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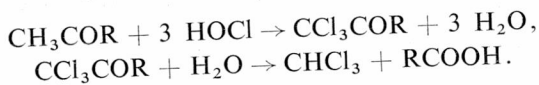
STUDIES ON HALOFORM FORMATION IN CERTAIN GROUND
AND SURFACE WATERS IN POLAND**

Chlorination has long been recognized as the cause of haloform formation in natural waters. The paper is aimed at determining which fraction of the humus in water can be regarded as the precursor of trihalomethane and at explaining the kinetics of its formation.

1. INTRODUCTION

The problem of haloform formation in the natural waters due to chlorination procedure has been extensively studied since the publication of the first papers dealing with this subject [1, 5]. The chlorinated water contains chiefly chloroform (CHCl_3) and smaller amounts of dibromochloromethane (CHBr_2Cl), bromodichloromethane (CHBrCl_2) and bromoform (CHBr_3). Dichloriodomethane (CHCl_2I) has been detected occasionally, but no other haloforms have been found [8].

According to MORRIS and MCKAY [4] the haloform reaction between halogens and organic components containing acetyl or other groups which can be oxidized to the acetyl group is responsible for the formation of trihalomethanes in the natural waters. In that reaction, three hydrogen atoms of the methyl group are substituted successively by chlorine atoms (or atoms of other halogens), resulting in formation of haloform and a carboxyl acid. The reaction can be presented briefly as follows:



ROOK [6] demonstrated that the aromatic nucleus with two $-\text{OH}$ groups in the meta position is susceptible to haloform reaction. In view of the fact that acceleration of haloform reaction occurs at $\text{pH} = 11$, as demonstrated by ROOK and other authors [7], ROOK

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proposed reaction pathway in which like in the case of aliphatic ketones the haloform reaction is preceded by enolization.

The probable course of haloform formation has been generally accepted; there is, however, no unanimity regarding the question which organic components occurring in the waters produce haloform in the reaction with chlorine or other halogens. The hypothesis that simple organic compounds of low molecular weight, such as ethanol [1], can be haloform precursors has not been confirmed experimentally [6]. STEVENS et al. [7] using a commercial preparation of humic acids demonstrated that the quality of haloforms produced was proportional to the concentration of organic carbon in the preparation, as well as to the concentration of organic carbon contained in the non-identified organic substances occurring in the water of Ohio River. This has led the author to the conclusion that humic acids are trihalomethane precursors in the water.

ROOK [6] examined a number of organic compounds and a preparation of fulvic acids extracted from peat. He found that among the substances occurring potentially in the natural waters, resorcin and fulvic acids could be haloform precursors. It can be seen that these authors represent various opinions concerning the question which fraction of humus can be regarded as haloform precursor. These fractions are chemical compounds not clearly determined and both the commercial preparation of humic acids used by STEVENS [7], as well as the preparation of fulvic acids extracted from peat by ROOK [6], may not be typical representatives of these fractions in the natural waters.

MORRIS and MCKAY [4] have elaborated an extensive review of organic compounds occurring in the natural waters, taking into account their susceptibility to the haloform reaction. Among the most probable haloform precursors they listed: humic substances; aliphatic hydroxy acids occurring in minute quantities; mono-, di- and tricarboxylic acids; aromatic carboxylic acids, as well as chemical compounds belonging to the groups of terpenoids, isoprenoids and carotenoids, however their occurrence in the natural waters has not been proved. It can be concluded that among the potential precursors of trihalomethanes, the humus substances occur in water in the largest amounts.

The aims of the studies reported in this paper were:

1. to determine which fraction of humus occurring in the natural waters can be regarded as the most probable trihalomethane precursor,
2. to characterize the kinetics of trihalomethane formation.

The studies were carried out on 18 samples of natural surface and underground waters.

