/dm³ (Van Steenderen, 1976; Van Steenderen, 1979a).

A TOC method initiated by Goulden and Brooksbank (1975) and further improved at the NIWR involves wet chemical oxidation with infrared measurement of the liberated carbon dioxide (Van Steenderen *et al.*, 1979). Sample volume was 6 cm³ and the minimum detection limit was 50 $\mu\text{g/dm}^3$ C. The sampling rate was 20/h. In the present study, silver peroxydisulphate oxidation at 75 °C was employed. The cost for the construction of this TOC system amounted to approximately one third the price of an equally effective commercially marketed instrument (if one assumes the manufacturer's specifications to be valid). Sixty per cent of the cost was attributed to purchase of

a Beckman infrared analyser.

Instrumental development for TOH analysis

Although the nature of the entire organic content of drinking-water is of interest (numerous methods have been developed for the isolation, identification and quantification of complex mixtures of organic compounds in drinking-waters) it is neither technologically nor economically feasible to perform such a comprehensive analysis on every sample. Determinands are therefore required which can provide significant information without requiring complicated analytical procedures that cannot be used on a routine basis. One such determinand is that of TOH, which amongst other techniques can best be determined by coulometric titration. The technique firstly involves sample concentration by means of solvent extraction. An aliquot of the sample extract is injected into a pyrolysis tube and mixed with reactant gas. The gas is then eluted through a heated capillary into a coulometric titration cell where the halides formed are coulometrically titrated and quantitatively determined by mea-

TABLE 3

CONSTITUENTS MEASURED IN THE BOD, COD AND TCA DETERMINATIONS (HILL, 1969)

Material detected in water	Method		
	BOD ¹	COD	TCA
Organic carbon	Yes	Yes	Yes
Organic nitrogen	Yes	No	No
Aromatics	Yes ²	No	Yes
ABS plastics	No ²	Yes	Yes
Cellulose	No	Yes	Yes ⁵
Ammonia	Yes	No	No
Nitrites	Yes	Yes	No
Carbonate	No	No	Yes
CO ₂	No	No	Yes
Ferrous iron		Yes	No
Sulphides	Yes ³	Yes	No
Sulphites	Yes ³	Yes	No
Halides	No	Yes ⁴	No
Sulphate	No	No	No
Phosphate	No	No	No
Nitrate	6	No	No
Oxygen	7	No	No

NOTES:

- 5-day BOD test.
- Oxidized slowly, but eventually degraded.
- Included only if test based on initial dissolved oxygen demand (DOD).
- Can be partially eliminated by complexing with mercuric sulphate.
- Provided particles are small enough to be decomposed during short contact time.
- Reduces oxygen demand.
- Not applicable.

TCA = Total carbon analysis

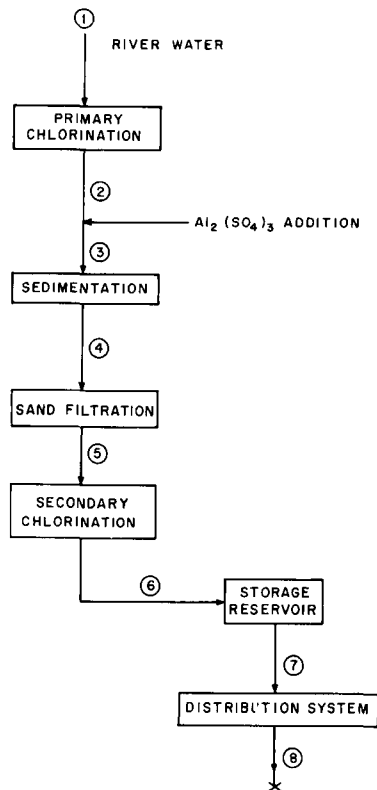


Figure 1
Water purification plant I (Sampling points)

asuring the amount of electricity (in coulombs) necessary to complete the titration. Such a system has been built at the NIWR for approximately R6 000 and its construction details have been tabulated (Van Steenderen, 1979b). The rate of analysis was between 3 and 4 min per sample using a 10 mm³ sample extract volume. The minimum detection limit in water was 1 µg/dm³ halogens using the technique of sample extraction *without* headspace (extraction flasks completely filled).

