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Potential of capillary electrophoresis mass spectrometry for the characterization and monitoring of amine-derivatized naphthenic acids from oil sands process-affected water

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ABSTRACT

Capillary electrophoresis coupled to mass spectrometry (CE–MS) was used for the analysis of naphthenic acid fraction compounds (NAFCs) of oil sands process-affected water (OSPW). A standard mixture of amine-derivatized naphthenic acids is injected directly onto the CE column and analyzed by CE–MS in less than 15 min. Time of flight MS analysis (TOFMS), optimized for high molecular weight ions, showed NAFCs between 250 and 800 *m/z*. With a quadrupole mass analyzer, only low-molecular weight NAFCs (between 100 and 450 *m/z*) are visible under our experimental conditions. Derivatization of NAFCs consisted of two-step amidation reactions mediated by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), or mediated by a mixture of EDC and *N*-hydroxysuccinimide, in dimethyl sulfoxide, dichloromethane or ethyl acetate. The optimum background electrolyte composition was determined to be 30% (*V/V*) methanol in water and 2% (*V/V*) formic acid. NAFCs extracted from OSPW in the Athabasca oil sands region were used to demonstrate the feasibility of CE–MS for the analysis of NAFCs in environmental samples, showing that the labeled naphthenic acids are in the mass range of 350 to 1500 *m/z*.
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Introduction

More than 170 billion barrels of crude oil are considered to be economically viable for recovery in the Athabasca oil sands in Northern Alberta, Canada (Headley et al., 2013a, b). For every 1 barrel of synthetic crude extracted from the oil sands, 3.3 barrels of process water ("tailings") are produced (Headley et al., 2013a, b). Process water from oil sands mining is stored in large tailing ponds, whose total volume has already surpassed 720 billion L (McKenzie et al., 2014). Fresh oil sands process-affected water (OSPW) has been demonstrated to be acutely toxic toward a number of animal species, due in part to the presence of a class of organic contaminants called naphthenic acids (NAs) at concentrations as high as 100 mg/L in tailing ponds (McKenzie et al., 2014; Allen, 2008).

The term "naphthenic acids" suggests the acids of naphthenes (*i.e.*, cycloalkanes) (IUPAC, 1997; Nic et al., 2006; Senning, 2007). In fact, the class of compounds referred to as

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NAs consists of a mixture of aliphatic and alicyclic hydrocarbon carboxylic acids, usually containing 10 to 30 carbons and N, O, and S as ring heteroatoms and functional moieties. A small subset of possible NA structures with $C_{8–26}$ is shown in Fig. 1.

NAs mixture compositions vary according to the geographical location of the crude deposit. Additionally, NAs found in OSPW may have altered molecular structures and toxicity from those found naturally in bitumen (Rowland et al., 2011). Identification of the source of a particular NAs sample is therefore an important challenge for environmental forensics. Currently, there is no standard monitoring system for NA levels in water. This is due in part to the fact that current chromatographic separation methods cannot resolve individual NAs species, including isomers, from the complex mixtures that exist in the environment (Proposal to Add Naphthenic Acids to the NPRI for the 2012 Reporting Year Recommendations of the NPRI Multi-Stakeholder Work Group, 2012).

Currently there are several methods that are used for the characterization of NAs. High-resolution mass spectrometry has shown remarkable success in identifying possible chemical structures (Headley et al., 2016). More recently, liquid chromatography–mass spectrometry (LC–MS) has also been used to further characterize the different species, including those containing oxygen, sulfur, and nitrogen species (Martin et al., 2010). Capillary electrophoresis coupled with mass spectrometry has shown important complementarity with LC–MS in proteomics and metabolomics research (Sun et al., 2016).