2. ANALYTICAL METHODS

Quantitative determination of the humus fraction was performed basing on the method of HOFFMAN [3]. Absorption in alkaline water solution of humus was measured at $420\mu\text{m}$ after previous humus extraction with amyl alcohol from an acid solution. The extract of the non-precipitable part of humus due to acidification (soluble in alkalies) was used for the determination of fulvic acids. The total amount of humic and hmatomelanic

acids was calculated by subtraction of the amount of fulvic acids from the total amount of humus.

The course of haloform reaction was studied as follows. Solution of gaseous chlorine in distilled water was added to the examined water samples. The content of free chlorine in the water examined was maintained at the level of at least 2.0 mg/dm³. The reaction was carried out in darkness, at the temperature of 293±1°K. The reaction was interrupted with ascorbic acid solution in 0.5, 4, 24, 96 and 240 h after addition of chlorine.

Quantitative determination of trihalomethanes was performed by gas chromatography. The chromatographic analysis was preceded by initial extraction of samples with n-pentane [9]. Method sensitivity at sample volume of 5 to 10 cm³ was 1 µg/dm³. Chloroform, dibromochloromethane, bromodichloromethane and bromoform were determined.

The other measurements i.e. of colour, pH and COD were carried out according to the official methods used in Poland and published in the Polish Standards.

3. RESULTS AND DISCUSSION

Among the 18 water samples analysed there were 8 surface waters and 10 ground waters. The qualitative characteristics of waters are shown in table 1. The samples were selected taking into account the possibly great variances in colour and humus content.

Table 1
Characteristics of waters examined and haloform reaction output
Charakterystyka badanych wód i wydajności reakcji haloformowych

Sample No.	Water sample origin	Colour °Pt	COD mg O ₂ /dm ³	Humic substances mg/dm ³	Humic + hymato-melanic acids mg/dm ³	Fulvic acids mg/dm ³	Total THM* µg/dm ³
1	surface — reservoir	30	40	4.4	0.3	4.1	132.5
2	surface — river	32	38	4.2	0.2	4.0	184.4
3	surface — reservoir	25	33	3.7	0.0	3.7	142.8
4	surface — peatbog	300	135	58.0	19.5	38.5	133.7
5	surface — river	25	29	4.2	0.4	3.8	127.8
6	surface — river	35	38	4.9	0.6	4.3	76.9
7	ground — miocene	650	76	160.0	153.5	6.5	615.0
8	ground — miocene	70	20	16.0	15.0	1.0	187.5
9	ground — miocene	605	83	255.0	252.0	3.0	1140.0
10	surface — river	70	38	4.1	1.4	2.7	146.4
11	ground — miocene	500	70	68.0	65.0	3.0	525.6
12	ground — miocene	135	21	44.0	42.1	1.9	233.2
13	surface — river	27	36	3.9	0.7	3.2	179.7
14	ground — infiltration	17	15	2.7	0.5	2.2	165.5
15	ground	30	14	2.1	0.0	2.1	84.0
16	ground	30	15	3.0	0.5	2.5	82.7
17	ground	25	12	2.5	0.4	2.1	112.6
18	ground — miocene	640	66	94.0	88.5	9.5	812.5

* After 24 h of reaction.

The content of humus substances in the ground waters ranged from 2.1 to 255 mg/dm³, and in the surface waters from 3.7 to 58 mg/dm³. In the surface waters and in slightly coloured ground waters the fraction of fulvic acids predominated quantitatively, while in the dark coloured ground waters the predominating part was the fraction of humic and hymetomelanic acids determined as the total amount.

Due to the reaction with chlorine, chloroform, bromodichloromethane and in one case dibromochloromethane occurred in the water samples examined. Bromoform was seldom found and in quantities being close to the identification limit. Total quantities of trihalomethanes which were formed after 24 h of reaction are shown in table 1. They amounted from 76.9 to 1 140 µg/dm³.

Correlation coefficients between the total content of humic substances, fulvic acids, total amount of humic and hymetomelanic acids, colour, COD and trihalomethanes content were calculated (table 2). Equations of regression straight lines were also found.

