



Coupling of supercritical fluid chromatography to mass spectrometry for the analysis of Dechlorane Plus: Examination of relevant negative ion atmospheric pressure chemical ionization mechanisms

Nicole Riddell^{a,b,*}, Bert van Bavel^{b,c}, Ingrid Ericson Jogsten^b, Robert McCrindle^d, Alan McAlees^a, Brock Chittim^a

^a Wellington Laboratories Inc., 345 Southgate Drive, Guelph, Ontario, Canada N1G 3M5

^b Man-Technology-Environment (MTM) Research Center, Örebro University, Örebro 70182 Sweden

^c Norwegian Institute for Water Research, NO-349 Oslo, Norway

^d Chemistry Department, University of Guelph, Guelph, ON, Canada N1G 2W1

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ABSTRACT

During an investigation of the potential associated with coupling packed column supercritical fluid chromatography (pSFC) to mass spectrometry for the analysis of Dechlorane Plus and related compounds, it was found that negative ion atmospheric pressure chemical ionization (APCI) was a promising ionization technique. In the course of maximizing the responses associated with the target analytes, it proved useful to examine some aspects of the complex nature and reactivity of the corona discharge plasma generated to explain the observed ionization products. Various dopants/reagents were screened for both APCI and atmospheric pressure photoionization (APPI) in negative ion mode and mechanisms of ionization involving superoxide were elucidated based on the results obtained. Superoxide formation was found to be temperature dependent and directly related to the intensity of the ion cluster $[M-Cl+O]^-$ obtained for the target DP analytes. Furthermore, triethylamine was identified as a reagent capable of suppressing unwanted side reactions during the ionization process and maximizing response associated with the analytes of interest. The applicability of pSFC-APCI/MS for the separation and detection of Dechlorane Plus and related compounds was demonstrated by analyzing Lake Ontario sediment and comparing the results with values reported in the scientific literature.

1. Introduction

Dechlorane Plus (DP) is a highly chlorinated additive flame retardant that is produced globally and utilized in a variety of applications such as electrical wire and cable coatings, computer connectors, and roofing materials [1]. It exists in two isomeric forms (syn and anti; see Fig. 1) and was first detected in the environment in 2006, in air and sediment samples from the Great Lakes region of North America, using gas chromatography (GC) coupled to electron capture negative ionization (ECNI) mass spectrometry (MS) [2]. The authors of this study favoured this method of ionization over electron ionization (EI) due to the observation of extensive fragmentation and extremely low intensity of the molecular ion using the latter technique. DP is now being widely used, presumably because it offers several advantages over brominated flame retardants such as increased thermal and photochemical stability and lower cost [1], resulting in its detection in both indoor [3,4] and outdoor [5–9] environmental

matrices. Although the most widely used analytical technique for the detection of DP in environmental samples remains GC/ECNI-MS, other methods of separation and ionization have been reported, such as liquid chromatography (LC) coupled with atmospheric pressure ionization (API) MS [10,11], for the simultaneous analysis of DP with LC amenable analytes.

The present study investigates the applicability of packed column supercritical fluid chromatography (pSFC), a separation technique amenable to compounds traditionally run by both LC [12] and GC [13], to the separation of DP and related compounds. Available instrumentation for pSFC separations are typically coupled with mass spectrometers equipped with atmospheric pressure ionization sources. The introduction of significant quantities of carbon dioxide into the MS source can complicate ionization and optimization is a vital part of method development. In order to maximize detection limits, relevant API mechanisms, which could be applicable to other halogenated environmental contaminants, were investigated. Literature reports of

* Corresponding author at: Wellington Laboratories Inc., 345 Southgate Drive, Guelph, Ontario, Canada N1G 3M5.
E-mail address: nicole@well-labs.com (N. Riddell).

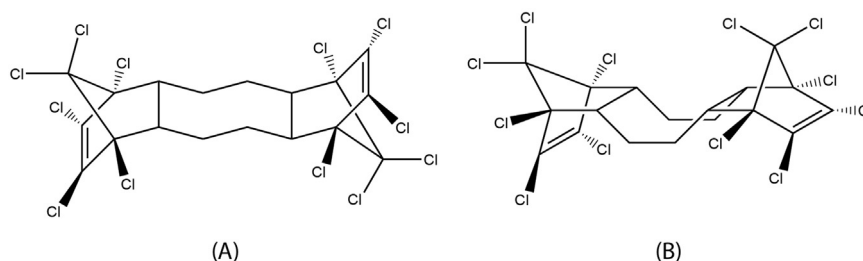
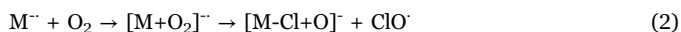


Fig. 1. Structures of the (A) anti- and (B) syn-isomers of Dechlorane Plus.

the APCI of DP describe the formation of a $[M-Cl+O]^-$ cluster [10,11,14]. In 1975, it was reported by Dzidic et al. that phenoxide ions, $[M-Cl+O]^-$, were formed during API mass spectrometry of chlorinated aromatic compounds, possibly through reaction with superoxide (see Eq. (1)). The authors proposed that this ionization process occurred in the API source in the presence of nitrogen containing 0.5 ppm oxygen and also in air [15].



