

Total Trihalomethane Measurement using a Reagentless and Contactless Analyser developed by Multisensor Systems Ltd.

Krishna C. Persaud, School of Chemical Engineering and Analytical Science, The University of Manchester, Manchester, UK krishna.persaud@manchester.ac.uk

Abstract

Awareness of risks associated with THMs in drinking water has increased steadily over the course of the last three decades. A number of technologies have been developed to provide Water Treatment Plants with the tools to perform on-line monitoring of THMs in drinking water. This article describes the state of art of on-line THM analysers and focuses on the e-nose based system. Data from real-life installations are presented with a detailed explanation of the measurement process.

Introduction

Chlorine has been used for disinfecting water around the world for over a century. It is easy to manufacture and store and the disinfected water is left with a level of chlorine that keeps it disinfected within the distribution network until it reaches the tap.

One of the main benefits of water chlorination is the drastic reduction of infection by bacterial, viral and parasitic diseases.

The main disadvantage of chlorine disinfection is the potential for the **formation of trihalomethane compounds (THMs)**. There are a number of other disinfection methods, such as ozone or UV treatment which do not present this problem, however, they are all significantly more expensive to implement and run. This means chlorination continues to be the most common technique for larger operations.

THMs are generated during the disinfection of water through the reaction of chlorine (or chlorine dioxide/hypochlorite) with **naturally occurring organic matter (NOM)**[1] present in the water, such as humic acid and fulvic acid. The concentration of THMs in the water will depend upon on the amount of chlorine present, the contact time of the chlorine with the organic matter, the amount of organic matter present, the concentration of bromide compounds in the water, the pH and the temperature .

The compounds that lead to the formation of THMs, "**THM Precursors**", are dissolved organic matter which naturally occur in water. This organic matter contains a heterogeneous mixture from the breakdown of organic materials (plants, bacteria etc.). Studies suggest that compounds containing aromatic structures are often the precursors for THM formation, however the mechanism is complicated by a number of additional factors including:

1. The distinctive chemical characteristics of the precursor solution. These tend to lead to chloroform being formed as the most abundant by-product as the majority of water sources do not contain significant concentrations of brominated species.
2. Seasonal dependencies connected to the life cycles of flora and fauna in the water source.
3. Residency time of chlorine in in the water source. For example, during the "first rain", a high concentration of organic compounds which have

accumulated in the ground are washed into the river. This leads to higher levels of THMs[2]. Moreover, the longer the chlorine has to interact with the organic compounds results in demand patterns influencing the levels of THM.

4. Hydrological and biogeochemical processes.

THMs and Risks to Public Health

Studies concerning the formation of Trihalomethanes as a consequence of adding chlorine to water were first carried out in the United States in the 1970s. In these experiments gas chromatography and mass spectrometry were used on water samples. Subsequent epidemiological studies associate exposure to disinfection by-products, mostly THMs, with health effects such as bladder cancer and birth defects in newborns of exposed mothers.[3]

Studies into bladder cancer found an increased risk with long exposures to THM (more than 30 years). The US EPA classifies chloroform and bromoform as probable carcinogens and dibromochloromethane as a carcinogen for humans under certain exposure conditions.

According to the World Health Organization (WHO), the potential risks posed by THMs are greatly outweighed by the dangers of not chlorinating drinking water supplies. The risk posed by THMs is considered long-term, since it would require the consumption of water over a lifetime, to create problems. According to the WHO, THMs lead to one case of cancer per 100,000 people who consume water for a minimum period of 70 years. In the European Union, the risk is considered to be 1 case in one million.

Some recent studies have shown a strong association between bladder cancer and THMs in Europe. The research associated one in 5 bladder cancers studied to THMs.[4]

As an alternative, some developed countries are using sodium chlorite as a replacement for sodium hypochlorite, thus avoiding the production of THM in the purification of water.

THMs can be absorbed into the human body through several routes: **ingestion of tap water, inhalation of evaporated THMs and dermal absorption.** Many daily activities such as bathing or showering and swimming in the pool can also contribute to the total exposure to THM.