Tabele 2

Correlations between haloform reaction output and COD, colour, humus and humus fractions content
Korelacje między wydajnością reakcji haloformowej a ChZT, kolorem, humusem i zawartością frakcji humusowej

Independent variable	Correlation coefficients after reaction time hours					Regression equation**
	0.5	4	24	96	240	
COD	—	—	0.505	—	—	$y = 4.6x + 77.6$
Colour	0.697	0.743	0.888	0.906	0.963	$y = 2.1x + 211.4$
Humic substances	0.677	0.760	0.857	0.839	0.966	$y = 5.8x + 284.8$
Humic + hymetomel- anic acids	0.681	0.765	0.862	0.879	0.969	$y = 5.8x + 322.8$
Fulvic acids	0.052*	0.024*	-0.001*	0.004*	-0.084*	

* There is no reason to reject the hypothesis that the correlation coefficient $r = 0$.

** Estimated for the longest reaction time.

The calculated correlation coefficients for various reaction times are presented in table 2. They point to the correlations (significance level $\alpha = 0.05$) between the amounts of trihalomethanes and colour, humus content, hymetomelanic and humic acids contents and COD. Lower correlation coefficients were associated with longer reaction time and indicated the decreasing differences in the reaction rate between various waters. No correlation was found in regard to the amount of fulvic acids occurring in water.

Kinetics of reactions are shown as diagrams in figures 1-4. They demonstrate the amounts of chloroform and bromodichloromethane formed in the surface (figs. 1 and 2) and ground (figs. 3 and 4) waters as a function of time. The diagrams were made for the typical representatives of surface waters and coloured ground waters. In the same figures the calculated values of $\ln C$, $1/C$ and $1/C^2$ as a function of time were drawn to determine

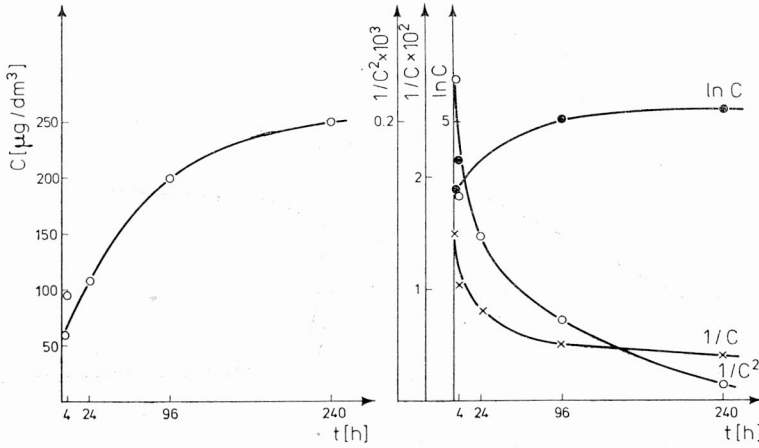


Fig. 1. Kinetics of chloroform formation in coloured surface water (Drwęca river)
 Rys. 1. Kinetyka powstawania chloroformu w zabarwionej wodzie powierzchniowej (Drwęca)

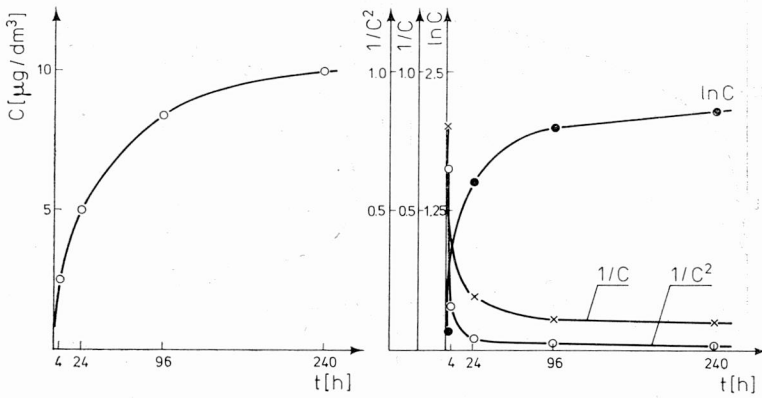


Fig. 2. Kinetics of bromodichloromethane formation in coloured surface water (Poznań, miocene water)
 Rys. 2. Kinetyka powstawania bromodwuchlorometanu w zabarwionej wodzie powierzchniowej (Poznań, woda miocenska)