Further work on this ionization process was completed by Lépine et al. that focused on chlorinated compounds, such as polychlorinated biphenyls, which undergo oxygen addition-induced dechlorination reactions during electron capture negative chemical ionization [16]. The authors suggest that this process might be relevant for other atmospheric pressure ionization sources as well and report that many chlorinated compounds show ions with mass-to-charge (m/z) ratios that are lower than the expected molecular ion cluster by 19. The mechanism associated with this reaction sequence has not been definitively determined, but the following process (see Eq. (2)) proceeding through a radical intermediate has been proposed [17]:



In the field of environmental chemistry, mass spectrometry is a widely used detection technique due to its inherent sensitivity and selectivity. The use of GC and LC instrumentation interfaced to MS detectors for the analytical measurement of environmental contaminants is common, but pSFC introduces new challenges when attempting to do comparable low level analytical work. The utilization of API techniques for the ionization of halogenated environmental contaminants (both aromatic and non-aromatic) has been established [14,18–20]. However, due to the complexity of chemical reactions that can occur in an MS source, an understanding of the factors affecting ionization pathway promotion and quenching may aid in the promotion of a single species for optimal detection limits. In this work, optimal ionization parameters were determined for the syn- and anti-isomers of DP based on the formation of $[M-Cl+O]^-$ ion clusters in both negative-ion atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI) modes when pSFC was utilized as the separation technique. Possible mechanisms of action are proposed for the optimized ionization parameters and developed ionization conditions were tested for relevance at environmental levels of DP by extracting and analyzing lake sediment obtained from the Great Lakes Region of Ontario, Canada.

2. Materials and methods

2.1. Chemicals

Individual certified reference standards of syn- and anti-Dechlorane Plus (s-DP and a-DP respectively) as well as anti isomers of both Cl_{10} and Cl_{11} analogues of DP (aCl10DP and aCl11DP respectively) were obtained from Wellington Laboratories Inc. (Guelph, ON, Canada). A mass-labelled syn-DP reference standard (Dechlorane Plus Syn (bis-

cyclopentene- $^{13}C_{10}$) was obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Homogeneous lake sediment collected from Lake Ontario for organic contaminant analysis (WMS-01) was obtained from Wellington Laboratories Inc. (Guelph, ON, Canada). HPLC grade methanol, acetonitrile, cyclohexane, as well as distilled in glass grade acetone, ethyl acetate, toluene, nonane, 2-propanol and reagent grade ammonium hydroxide were purchased from Caledon (Guelph, ON, Canada). Reagent grade anisole and triethylamine were purchased from Sigma Aldrich (Oakville, ON, Canada). Reagent grade tetrabutylammonium hydroxide was purchased from Fisher Scientific (Ottawa, ON, Canada). Food grade carbon dioxide was purchased from Linde Canada Industrial Gases (Guelph, ON, Canada). The nitrogen gas utilized for desolvation purposes in these experiments was produced using a Parker Balston N2-14 nitrogen generator and has a reported purity range between 95.0–99.5% with the purity of the nitrogen being dependent on the temperature and pressure of the inlet compressed air.

2.2. Chromatographic systems and conditions

All pSFC separations were carried out using a Waters Acquity UltraPerformance Convergence Chromatograph (UPC²) (Waters Corp., Milford, MA, USA) system equipped with an Acquity Photodiode array (PDA) Detector, Acquity Convergence Manager, Acquity UPC² Binary Solvent Manager, Isocratic Solvent Manager, Acquity Sample Manager, and an Acquity Column Manager. The UPC² was coupled to a Micromass Quattro micro atmospheric pressure ionization (API) Mass Spectrometer (MS) (Waters Corp., Milford, MA, USA) and data were processed using Waters MassLynx software.

2.3. Infusion experiments for the optimization of negative-ion API parameters

For optimization of the ionization parameters of DP, the anti isomer was chosen as the test compound. The MS was configured in dual negative-ion APCI/APPI mode and the listed tune parameters were varied until the following optimized parameters were determined for the formation of the $[M-Cl+O]^-$ ions: krypton lamp (eV) =10.6, repeller voltage (kV) =1.0, corona needle (μA) =6.0; cone voltage (V) =20.0; cone gas flow (L/h) =100; desolvation gas flow (L/h) =500; desolvation temperature ($^{\circ}C$) =350; source temperature ($^{\circ}C$) =100. The MS make-up solvents containing dopants/reagents that were investigated (acetonitrile with 5% acetone, acetonitrile with 5% ethyl acetate, acetonitrile with 5% anisole, acetonitrile with 0.05 – 0.2% ammonium hydroxide, methanol with 0.1% ammonium hydroxide, acetonitrile with 0.1% tetrabutylammonium hydroxide, and 0.1–0.5% triethylamine; see Table S1) were added to the split from the UPC² at a flow-rate of 0.4 mL/min. All data for infusion experiments were acquired in full scan mode by introducing a 5 $\mu g/mL$ a-DP standard (in acetonitrile) directly into the UPC² eluent/MS make-up solvent at a rate of 10 $\mu L/min$. Data were collected for one minute and all spectra were averaged, smoothed (Savitzky Golay, $N=2$), and centered. The UPC² eluent was comprised of 90% CO_2 and 10% acetonitrile at a flow-rate of 0.45 mL/min with an automated back pressure regulator (ABPR) setting of

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