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RAMAN SPECTROSCOPY IN ESTIMATING
THM FORMATION POTENTIAL IN WATER PIPE NETWORK

About 250 disinfection by-products (DBPs) have been identified; however, only 20 DBPs including four basic trihalomethanes (chloroform, bromoform, bromodichloromethane, dibromochloromethane) are well-known taking into consideration their behavioral profile. There have been made many attempts to predict the occurrence of DBPs in drinking water. The models developed are generally based on the data generated in laboratory scale. However, their practical application in management of water treatment processes and water supply system exploitation seems to be insignificant. Only a few of them have been made in field-scaled investigations. In this paper the results of laboratory studies, including the possibilities of applying a Raman spectroscopy to THMs precursors identification, are presented. Based on the results obtained, the mathematical models describing the level of PTHM potential are constructed.

1. INTRODUCTION

It has been known for a long time that water as a basic medium necessary to people's life is the environment of many heterotrophic microorganisms, bacteria of cola group, invertebrates and such opportunistic pathogens as: *Pseudomonas, Mycobacterium, Klebsiella, Legionella, Erdwarsiella* or *Serriatia.* The organisms mentioned above cause mass diseases spread through water (cholera, typhus, typhoid fever). Therefore the water free of microorganisms is the most important aim of its treatment processes. Water disinfection is one of the methods of eradicating diseases spread through water. It proved to be the most effective step to prevent some epidemics spread through water. It consists, on the one hand, in killing all both live and spore forms of pathogenic organisms, but on the other one, in protecting us from their reactivation inside a widespread water supply network. In the process of disinfection,

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the commonly used agent is chlorine. It is very effective technologically and relatively cheap, both from the investment and operation points of view. It proved to be cheaper than some alternative methods of chemical disinfection of water with chlorine dioxide or ozone.

Chlorine usage in water treatment has some disadvantages, i.e. formation of disinfection by-products (DBPs) such as: trihalomethanes (THM), haloacetic acids (HAA), haloacetonitrile (HAN), chlorophenols, MX or aldehydes [1]–[3]. The main precursors of DBPs are as follows: humic acids, chlorophyll *a*, metabolites of aqueous organisms, aliphatic hydroxy acids, aromatic carboxylic acids and some inorganic compounds as bromates. DBPs are formed in small quantities, but they have toxic, mutagenic, carcinogenic or teratogenic properties. Therefore they must be taken into consideration in a final water quality assessment. Moreover, the operation of wide spread water-pipe network often causes a significant increase in DBPs in water delivered directly to the customer. The drinking of water polluted with disinfection by-products poses a threat to public health as it can be responsible for tumour diseases of kidneys, an urinary bladder, intestines and a liver; such skin diseases as: irritations, dryness and breaks, lowering skin immunity to infections caused by fungi and yeast as well as headache. Additionally, water with DBPs is very dangerous for pregnant women, infants, elderly people and people with injured immune system [4]–[7]. These facts speak for themselves, hence the World Health Organization, based on the International Agency for Research for Cancer proposal, qualified chloroform (the most often generated THM in water after chlorination) to B2 group. That group contains probable carcinogens. Chloroform classified as a human carcinogen in legislative acts in Poland belongs to the carcinogens of the third category (Decree of Health Minister of February 28, 2005 according to the list of dangerous substance together with their classification and marking – Official Journal no. 201, item 1674, 2005).

The discovery of trihalomethanes [8], [9] in chlorinated water in 1974 and a significant development of analytical methods, especially gas chromatography, electron capture detector and mass spectrometry, inclined the scientists to carry out in-depth and extensive research on the mechanism of those compounds' formation, factors affecting this formation, identification of their precursors, and also their negative influence on live organisms. The review of literature showed [1], [2], [10]–[13] that a few trials of constructing a mathematical model for determining the level of THM formation with time have been taken so far. The models made are generally based on data generated in a laboratory scale. Only a few of them have been constructed under real conditions of water supply network. The first who explored the possibility of determining THMs based on the parameters of water quality and reaction conditions were Amy, Chadik and Chowdhury. In their model, the quantity of predicted concentration of *PTHM* (μmol/dm^3) was represented by the function of total organic matter (TOC (mg C/dm^3)), UV absorbance at 254 nm, chlorine dose (D_{Cl_2} (mg Cl$_2$/dm^3)), the time of the water contact with residual chlorine (*t* (h)), water temperature (*T* (ºC)) and pH as

well as the concentration of bromide ion (Br (mg Br/dm^3)) [10]:

$$PTHM = 0.00309(UV \cdot TOC)^{0.44}(D_{Cl_2})^{0.409}(t)^{0.205}(T)^{1.06}(pH - 2.6)^{0.715}(Br + 1)^{0.0356}.$$