graphically the reaction order [2]. The curves shown in figures 1-4 indicate that the reaction of trihalomethane formation is performed at the highest rate during the first 24 h, however, over the whole experimental period (240 h) a further increase of trihalomethane concentration was observed. An attempt at a graphical estimation of reaction order was unsuccessful in all cases. This indicated that the reaction of trihalomethane formation corresponded with the kinetic equations described with more complex algebraic formulae than the simple equations of the 1st, 2nd or 3rd order [2]. This confirms, indirectly, the multistage mechanism of reaction as proposed by MORRIS and MCKAY [4].

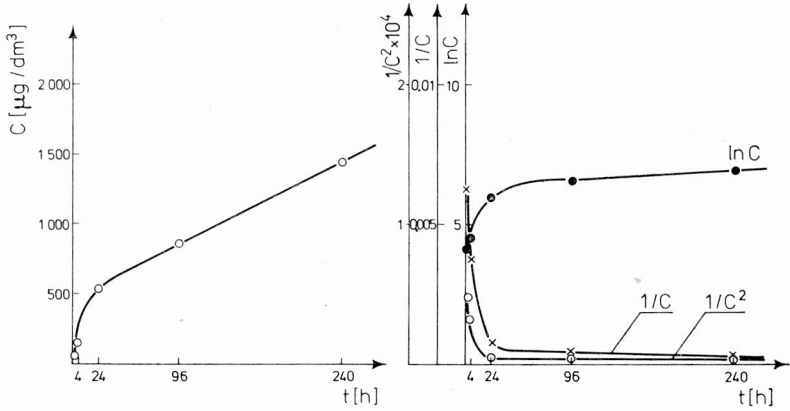


Fig. 3. Kinetics of chloroform formation in coloured ground water (Poznań, miocene water)
Rys. 3. Kinetyka powstawania chloroformu w zabarwionej wodzie gruntowej (Poznań, woda mioceńska)

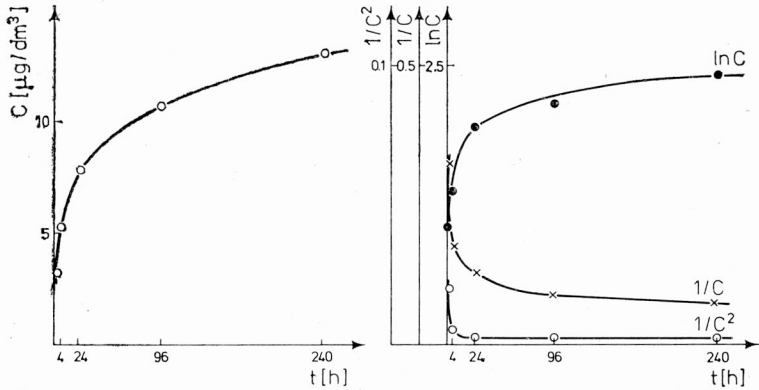


Fig. 4. Kinetics of bromodichloromethane formation in coloured ground water (Drwęca river)
Rys. 4. Kinetyka powstawania bromodwuchlorometanu w zabarwionej wodzie gruntowej (Drwęca)

4. CONCLUSIONS

The experimental results indicate that:

1. Trihalomethanes are formed in the natural waters due to a multistage reaction between chlorine and organic substances, as indicated by the negative result of a test concerning the estimation of reaction order using simple kinetic equations.

2. Humic and hymetomelanic acids are more probable trihalomethane precursors than the fulvic acids.

5. SUMMARY

In the samples of natural, coloured ground waters and surface waters, the contents of humus and its fractions, humic and hymetomelanic acids and fulvic acids were determined. The amount of trihalomethanes (THM), occurring in the water due to chlorination procedure was also determined.