Current regulations and limits

The WHO provides recommended maximum guide values for individual THMs in water for human consumption. The guide values represent the maximum concentration of a compound that should not result in any significant risk to health through lifelong consumption. These are:

- Chloroform: 300 µg/L
- Bromodichloromethane (BDCM): 60 µg/L
- Dibromochloromethane (DBCM): 100 µg/L
- Bromoform: 100 µg/L

According to the WHO, calculation of the combined toxicity of all THMs can be achieved using the following equation:

$$\frac{C_{bromoform}}{GV_{bromoform}} + \frac{C_{DBCM}}{GV_{DBCM}} + \frac{C_{BDCM}}{GV_{BDCM}} + \frac{C_{chloroform}}{GV_{chloroform}} \leq 1$$

Where C is the concentration and GV is the guideline value.

Current State of Monitoring Technology

The level of awareness of control and **monitoring technology for THMs** in drinking water varies significantly around the world, despite strengthening regulations globally. In some places THMs are considered not an important (or even known) issue.

Many other water treatment plants rely on a bi-annual or monthly laboratory analysis of the THM levels. This usually consists of sampling the water, transporting it to a laboratory, analysing it via Gas Chromatography / Mass Spectroscopy (GCMS) techniques. The elapsed time for this approach can be **up to two weeks**.

When THM levels are consistently and historically low (i.e. < 10 ppb of Total THMs) this approach is generally thought to be sufficient to comply with current regulations. This approach means that the operators are relying on a very **limited sample** to determine the overall levels, however, which has obvious disadvantages. A spot sample every month or six months is not likely to be representative and will almost certainly miss random fluctuations and unusual peak activity.

Finally, there are plants/regions where, due to the characteristics of the source water, THMs are a significant issue and need to be closely monitored. For these applications it is very important to strike a balance between the accuracy of the system, the cost of the purchase, the running costs and the ease of operation. This level of analysis is usually necessary when total THM concentrations are on average around 30 ppb. This is because there is always a risk of the **THMs exceeding** the 80 - 100 ppb limit and it is in the interest of the water treatment plant (WTP) to keep levels as low as possible.

Following international trends, regulation of THM concentrations is likely to become stricter in the future, so whilst 100 ppb is on the limit of acceptability today (2019), in many parts of the world it is very likely that this will not be the case in a few years time when legislators and consumers will expect much higher standards of water quality.

Several different technologies are available on the market for **THM analysis**. Each system has strengths and weaknesses. Particular interest should be given to the following criteria before purchasing an instrument:

- Level of maintenance
- Cost of ownership

- Ease of use
- Accuracy/Reliability of the measurement
- Measurement frequency

Purge Trap with Colorimetric technique

This is an **on-line technique** that can give a reading every 4 hours or more.

In this method the instrument extracts THMs from the water sample using an adsorbent material and concentrates them over time (known as purge and trap). The THMs are subsequently desorbed into a proprietary reagent mixture that generates a coloured solution which is measured by spectroscopy (colorimetry).

The system is very expensive to run, primarily due to the cost of reagents, and can be up to tens of thousands of dollars per year. The system is also slow and is not able to give measurements every hour. The method also means that the instrument has an inherent complexity and many different components, which can lead to expensive repairs and ongoing issues.

Purge/Trap – Gas Chromatography – Surface Acoustic Wave Detector

This is a laboratory instrument which has been adapted for on-site application.

The analyser is an integrated purge-and-trap system connected to a compact gas chromatograph column and a surface acoustic wave (SAW) detector. The system requires helium gas, an external manual calibration and needs to be operated by skilled technicians.

Also, because of the nature of the technology it is impractical to use it as an on-line system: the operator will have to go on site, take a sample, wait 30 minutes and get the result.

Membrane Permeation – Gas Chromatography – Electron Capture Detector

This is an experimental method, not yet widely accepted in industry

In this kind of system, THMs are extracted from a water sample into a carrier gas. This is achieved by forcing the water through a permeable membrane, then adsorbing the THMs onto a trap, followed by separation on a GC column. Finally, the trihalomethanes are detected by an Electron Capture detector. Using a gas chromatograph for online monitoring generates problems such as stability, retention times, calibration and system validation.

Extraction through a semi-permeable membrane has a huge impact on sample matrix including ionic strength, pH and temperature. Fouling of the membranes is a significant problem that can arise in this kind of system. The use of the radioactive element ^{63}Ni in the detector may be problematic and requires careful monitoring. The system also requires an expensive carrier gas.

Fluorescence Detector with Membrane Permeation and Chemical Reaction

This is an experimental method, not widely accepted in the industry.