Direct Application of the TOC and TOH Analysers on Three Water Purification Plants in the Pretoria Area

Prior to a proposed nationwide survey of water purification plants, experiments were carried out at three easily accessible plants where surface water was purified to drinking-water quality. The source of raw water for the first purification plant was dam water and for the second plant, river water. Both these sources were recipients of purified sewage effluent. The source of raw water for the third purification plant was activated sludge plant effluent. Sampling points (retention time of the works taken into account) are shown in Figures 1, 2 and 3. Studies carried out (Van Steenderen, 1979c) illustrated that, although none of the raw water sources were completely free from halogenated organic compounds, the bulk of these com-

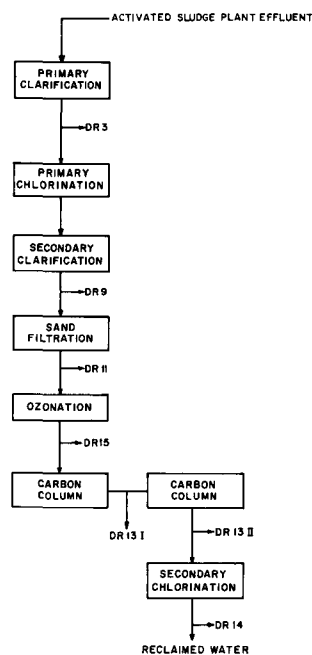


Figure 2
Water purification plant II (Sampling points)

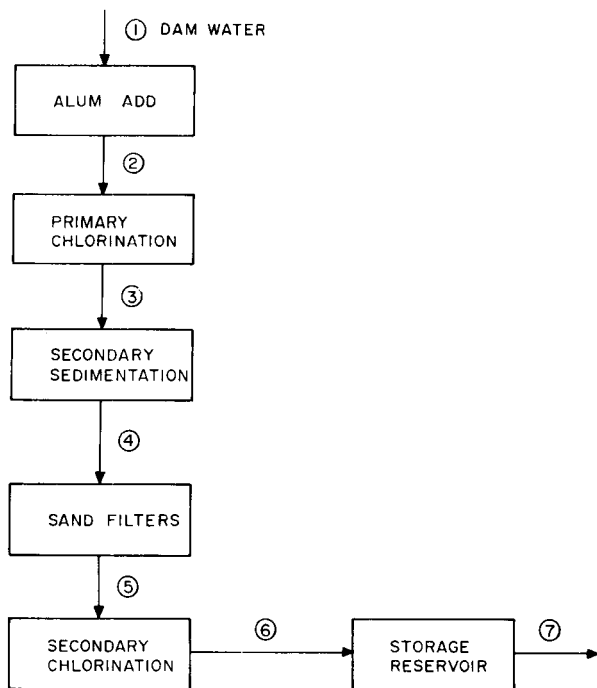


Figure 3
Water purification plant III (Sampling points)