Humus content ranged from 2.1 to 255 mg/dm³ and the total content of THM formed 4 h after chlorination varied from 76.9 to 1140 µg/dm³. Correlation was found between humus content, the total content of humic and hymetomelanic acids and the amount of trihalomethanes in the water. No correlation was observed in regard to the fulvic acids.

Investigations on reaction kinetics of THM formation demonstrated that it should be described by equations of more complex nature than the simple equations of reaction of the 1st, 2nd and 3rd order.

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BADANIA NAD POWSTAWANIEM TRÓJHALOMETANÓW W PEWNYCH GRUNTOWYCH I POWIERZCHNIOWYCH WODACH POLSKI

W próbkach naturalnych, barwnych wód podziemnych i powierzchniowych oznaczono zawartość substancji humusowych oraz ich frakcji: kwasów huminowych wraz z hymatomelanowymi oraz kwasów fulwowych. Oznaczono również ilość trójhalometanów (THM) tworzących się w tych wodach wskutek chlorowania.

Zawartość substancji humusowych wynosiła od 2,1 do 255 mg/dm³, a suma THM tworzących się po 24 godzinach reakcji z chlorem — od 76,9 do 1140 µg/dm³.

Stwierdzono korelację między zawartością humusów oraz sumy kwasów huminowych i hymatomelanowych a ilością tworzących się THM; w przypadku kwasów fulwowych brak takiej korelacji. Badania

kinetyki reakcji tworzenia się THM wykazały, że opisują ją równania bardziej złożone niż proste równania reakcji I, II lub III rzędu.

UNTERSUCHUNGEN ZUR ENTSTEHUNG VON TRIHALOMETHANEN (THM) IN BESTIMMTEN GROUND- UND OBERFLÄCHENWÄSSERN POLENS

In frischen Proben stark gefärbter Grund- und Oberflächenwässer wurde die Konzentration von humusartigen Substanzen sowie deren nachstehende Fraktionen bestimmt: Huminsäuren gemeinsam mit Hymatomelansäuren und Fulvicsäuren. Bestimmt wurde auch die Gesamtmenge von THM die bei der Chlorung dieser Wässer entstehen.

Die Konzentration der humusartigen Substanzen betrug 2,1 bis 255 mg/dm³ und die Summenkonzentration von THM, nach einer 24-stündiger Reaktionszeit mit Chlor 76,9 — 1 140 µg/dm³.

Es besteht eine Korrelation zwischen der Humusmenge, der Gesamtmenge von Humin- und Hymatomelansäuren und der entstandenen THM-Menge. Für Fulvicsäuren trifft das nicht zu. Zur Kinetik der THM-Bildung ist zu sagen, daß hier Reaktionen höherer Ordnung eine Rolle zu spielen scheinen als die der I., II. und III. Ordnung.

ИССЛЕДОВАНИЯ ОБРАЗОВАНИЯ ТРИГАЛОМЕТАНОВ В НЕКОТОРЫХ ГРУНТОВЫХ И ПОВЕРХНОСТНЫХ ВОДАХ ПОЛЬШИ

В естественных пробах окрашенных подземных и поверхностных вод было определено содержание гумусовых веществ, а также фракций: гуминовых кислот вместе с гиматомелановыми кислотами и фульвокислот. Обозначалось также количество тригалометанов, образующихся в этих водах вследствие хлорирования.

Содержание гумусовых веществ составляло от 2,1 до 255 мг/дм³, а сумма тригалометанов, образующихся в течение 24 часов реакции с хлором, составляла от 76,9 до 1 140 µг/дм³.

Была отмечена корреляция между содержанием гумусов, а также суммы гуминовых и гиматомелановых кислот, с одной стороны, и количеством образующихся тригалометанов, с другой, в случае фульвокислот такая корреляция отсутствует. Исследования кинетики реакции образования тригалометанов показали, что эту кинетику описывают более сложные уравнения, чем простые уравнения реакции I, II или III порядка.