APPLICATION TO THE MALASPINA RESEARCH FUND

1. Date of Submission: **Nov. 15th, 2002**

2. Project Title: **Rapid Measurement of Dis-Infection By-Products in Drinking Water**

3. Submitted by: **Dr. Erik Krogh* and Dr. Chris Gill**

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4. Project Summary:

This project aims to develop a novel method for the detection of an important class of potentially harmful molecules known collectively as dis-infection by-products (DBP's). These molecules are formed unintentionally depending on the levels of pre-cursor species present in source waters and are currently the focus of a great deal of toxicological research. We propose to develop membrane introduction mass spectrometry (MIMS) as a rapid measurement device capable of real-time identification and ultra-low level detection of DBP's.

5. Research Abstract:

The work to be conducted by the successful funding of this proposal will be to evaluate the appropriateness of MIMS as a real time monitor for DBP's produced by oxidation based water purification processes (chlorination, ozonation and chlorine dioxide) in the presence of dissolved humic materials from Vancouver Island as well as other regions. In addition to the MIMS work, the role of several other chemical determinants in the formation of DBP's will be addressed by this work: (1) quantification of humic materials (HM's) naturally present in coastal watersheds (including Nanaimo water district) using TOC analysis; and (2) characterization of these HM's using UV absorption and fluorescence emission spectroscopy; (3) the role of naturally occurring interferents (i.e. carbonates) and naturally occurring accelerants (i.e. bromides) will be monitored using off line measurement before/after treatment(s) by ion chromatography.

The ultimate aim of this research is to provide a new analytical tool that will contribute to the maintenance of safe pathogen-free drinking water supply, while minimizing unintentional risks due to chemical DBP's.

6. Statement of potential impact and significance of research:

The importance of dis-infection to protect drinking water from pathogenic micro-organisms cannot be understated. It is estimated that chlorination alone is responsible for saving hundreds of thousands of lives world wide annually[1]. A number of the dis-infection strategies are employed globally and many of these have been shown to lead to the formation of minute quantities of Dis-infection By-Products (DBP's).[2,3] This research proposal is in direct response to the growing concern over adverse health affects of ultra-low concentrations of DBP's.[1] The current DBP regulations are based on aggregate measure class sums, such as total trihalomethanes (THM's) and sum of haloacetic acids (HAA's)[4,5]. It is anticipated that future regulations will target individual DBP's suspected to be the largest contributor to adverse affects, such as bromodichloromethanes.[4] Some researchers have recently observed adverse effects of certain DBP's in aquatic organisms at concentrations below commonly available detection limits (Tony Farrell, personal communication, 2002). This presents a difficult situation to regulatory bodies and provides an impetus for the development of advanced analytical capability.

As research into both the short and long term affects of DBP exposures intensifies over the next decade, the ability to directly analyze these compounds in various water supplies, as well as blood and urine samples will present a tremendous advantage. This is particularly relevant to epidemiological and toxiciological studies. The ability to unequivocally identify and quantify trace levels of DBP's by a direct analysis technique such as MIMS will contribute to our understanding of the factors that control their formation, distribution and fate. Rapid screening techniques afforded by MIMS technology could be developed to provide 'real-time' data, which will allow water purveyors operational control of water purification processes and thus minimize DBP formation.[6]

7. Detailed Summary of Research Project

Introduction

Chlorination and other chemical disinfectants have long been recognized as effective treatments for the removal of pathogenic micro-organisms from drinking water supplies. However in some waters, particularly those high in natural organic matter (NOM), trace quantities of a number of disinfection by-products (DBP's) have been observed. Although several hundred DBP's have been identified,[1] most are relatively small, non-polar organic molecules and are well suited to any membrane introduction mass spectrometry (MIMS) as indicated by the major contributors listed in Table 1. Other DBP's identified in treated waters include those ionic species listed in Table 2.