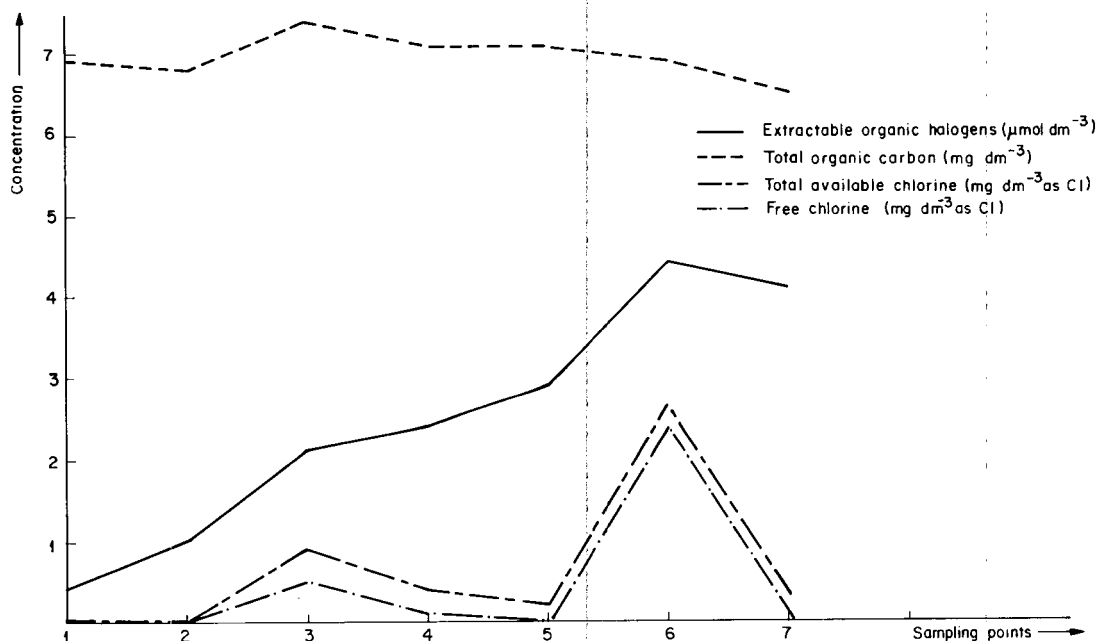


Figure 4
The relationship between organic halogens, organic carbon, and chlorine during various stages of water purification plant III

pounds were formed after the chlorination of these waters. It was also found that primary chlorination (chlorination of raw water) was highly detrimental with respect to the formation of halogenated organic compounds (Fig. 4) and that these compounds were sparingly removed by methods such as flocculation, sedimentation, sand filtration and ozonation (Fig. 5). Granular activated carbon (approximately 6 min contact time) removed nearly all these compounds that were formed during primary chlorination but not all the dissolved organic carbon (Fig. 5), which resulted in further organic halogen formation after secondary chlorination. It is this latter continued action which concerns the water consumer (Figs. 6 and 7).

It was furthermore found that bromoform was only formed after the chlorination of water and that the main contributors to the volatile halogenated compounds in descending order were trichloromethane, dichlorobromomethane, dibromochloromethane and tribromomethane (determined by gas chromatography). In all cases, the raw waters of the three plants tested showed that the total of these four volatile halogenated compounds amounted to less than 25 per cent of the total halogenated organic compounds, while for the final waters these volatile compounds represented 75 per cent or more of the total halogenated organic compounds. If one considers the highest halogen concentration found as per Figure 6 to be trichloromethane ($258 \mu\text{g}/\text{dm}^3$) we find that our treated waters are probably not much different from those waters in the USA (Table 1) or elsewhere in the world (Wegman and Greve, 1977).

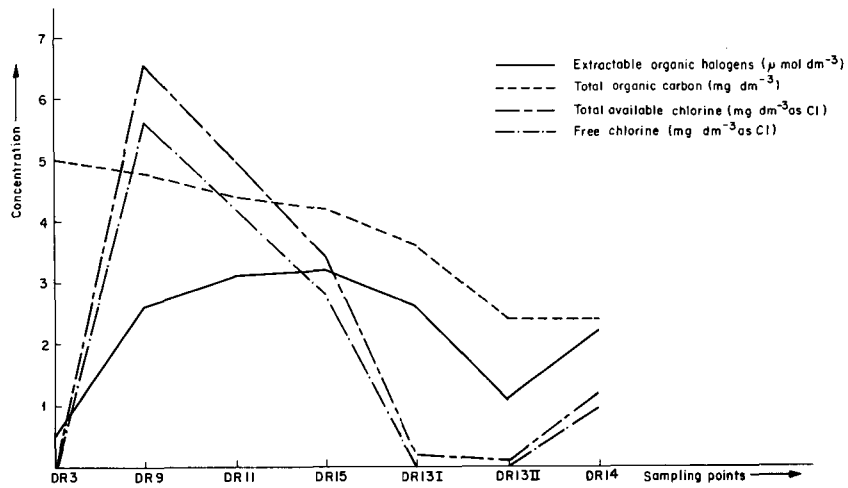


Figure 5
The relationship between organic halogens, organic carbon, and chlorine during various stages of water purification plant II