This mathematical formula was derived based on the research into model solutions with humic substances. Therefore it should be verified under real operating conditions of water supply systems. However, it is not a simple task and it causes practical difficulties in using such a formula for predicting THMs' level in every-day water supply practice.

2. APPLICATION OF RAMAN SPECTROSCOPY

The progress in water technology is strictly connected with the development of not only basic sciences, but also with the implementation of new technologies, computerization and more and more sensitive equipment and analytical methods for the research of molecular systems and their structures. Such structural research is based on infra-red absorption spectroscopy and Raman spectroscopy with its numerous varieties (RDS – Raman Difference Spectroscopy, CARS – Coherent Anti-Stokes Raman Spectroscopy, ROA – Raman Optical Activity, SERS – Surface-Enhanced Raman Spectroscopy, MOLE – Molecular Optical Laser Examiner). Nowadays the SERS technique is used in biomolecular examinations. It was used for the first time in 1980 by COTTON [14] and his team in the analysis of the Raman spectrum of concentrated solutions of cytochrome and myoglobin. At the same time, KOGLIN et al. [15] carried out analogical experiments in order to provide information on the structure of nucleic acids. Due to the positive effects of their research, Otton and Koglin began the era of using CARS and SERS techniques for the analysis of organic substances in various environments, including water.

The SERS technique is based on the intensity growth of the Raman bands of the substance tested, which is adsorbed and condensed on a metal electrode, mainly silver one, in solution. This way, the spectrum grows in intensity by 10^3–10^6 times which allows very diluted solutions to be tested [16].

Nowadays the Raman spectroscopy techniques are widely used for structural identification of organic compounds found in aquatic environment. For example, the resonant Raman spectra of photosynthetic pigment of chlorophyll occurring in plants, in photosynthetic bacteria or in blue-green algae were many times obtained. LUTZ [18], LUTZ and KLEO [19] and HOXTERMANN et al. [17] analyzed the Raman spectra of chlorophyll in vitro and in vivo in plants photosynthetic systems, in chloroplasts, in blue-green algae and in bacteria. Water and other chemical compounds different from chlorophylls in photosynthesis centers make classical spectra significantly richer which makes their interpretation more difficult. Therefore, the use of Raman resonator spectra and CARS spectra offers the possibility of eliminating the hindrances men-

tioned above, making it possible to interpret particular components of complex photo-synthetic system selectively and in detail (table 1). SERS makes it possible to eliminate disadvantageous fluorescence in the Raman research.

Wavenumbers and oscillation bands for resonance Raman spectra of chlorophyll

Wavenumbers (cm^{-1})	Type of vibrations
1620–1720	ν_{-COOH}
1520–1620	vibrations of the methylene bridge ($-CH_2$)
1200–1400	ν_{C-C}, ν_{C-N}
200–400	Mg–N stretching

ν – stretching vibrations.

The literature review of using Raman spectrophotometry in biological or medical research [14]–[19] encouraged the authors of this paper to apply those techniques of identifying organic compounds to the evaluation and characterization of the precursors of THMs in natural waters. Those waters are the source of water-supply systems.