Table 1: Dis-Infection By-Products Potentially Measured by MIMS

Compound Classification	**Representative Molecules**
Chloromethanes	CH_3Cl, $CHCl_3$, CH_2Cl_2, CCl_4
Bromochloromethanes	$CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$
Chloroacetonitriles	$ClCH_2CN$, Cl_2CHCN, Cl_3CCN
Chloramines	NH_2Cl, $NHCl_2$, NCl_3
Chlorophenols	2-chlorophenol, 2,4-dichlorophenol
	2,4,6-trichlorophenol

Table 2: Ionic Dis-Infection By-Products Investigated by Ion Chromatography

Bromate	**Chlorite**	**Haloacetic acids**
BrO_3^-	ClO_2^-	$ClCH_2CO_2H$
		Cl_2CHCO_2H
		Cl_3CO_2H

Epidemiological studies suggest that long term exposure to certain DBP's is correlated to increased numbers of stillbirths[7] and other adverse health impacts[8]. Concern over the formation of DBP's is furthered by the potential that some of these molecules are suspect carcinogens[9] (Table 3). It is suspected that some of these species may be detrimental at exceedingly low concentrations (in the parts-per-billion range).

Table 3: Classification of Chlorination DBP into Cancer Groups

Compound Name	Molecular Formula	Cancer Group
Chloroform	$CHCl_3$	B2
Dichlorobromomethane	$CHCl_2Br$	B2
Dibromochloromethane	$CHClBr_2$	C
Bromoform	$CHBr_3$	B2
Dichloroacetonitrile	$CHCl_2CN$	C
Dibromoacetonitrile	$CHBr_2CN$	C
2-chlorophenol	C_6H_4ClOH	D
2,4-dichlorophenol	$C_6H_3Cl_2OH$	B2

group B: probable human carcinogen (B1 epidemiological studies, B2 animal studies)
group C: possible human carcinogen
group D: not classifiable

Although disinfection by-products are correlated with NOM and naturally occurring bromide ion, the mechanisms of the reactions leading to DBP's are not precisely known.[9] This is partly due to the fact that it is problematic to carry out formation studies at the extremely low concentrations with current analytical techniques. Other work being carried out in our lab, involves the quantification and characterization of NOM from several coastal watersheds. We have also been involved in studies aimed at understanding the factors affecting both photochemical and microbial degradation of NOM. Since NOM includes a large assemblage of organic molecules with varying molecular structures depending on the vegetation of surrounding watershed, levels of algae present and time of year, we anticipate that the evolution of MIMS technology will allow us to investigate the distribution of DBP's as a function of quantity and type of NOM.

Membrane introduction mass spectrometry (MIMS) operates by placing a sample at a semi-permeable membrane interface. An inert gas stream flows on the inside of the hollow fibre membrane and is introduced directly into a quadrapole ion-trap mass spectrometer, which operates at relatively high internal pressures. Volatile and semi-volatile organic molecules pervaporate across this membrane interface and are sorted on the basis of their mass and quantified by a sensitive ion collector. This method is rapid, inherently simple and does not suffer from background contamination due to sample handling.[10] We believe that MIMS technology is particularly well suited for ultra-trace level quantification of the DBP's listed in Table 1.

Recent initial results from work conducted by our group (Gill MRF Final Report 2002, Gill JSRC Final Report 2001) have demonstrated the use of hollow fiber MIMS as a powerful analytical technique for several molecules including trichloromethane (chloroform). This work demonstrated direct, real time measurements with detection limits of approximately 1 part-per-trillion (pptr = 1 ng/L) and rise times of approximately 2 minutes. Figures 1 and 2 below illustrate these preliminary findings.