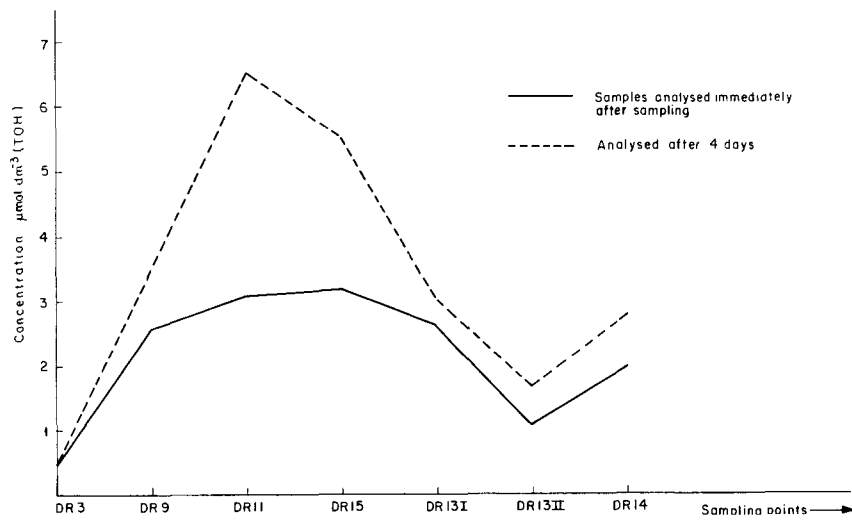


Figure 6
The effect of sample storage on the organic halogen concentration of chlorinated water samples. Samples stored in sealed bottles without headspace at 5 °C for 4 days. Water purification plant II

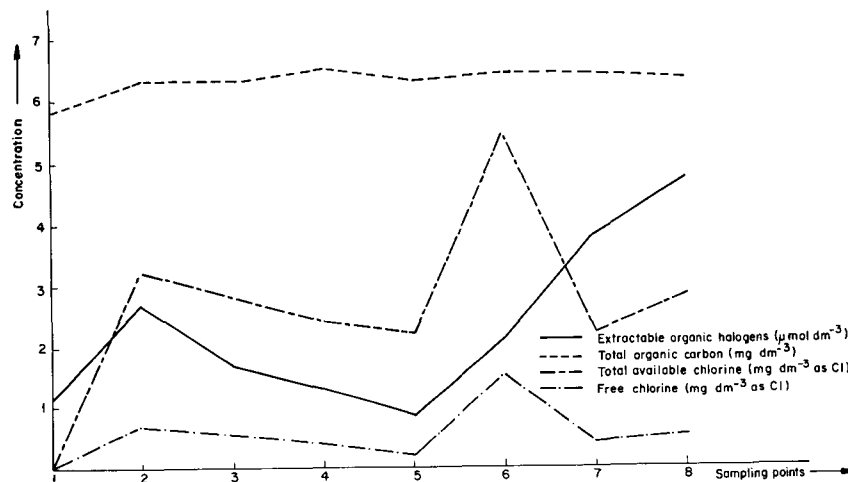


Figure 7
The relationship between organic halogens, organic carbon, during various stages of water purification plant I

Conclusion

A considerable contribution has been made to the already well established organic pollution determinands BOD and COD by the introduction of TOC and TOH. Instrumentation for the measurement of TOC and TOH in *potable waters* has been developed at the NIWR. Preliminary studies indicated that halogenated organic compounds were readily formed as a result of chlorination practice. These compounds persisted in the municipal distribution system and increased in concentration with retention time.

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