In this method, the trihalomethanes move from the water into the chemical reaction mixture through a semi-permeable membrane. A continuous flow of reagents is used and the fluorescence generated by the reaction of the THMs with alkaline nicotinamide is measured. This system uses a large volume of reagents and extraction through a semi-permeable membrane has a huge impact on the sample matrix including ionic strength, pH and temperature. As with a previous method, fouling of the semi-permeable membrane is a significant problem that could arise in this kind of systems.

Process gas chromatograph (GC) with TID (Thermal Ionization Detector) or PID (Photo Ionization Detector)

This system is a traditional process gas chromatograph with TID or PID technology. This technology is highly accurate and allows for speciation between the four THM

compounds. Given the complexity of the instrument it demands a high purchasing cost and frequent recalibration (once per month). The instrumentation requires a source of compressed air and must be operated by a skilled technician.

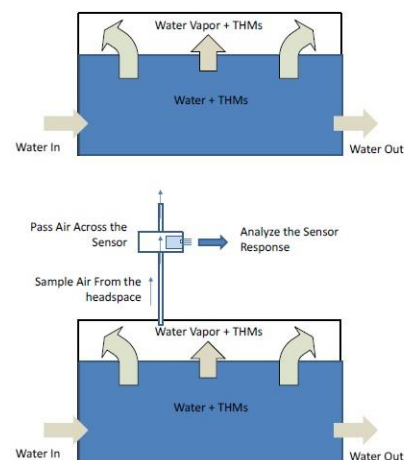
Electronic Nose

Artificial olfactory systems are of growing importance for the development of modern industry and raising the quality of everyday life. Their application increases manufacturing efficiency and environmental safety and makes it possible to control the quality of many products used in medicine and housekeeping. The concept of the electronic nose (EN) is one of the most efficient approaches for rapid screening of complex mixtures[5].

In most cases the EN involves the following functional elements: (i) a sample preparation and injection module that ensures contact between the sensors and sample; (ii) a recovery system that is responsible for cleaning the sensor and measuring cell; (iii) a data recording unit that records sensor signals and transforms them to a form acceptable for further processing; (iv) a data processing system that executes classification, identification and other operations, depending on the assigned task.

Principle of Operation of the MS2000 Total THM analyser

The UK based company, Multisensor Systems Ltd., has developed an e-nose based analyser for the measurement of Total THMs in water. In its implementation of the EN technology this system samples headspace gases from above a moving body of water in a



sample tank before passing these gases over sensors sensitive to the total concentration of THM compounds.



The advantage of the electronic nose technology is that it lends itself to on-line operation, is robust in a variety of environments and it does not use any reagents. The sample presentation is also simple, reducing the possibility of fouling. Being a non-contact technique, cleaning of the sensors is not necessary.

Henry's Law dictates that the concentration of THMs in the gas of the headspace is proportional to the concentration of the THMs dissolved in the water. The MS2000 works by passing a continuous flow of water through the sample tank as shown in the image below. The volatile components in the water will pass into the headspace above the water until an equilibrium is reached. A sample of the headspace gases is then passed across sensors

in the MS2000 THM Analyser sensor head, which respond to the THMs in the headspace. This response is then analysed by the instrument and a concentration value is generated based upon the relationship between the concentration present in the headspace and that in the water.

Field data from Spain

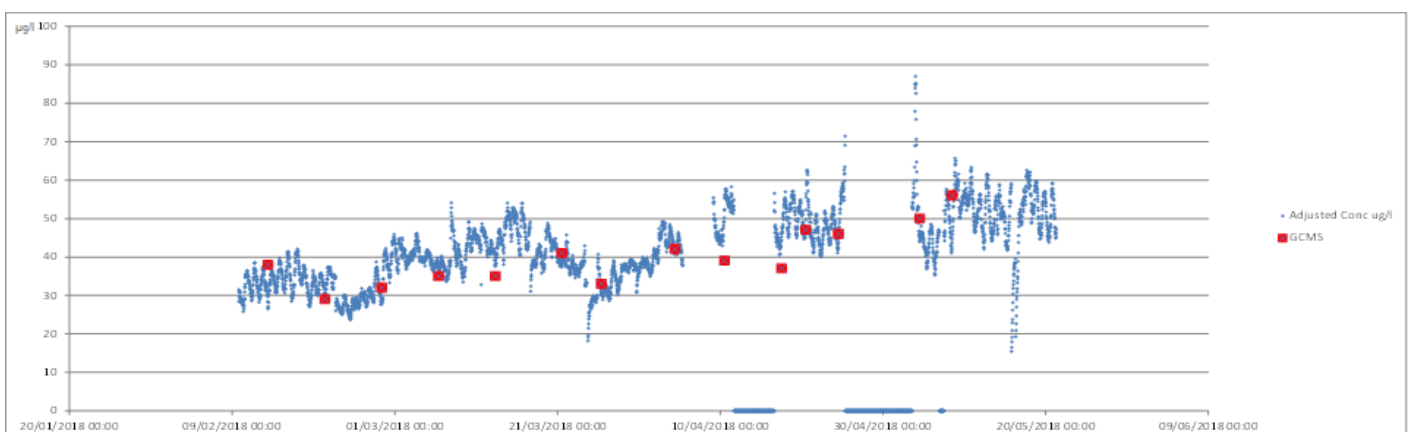
With many installations around the world Multisensor has been able to collect some relevant data from field installations and trials.