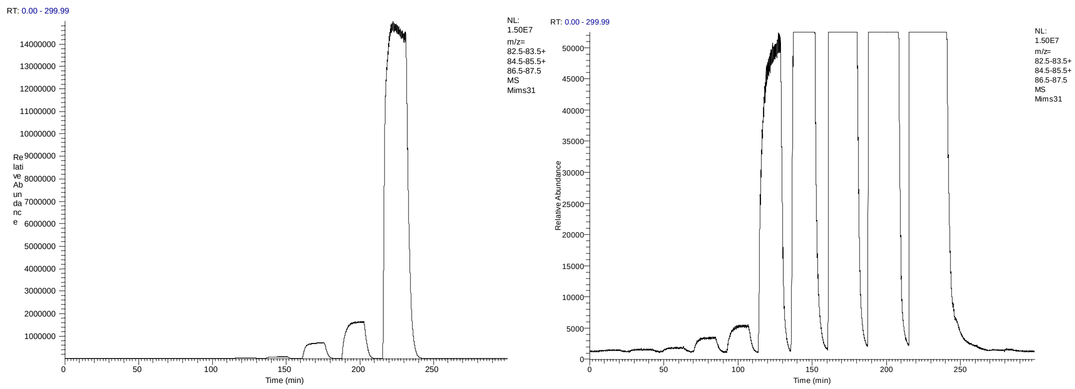
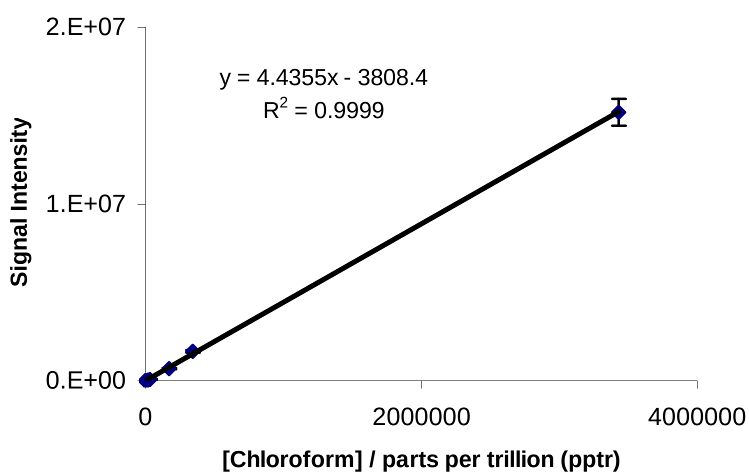


Figure 1: MIMS instrument response for aqueous chloroform standards. The left trace shows the raw signal at full scale, whereas the right trace has been vertically expanded to show analytical signals for trace components not evident at full scale.



conc (pptr)	Intensity
171	200
343	350
686	600
1713	2250
3430	4150
17130	50900
34300	89400
171300	698400
343000	1668400
3430000	15198400

Figure 2: Typical calibration curve (ion count vs concentration) for chloroform. Concentration of chloroform measured ranges from 171 pptr to 3 ppm.

Proposed Research

The work to be conducted by the successful funding of this proposal will be to evaluate the appropriateness of MIMS as a real time monitor for DBPs produced by oxidation based water purification processes (Cl_2, O_3, ClO_2) in the presence of dissolved humic materials from Vancouver Island as well as other coastal regions. The work outlined in this proposal extends well beyond the scope of the previous investigation (discussed above) through the examination of five classes of DBP's produced in water dis-infection (Table 1) by using MIMS as a real time monitoring method. To illustrate the versatility and sensitivity of MIMS for DBP molecules, the advantage of using a quadrupole ion trap operated in Selected Ion Monitoring (SIM) will be employed. SIM operation in an ion trap selectively stores only the ions of interest from a sample, rejecting any ions from unwanted/potentially interfering sample matrix molecules. This results in enhanced sensitivity for analyte species when compared to measurements made using linear quadrupole mass spectrometers. SIM mass spectrometric measurements also facilitate simultaneous monitoring of a variety of DBP's, which can be useful in characterizing the dis-infection process**.** In addition to the MIMS work, several other chemical parameters will also be addressed by this work: (1) the role of naturally occurring interferents (i.e. carbonates) and naturally occurring accelerants (i.e. bromides) will be monitored in conjunction with this work using off line measurement before/after treatment(s) by ion chromatography (IC); (2) quantification of humic materials (HM's) naturally present in coastal watersheds (including Nanaimo water district) using total organic carbon analysis; and (3) characterization of these HM's using UV absorption and fluorescence emission spectroscopy. The experimental design is outlined in the following sequence. All of these measurements will be conducted at Malaspina in the Applied Environmental Research Laboratories.