3. EXPERIMENTAL PROCEDURES AND METHODS

Many papers [20]–[22] point out that one of the parameters of potential reactivity of organic matter with chlorine and other oxidants can be their absorbance in ultraviolet. For example, the values of the absorbance at 254 nm wavelength (standard measurement) and 272 nm wavelength testify to the presence of activated aromatic rings and unsaturated double bonds in the structure of organic compounds. Thus, the absorbance value can be very significant in the evaluation of water treatment efficiency. Those processes are connected with the elimination of organic fouling. Therefore the evaluation of organic matter removal (expressed by TOC, COD and UV_{254}) related to the level of THM formation in treated water at the output of water treatment plant (WTP) as well as in the distribution subsystem was made for three water supply systems: in Kraków (Raba WTP), in Wrocław (Mokry Dwór WTP) and in Kobiernice (Czaniec WTP). The research was based on a laboratory qualitive analysis of the parameters of both raw and treated water carried out during 2000–2005. Water supply system exploitation practice shows that insignificant amounts of organic matter (table 2) remain in treated water until the level required by the Decree of Health Minister is reached which guarantees a significant content of THM in customer's water.

Selected parameters of output water quality

Factor		WTP		
		Raba	Mokry Dwór	Czaniec
Chemical oxygen demand ($mg\ O_2/dm^3$)	average	1.76	2.43	1.30
	minimum	0.00	1.31	0.50
	maximum	3.2	3.90	2.30
TOC ($mg\ C/dm^3$)	average	2.13	3.16	1.68
	minimum	1.2	1.92	0.69
	maximum	3.4	4.71	2.52
$UV_{254\,nm}^{1\,cm}$	average	0.025	0.039	0.024
	minimum	0.000	0.006	0.00
	maximum	0.040	0.079	0.076
Σ THM ($\mu g/dm^3$)	average	6.01	8.97	7.70
	minimum	0.00	0.40	3.30
	maximum	25.2	59.7	17.9

In view of the above, some research has been undertaken as the Research Project [23]. It is focused on looking for the parameter of water quality that will be the best factor of predicting THMs concentration in water-pipe network. This parameter would allow the operator of Water Treatment Plant to determine the range of water quality change in water supply system, based on raw water analysis at water intake, in the function of THM formation as a side-effect of water chlorination. In 2006, a series of laboratory tests were carried out in order to analyse the Raman spectra that represent organic compounds (precursors of DBPs) controlling the level of THM formation in water.

The levels of TOC and PTHM in water samples

Sample symbol	Water supply system	Date	Concentration level	TOC ($mg\ C/dm^3$)	PTHM ($\mu g/dm^3$)
W_1	Kraków	24.08.2006	20×	2.11	89.6
W_2	Kobiernice	18.09.2006	50×	1.74	152.1
W_3	Kobiernice	25.09.2006	50×	3.66	157.3
W_4	Wrocław	06.12.2006	50×	3.04	121.0
W_5	Wrocław	15.12.2006	50×	2.11	72.2

The water samples for the tests were taken from rapid filters of a technological system in three water supply systems: Kraków, Wrocław and Kobiernice. The water samples were concentrated to obtain the volumes 50 times smaller (for W1 water sam-

ple for Kraków, 20 times smaller) in a flow system with a membrane. In the water samples, TOC was determined (according to PN-EN-1484-1999) and then also the concentration of PTHM (according to 75-PB-NJL-W-06), table 3. In analytical procedures of PTHM determination, a dose of 10 mg/dm^3 chlorine was used at the maximum reaction time of 72 hours. In those samples, the concentrations of the remaining chlorine (according to PN-ISO 7393-2:1997) and THM were determined after 0.5, 1, 2, 8, 24, 48 and 72 hours of reaction.

The tests were carried using the following analytical and measuring methods:

• Raman spectrometry: spectrometer manufactured by BIO-RAD, model FTS 175C, with Raman attachment equipped with Ng-YAG laser (1024-nm excitation line), laser power of 235 mW, 180 scans, 90° geometry, measuring range of 500–4000 cm^{-1}, resolution of 8 cm^{-1},

• SERS surface: the SERS surface was obtained by silver reduction with dextrose in alkaline solution: one drop of 26% NH$_3$ was added to 5 cm^3 of 10–3 M water solution of AgNO$_3$. Then 3 cm^3 of 1% dextrose solution were added. The solution obtained was mixed and immediately poured into test tubes, ~7 mm in diameter, with bulbs blown on their ends. A silver layer covers a vertical half of the bulb surface. After the reaction had finished, the surface was washed with deionized water 50 times.

