



Project Summary

Multispectral Identification of Potentially Hazardous Byproducts of Ozonation and Chlorination: Part I, Studies of Chromatographic and Spectroscopic Properties of MX

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The gas chromatographic (GC) and Fourier transform infrared and mass spectroscopic (FT-IR and MS, respectively) properties of (Z)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (MX) (a highly mutagenic byproduct of drinking water chlorination) and several related compounds were studied. Specifically, MX, the methyl ester of MX (MX-OMe), and three MX-model compounds [mucochloric acid (MCA), mucobromic acid (MBA), and 2,4-(3H,5H)-furanedione (24FD)] were analyzed on our GC/FT-IR and GC/MS systems. A concentration study of MX on the GC/FT-IR system revealed a minimum identifiable quantity of approximately 10 ng, with linear response over the range of 10 to 600 ng. MX was stable to approximately 260°C. The thermal decomposition product produced above that temperature was tentatively identified by GC/MS as 2-(dichloromethyl)-3-chloro-2-propenal. The GC/FT-IR detector response for 600 ng of MX was compared to that of 600 ng of MX that had been methylated. The ratio of the detector responses indicated that the methylation efficiency was, at best, 40%.

Additionally, several extracts of chlorinations of dissolved organic material (DOM) were analyzed by GC/FT-IR and GC/MS. No MX was detected in any of these extracts. The approximate extraction efficiencies of MX and MCA were determined for several organic solvents, of which ethyl acetate was the most efficient for both compounds. A direct aqueous injection of the water

fraction from a DOM chlorination study was made on the GC/FT-IR system. Only simple aliphatic acids were detected. A preliminary alkaline hydrolysis study was undertaken with MCA at a reaction pH of 9.6 at 85°C. No MCA was detected after 1 hour.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Research Perspective

The goal of this research is to identify and determine the frequency of occurrence of potentially harmful contaminants in drinking water. The byproducts of disinfection (primarily chlorination and ozonation) are of principal concern, due to their ubiquity. The focus of the current work was to evaluate analytical methods for the identification of MX, by GC/FT-IR and GC/MS. Identification schemes for MX have previously involved either methylation or PFBOA derivatization. Although not complete, our studies indicate that, if MX can be extracted from water with more than 40% efficiency, it is more easily identified when not methylated or derivatized. Both GC/FT-IR and GC/MS are capable of identifying MX in the very low nanogram range. MX is thermally stable below about 260°C, and can be chromatographed easily with maximum oven and injector temperatures below this level. When the best analytical method for MX has been determined, we will investigate the possibility of



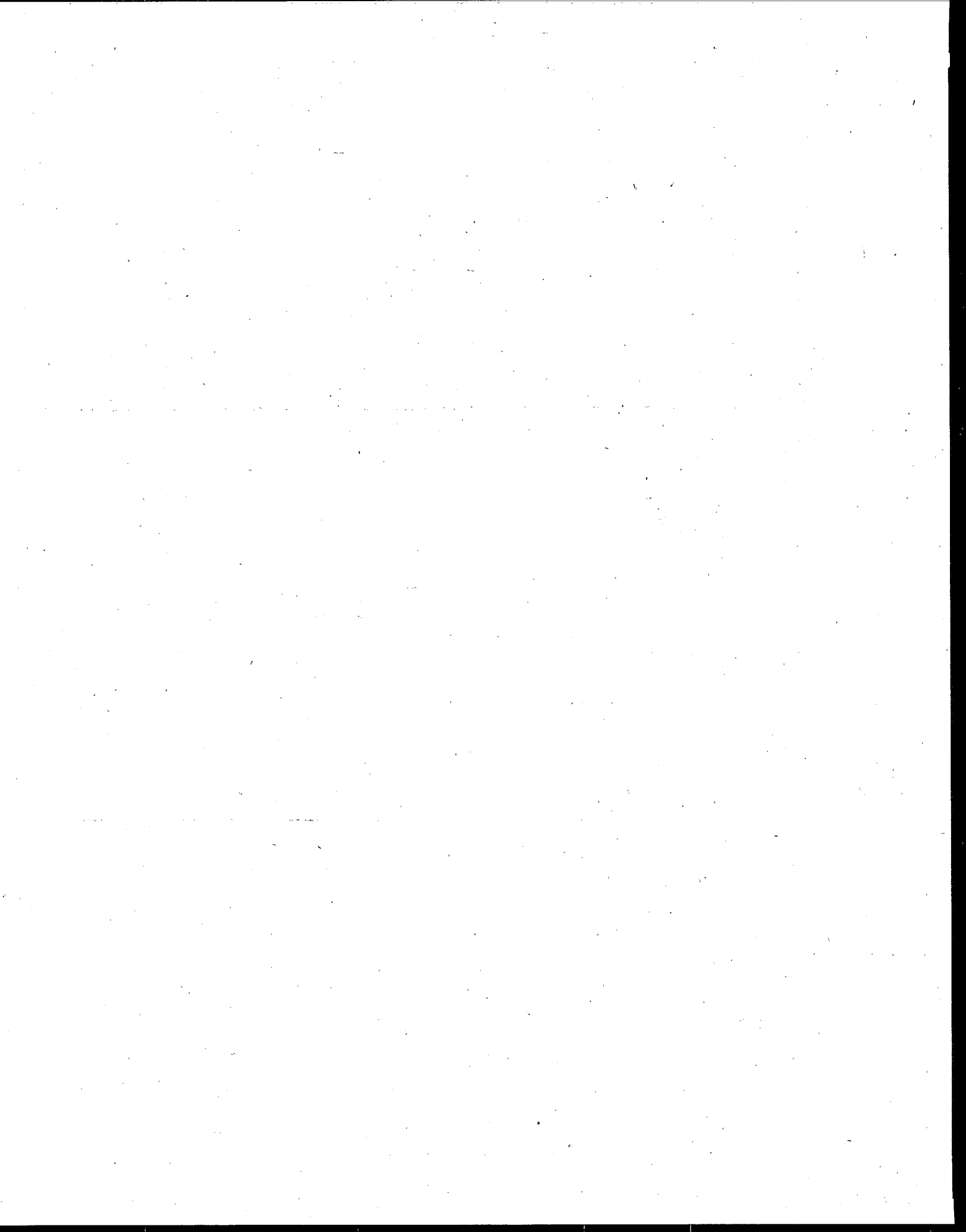
MX (or related mutagenic compound) formation on ozonation. The results of these studies could have an important impact on the consideration of alternatives to chlorine disinfection.