Instrument Optimization

At least one member from each of the DBP categories listed in Table 2 will be investigated individually in order to optimize mass spectral detection parameters and best monitoring regimes. This will include ionization parameters, major ion selection and MS/MS routines that will unambiguously identify each DBP. Method response times and minimum detection limits will be quantified for each representative DBP. Ultra-low level monitoring of $CHBrCl_2$ and NH_2Cl will be targeted because of the special interest these compounds have received in the literature relating to adverse human health and aquatic toxicity, respectively.[4]

Membrane Conditioning

The effect of temperature, pH and ionic strength of pervaporation processes will be assessed for representative DBP compounds.

Interferents/Interactions

Method response times and minimum detection limits will be investigated for various mixtures of DBP's and mixtures of DBP's in natural waters containing various amounts of NOM and naturally occurring ions. NOM levels will be quantified using a total organic carbon combustion analyzer and characterized using ultraviolet-visible spectrophotometry and fluorescence spectroscopy. Inorganic ion concentrations will be assessed using ion chromatograpghy.

DBP Formation Studies

Natural and artificial water samples with varying dissolved organic carbon (0 – 25 ppm) and bromide ion (0 – 5 ppm) will be dosed with chlorine (1 – 2 ppm) for 30 minutes in a benchtop reactor to simulate disinfection conditions. The concentrations of several neutral DBP's will be monitored simultaneously by MIMS in real-time and the ionic DBP's (Table 2) quantified by ion chromatography. The concentration of each DBP will be correlated with level and character of NOM and bromide. These results can be compared to similar disinfection trials using ozone.

Collaborations:

Drs. Erik Krogh and Chris Gill will lead a research team involving AERL students, technician, additional faculty (Dr. Duane Friesen) and Dr. Max Bothwell (National Water Research Institute, Environment Canada).

8. Detailed Budget Breakdown

Costs

Supplies:

Chemical reagents, standards, and pre-cursors $1,600.00

Gases and consumable supplies for instrumental methods: $1,000.00

Mass Spectrometry, Total Organic Carbon and Ion Chromatography

Salary: $5,865.00

Summer Research Assistant ($10.50/hr x 35 hr x 14 wks + 14%)

Travel/incidental: $1000.00

Discuss preliminary results and collaborate with researchers and water district managers including travel to UVic in Victoria and SFU, Env. Canada in Vancouver and the BC Freshwater Institute in Kelowna.

Total Costs of Project **$9,265**

Contributions

AERL in-kind $1,600.00

Gases and consumable supplies for instrumental methods

Environment Canada in-kind (anticipated) $400.00

DBP standard reference materials

Federal government wage subsidy $1,960.00

Summer Research Assistant ($4/hr x 35 hr x 14 wks)

MRF contribution $4,305.00

Technology Transfer Office (anticipated) $1,000.00

Travel and incidental costs

Projected Revenues of Project **$9,265**

Total Amount Requested from Malaspina Research Fund **$4,305**

9. Anticipated Timelines

This is anticipated to be a one year project. Preparatory work, such as the ordering of materials and preliminary MIMS testing will commence in the Spring semester of 2003. The majority of the research results will be generated in the summer of 2003, with a summary report to be written at the end of calendar year.

10. Names and addresses of suggested reviewers

Dr. Tony Farrell, Biological Sciences, Simon Fraser University
604-291-3647 Farrell@sfu.ca

Dr. John Pasternak, Environment Canada,
John.Pasternak@ec.gc.ca

11. This research project will not be associated with assisted/unassisted leave. This work will lead to publication in the peer reviewed literature. It is anticipated that the results of this project will be used to successfully apply for a major external grants from the Canadian Institute of Health Research and the American Water Works Association.

12. Other funding sources are outlined in the Detailed Budget (above).

Dean's Signature: ____

(Dr. David Drakeford, Dean of Science and Technology)

Acknowledgement:

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