The graph on this page was recently generated (2018) using data from an MS2000 Total THM analyser installed in a drinking water treatment plant in the east of Spain.

The local health authority had warned that the THMs level in the water supplied to households in the region was above or near the limit imposed by the law. For this reason, the local WTP was asked to install an on-line THM monitoring system and implement improved control of the process.

In this graph we can see a comparison between the data generated by the instrument (blue dots) and the corresponding GCMS analysis (red dots) which was done as a comparative test.

The data covers a 6 months period (from January to June) and we can see an upward trend in the levels of THMs as well as a good correlation between the GCMS results and the Total THM concentration reported by the



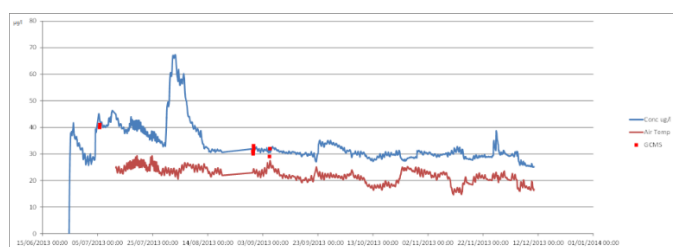
analyser.

In this specific case the customer was highly satisfied with the results and has planned the purchase of other 4 units that will be deployed throughout 2020 at 4 other sites in the area.

Data from France

Another more limited set of data can be observed here below.

This was produced in France in 2015 with the previous version of the TTHM monitor. We can see good comparisons with the few GCMS data points that were measured. Furthermore, we can see a significant peak in TTHM levels that were completely missed by the random GCMS sampling that the online monitoring by the MS2000 detected.



Conclusions

The monitoring of THMs in drinking water is becoming more important globally as drinking water standards increase. The monitoring of THMs cannot be left as a regulatory “chore” as it is vital in maintaining public confidence in water supply companies. There are many considerations in deciding which type of THM analysis technique should be used at a particular site. There are varying approaches with differing outcomes in terms of price, running costs, performance and reliability. Electronic nose technology has established itself as a cost effective method of monitoring THMs when measured against alternative techniques and is gaining growing acceptance in the market.

References

- [1] H. Wong, K. M. Mok, and X. J. Fan, “Natural organic matter and formation of trihalomethanes in two water treatment processes,” *Desalination*, 2007, doi: 10.1016/j.desal.2006.05.031.
- [2] E. Alkhatib and R. Peters, “Wet weather impact on trihalomethane formation potential in tributaries to drinking water reservoirs,” *Environ. Monit. Assess.*, 2008, doi: 10.1007/s10661-007-9823-y.
- [3] M. J. Nieuwenhuijsen, M. B. Toledano, N. E. Eaton, J. Fawell, and P. Elliott, “Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: A review,” *Occup. Environ. Med.*, vol. 57, no. 2, pp. 73–85, 2000, doi: 10.1136/oem.57.2.73.
- [4] I. Evlampidou *et al.*, “Trihalomethanes in Drinking Water and Bladder Cancer Burden in the European Union,” *Environ. Health Perspect.*, vol. 128, no. 1, p. 017001, Jan. 2020, doi: 10.1289/EHP4495.
- [5] K. C. Persaud, P. Wareham, A. M. Pisanelli, and E. Scorsone, “Electronic Nose’- New condition monitoring devices for environmental applications,” in *Chemical Senses*, 2005, doi: 10.1093/chemse/bjh210.