Here we propose to use a new method for the characterization of NAs based on capillary electrophoresis and mass spectrometry. Capillary electrophoresis (CE) is an analytical technique that separates analytes based on their differential rates of migration in an electric field, which is determined by the charge-to-size ratio of the analyte ions in solution. Because this mechanism of separation differs from that of chromatographic separations, in which separation is determined based on differential partitioning between a mobile and stationary phase, CE represents a complementary approach with several important advantages compared to chromatography: The most salient advantages of CE include (a) the possibility of high separation efficiency in order to resolve complex isomeric mixtures; (b) versatility in its ability to resolve a wide range of analytes (including neutral species) through the addition of additives to the background electrolyte; (c) low sample consumption (nanoliters) and low solvent consumption, which make it suitable for high-volume, routine analyses and environmental applications.

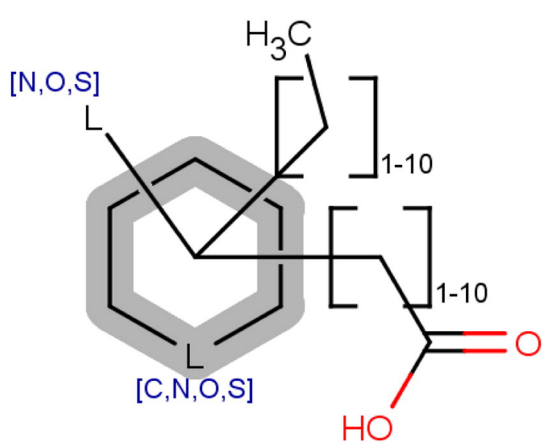

Fig. 1 – A small subset of possible naphthenic acid structures based on $C_{9–28}$, a single 6-membered ring, 3 heteroatom types at 2 locations (L in the diagram) and a single carboxylic acid group. This small subset contains approximately 259,000 members.

The power of CE can be further increased by coupling with mass spectrometry (MS), which provides an added dimension of resolution and information on the mass-to-charge ratio (*m/z*) of the separated species. While CE can be coupled to MS using a range of ionization modes (Maxwell and Chen, 2008), electrospray ionization (ESI) is by far the most common ionization and coupling method.

NAs exist as negatively charged ions in alkaline medium; however, the electrophoretic separation and negative-mode ESI–MS analysis of these molecules in basic aqueous medium has been challenging with the instrument we have. In the present study, three different types of chemical derivatization that convert the NAs into naphthenic amines were investigated to impart greater selectivity of acidic compounds from the sample matrix. The naphthenic amines, which existed as cations in acidic solution, were characterized by CE separation and ESI–MS analysis under positive ion mode. To our knowledge, this work is the first known application of capillary electrophoresis mass spectrometry to the analysis of NAs.

1. EDC/NHS-mediated chemical derivatization of NAs

Chemical derivatization is a common technique for increasing the selectivity, separation and sensitivity of detection of target analytes. The coupling of a carboxylic acid to a primary amine can be facilitated by the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS). Both EDC and NHS are widely used in bioconjugate chemistry and peptide chemistry. The general outline of such derivatizations is shown in Fig. 2a.

EDC and NHS activate carboxylic acids *via* different mechanisms. In the case of EDC, the carboxylic oxygen atoms donate electrons to the carbodiimide carbon on EDC, forming a C – O bond to make a transient *O*-acylisourea (Fig. 2b Step 1) (Mikołajczyk and Kiełbasiński, 1981; Williams and Ibrahim, 1981). Subsequent aminolysis of the *O*-acylisourea affords the amine-derivatized acid (Fig. 2b Step 2). In aqueous media, EDC degrades to the urea by-product. This degradation of EDC occurs rapidly in acidic, aqueous solutions (Gilles et al., 1990; Nakajima and Ikada, 1995).

By contrast, the mechanism of NHS activation involves a substitution to form a *N*-succinimidyl ester, with subsequent aminolysis of the ester to afford the amine-derivatized product. The aminolysis of the *N*-succinimidyl ester is first order with respect to [OH^-] (Cline and Hanna, 1988).

In concert, EDC and NHS, buffered at approximately pH 7, enhance each other's ability to mediate the amidation of carboxylic acids (Grabarek and Gergely, 1990; Staros et al., 1986).

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