• Concentration of water samples: membrane model: TW 30-2012-75 GDP, series No. JD 0701210, with pump Booster Pump PJ-V 6005.

• Determination of TOC: TOC analyser, 5050 Shimadzu.

• Determination of THM concentration: gas chromatograph HP-5890GC/5970MSD.

• Determination of chlorine: PC compact chlor photometer.

4. RESULTS AND DISCUSSION

On the Raman spectra of the samples tested (figure 1) the signals appear at 1826 cm^{-1} and 1703 cm^{-1} wave numbers characteristic of C=0 stretching vibrations in carbonyl group, probably of α-amino acid. The signal at 1530 cm^{-1} can be a result of C=C stretching vibrations in an aromatic ring. The signals at 514 cm^{-1}, 153 cm^{-1}, 103 cm^{-1} and 352 cm^{-1} correspond to deformation vibrations of a COO$^-$ group in a plane and to the torsion movements in the NH$_3^+$ system. A signal at 225 cm^{-1} is a results of Ag–Cl interaction, that is, the interaction between chlorine and SERS background. This testifies to the presence of chlorides in the water samples tested. A more accurate analysis of spectra is not possible because the number of signals is too small. However, it should be added that the spectrum shapes and their quality are comparable and in some cases even better compared with those reported so far [24]–[26].
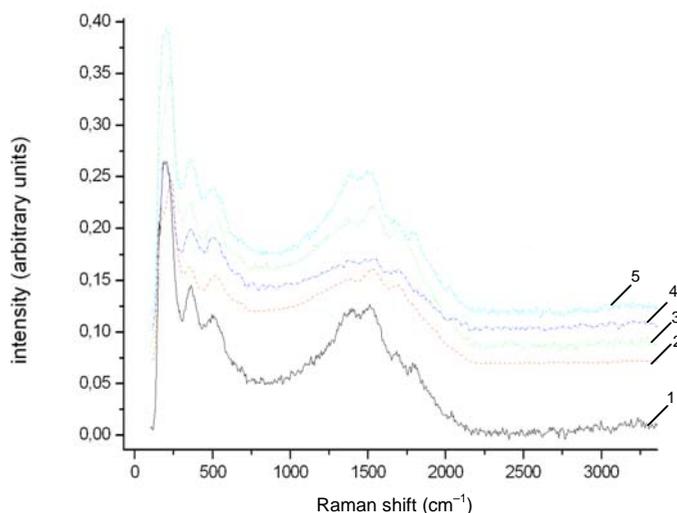
Fig. 1. The RM-SERS spectra of the samples analyzed
(for the explanation of the symbols see table 3)
1 – W1, 2 – W2, 3 – W3, 4 – W4, 5 – W5

It can be observed that the spectra recorded (figure 1) do not significantly differ from each other, but the ratio of signals' intensity is different, which can testify to a various compactness of particular functional groups in the samples analyzed. If the ratio of signal intensity at 1530 cm^{-1} corresponding to aromatic rings (which are quite stable elements of the structure) was juxtaposed with signal intensity at 225 cm^{-1}, this ratio would be helpful (after carrying out some detailed research) in assessing chloride content in particular samples. As is widely known, chloride concentration affects the level of THM generated in water. The ratio mentioned above can be a useful techno-logical parameter. In a further analysis, the correlations between the ratio of vibrations A_{Cl}/A_{Ar} intensity in RM-SERS spectra and the PTHM potential were found. The analysis carried out showed a great correlation between the variables tested, being corroborated by the correlation coefficient equal to 0.9887 (figure 2).