Corollary investigations on the fate of a MX-model compound indicate that the alkaline hydrolysis of this family is rapid. Further studies in this area may suggest procedures that could be incorporated in treatment and delivery systems to decrease the mutagenicity of drinking water.

Direct aqueous injection GC/FT-IR has been shown to be a feasible way of analyzing the water fractions of DOM chlorination studies, which have been neglected in most byproduct identification schemes. The use of this technique with fresh samples could be very informative. There is a possibility that the remaining 40 to 70% of drinking water mutagenicity (that not due to MX or other identified compounds) could be due to extremely hydrophilic compounds not identified because they have not been extracted from water. This technique offers a convenient, immediately applicable way of investigating this question.

Objectives and Accomplishments

- 1) We ran pure standards of five compounds (MX, methylated MX [MX-OMe], mucochloric acid [MCA], mucobromic acid [MBA], and 2,4-[3H,5H]-furanone [24FD]) on both our GC/MS and GC/FT-IR instruments to add their spectra to our libraries and determined their GC retention times. We chose the latter three compounds to serve as MX models.
- 2) We conducted a concentration study and generated a standard curve for MX on the GC/FT-IR. In contrast to GC/MS, detection limits for GC/FT-IR vary greatly for different classes of compounds. We, therefore, wanted to determine the minimum identifiable quantity (MIQ) for MX on our GC/FT-IR instrument. MIQ has been defined as the minimum quantity that must be injected to result in a spectral match that has the correct compound identification in the top five spectral matches.
- 3) We carried out a study of the thermal stability of MX. The GC/FT-IR response, as a function of heated splitless injector port temperature, was observed for separate, equal-volume injections to determine the temperature at which substantial degradation occurred. The tentative identity of the thermal degradation product was determined by GC/MS.
- 4) The GC/FT-IR detector response for a given injected quantity of MX was compared to that of an injection of an equal quantity of MX that was methylated (MX-OMe) and extracted. The goal of this experiment was to determine to what degree methylation facilitates GC/FT-IR detection of MX.
- 5) Several extracts of DOM chlorinations were analyzed by GC/MS and GC/FT-IR for MX and related compounds. One extract was from a sample that was methylated and reacted with PFBOA. The others were from samples that were solvent extracted after chlorination.
- 6) The approximate extraction efficiency of MX and MCA from water was determined for a number of organic solvents.
- 7) An auxiliary objective of this research was to identify the hydrophilic compounds that are left in the aqueous phase of chlorinated DOM, after all extractions have been performed. Although extensive derivatization and extraction procedures have been developed for these types of samples, to our knowledge no one has ever published identifications based on a direct analysis of the aqueous fraction. We are also interested in developing a direct aqueous analysis method for MX, as an alternative to extraction, methylation, or derivatization methods. In a preliminary feasibility study, we obtained the aqueous fraction from a chlorinated DOM sample and analyzed it by direct aqueous injection (DAI) GC/FT-IR.
- 8) Another auxiliary objective of this research was to determine the fate of MX in aqueous media over time periods characteristic of holding times in water supply distribution systems. We would like to determine whether MX is transformed via hydrolysis, and, if so, to what products. MX recently has been shown to degrade in the presence of excess chlorine. These are obviously important issues in determining the level of MX likely to be at the tap, depending on pH, residual chlorine, etc. Preliminary alkaline hydrolysis experiments have been performed with MCA, as a model for MX.



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The complete report, entitled "Multispectral Identification of Potentially Hazardous Byproducts of Ozonation and Chlorination: Part I, Studies of Chromatographic and Spectroscopic Properties of MX," (Order No. PB91-161 703/AS; Cost: \$17.00 subject to change) will be available only from:

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