Table 4

Vibration intensity ratio (A_{Cl}/A_{Ar}) in RM-SERS spectra

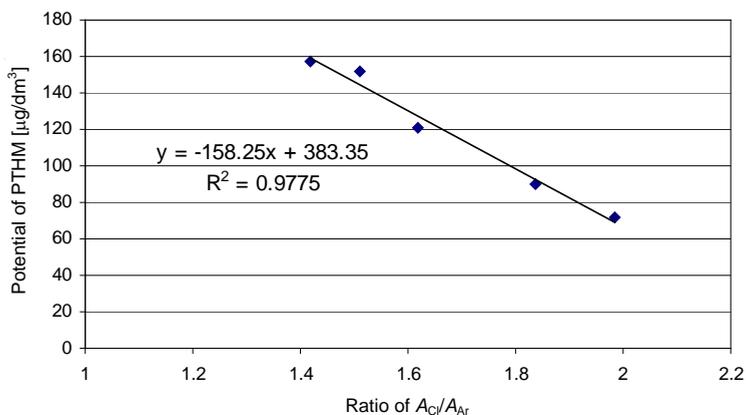| Sample symbol	A_{Cl}/A_{Ar} ratio
W_1	1.837
W_2	1.512
W_3	1.417
W_4	1.618
W_5	1.986

Fig. 2. Vibration intensity ratio (A_{Cl}/A_{Ar}) in RM-SERS spectra versus potential of PTHM
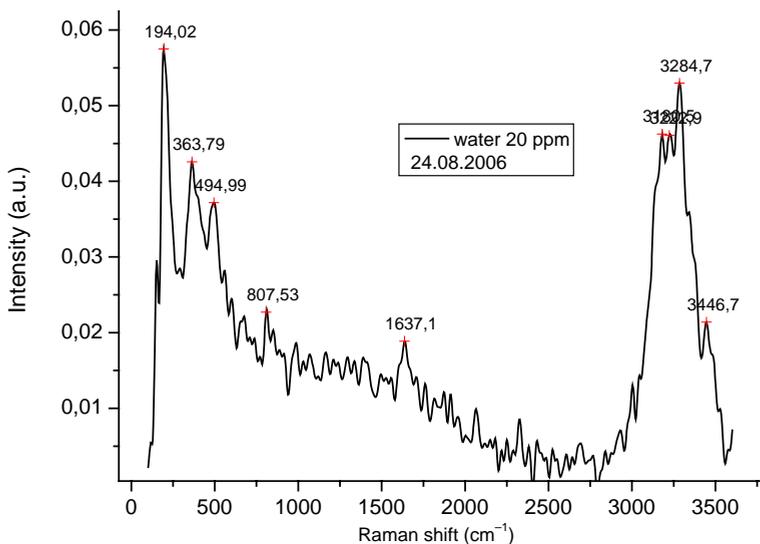

Fig. 3. Raman spectra of water sample W1 taken from technological system of Raba WTP

Traditional Raman spectra (figure 3) were recorded only for the W1 water sample from a technological system of the Raba WTP water-supply system. The signals corresponding to consecutive peaks can be characterized as follows:

• Peaks at 3446.7 cm^{-1}, 3284.7 cm^{-1} and 3222.9 cm^{-1} correspond to asymmetrical vibrations stretching N–H in primary amines.

• Peaks at 3180.5 cm^{-1} correspond to vibrations stretching C–H in aromatic ring.

• Peaks at 1637.1 cm^{-1} correspond to vibrations stretching C–C in aromatic ring (a singular signal, so the ring can be condensed).

• Peaks at 807.53 cm^{-1} correspond to "breathing" vibrations in a heteroaromatic ring, where heteroatom is nitrogen.

• Signals at 494.99 cm^{-1}, 363.79 cm^{-1} and 194.02 cm^{-1} correspond to vibrations connected with electronic displacement in a large system of conjugated π vibrations built in a skeleton of allyl or heteroaromatic molecule [27].

As can easily be noticed, traditional Raman spectrum provides much more information than SERS spectrum. However, it is very difficult to obtain that spectrum for very diluted samples of water. It is worth mentioning that its intensity is, on average, 11 times lower than the SERS spectra intensity.

5. CONCLUSION

Our preliminary tests undertaken in order to record the Raman spectra of water from technological treatment plants with three various water supply systems have brought about satisfactory results. These spectra allow the functional groups of organic compounds to be identified. The results obtained encourage us in our research on a wider scale.

A high correlation between the ratio (A_{Cl}/A_{Ar}) of vibrations intensity in RM-SERS spectra and the PTHM potential enables an assumption that the above relation can be a significant functional dependence useful in determining THM concentration in a water distribution network in a very simple and fast way. However, further numerous tests are necessary to confirm this dependence, based on a comprehensive numerical database allowing its statistical verification.

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