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Improved coverage of naphthenic acid fraction compounds by comprehensive two-dimensional gas chromatography coupled with high resolution mass spectrometry

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ABSTRACT

This study reports the first application of comprehensive two-dimensional gas chromatography coupled to a high-resolution quadrupole time-of-flight mass spectrometer (GC × GC/HRQTOF-MS) for the characterization of naphthenic acid fraction compounds (NAFCs) from the Alberta Oil Sands. High resolution mass spectrometry (HRMS) significantly increased the coverage of NAFCs in the mixture and allowed the differentiation of NAFCs from several chemical classes. It was demonstrated that GC × GC, in combination with the high mass accuracy and precision of the HRQTOF-MS, could distinguish chemical species with the C_3 vs SH_4 mass split at a much lower resolving power than required with direct infusion experiments. Mass defect plots were useful for visualizing the complex datasets generated by GC × GC/HRQTOF-MS and led to the identification of 1105 chemical species with unique elemental compositions (<5 ppm mass accuracy). Mass defect plots were shown to be a powerful screening tool and enabled the detection of extensive isomer series from the SO_2 chemical class, some of which have not been previously reported in oil sands related samples. The GC × GC/HRQTOF-MS approach is expected to improve NAFC monitoring programs since the technique allows the qualitative analysis of individual NAFCs and provides unique fingerprints via isomer distributions which may assist in future fingerprinting studies.

1. Introduction

The Athabasca oil sands are the third largest oil reserve in the world [1]. The caustic hot water extraction of bitumen from oil sands material results in the production of tailings [2,3]. The aqueous component of tailings, referred to as oil sands process-affected water (OSPW), has shown acute and chronic toxicity towards a variety of aquatic organisms. This toxicity is widely attributed to the presence of a complex mixture of organic compounds referred to as naphthenic acids (NAs) [4–10]. In accordance with Alberta's zero discharge policy, OSPW must be stored on site in tailing ponds and settling basins [2]. Since NAs are somewhat soluble in water, they have the potential to migrate into the greater environment via leakage into groundwater [11]. Therefore, it is critical that suitable analytical techniques are developed to not only monitor NAs, but also differentiate industrial NA sources from natural sources.

Naphthenic acids are one of the most complex organic mixtures in the world, and their characterization poses a tremendous challenge to analytical chemists [12]. The term "naphthenic acids" was originally used to define the complex mixture of aliphatic and alicyclic monocarboxylic acids ($C_nH_{2n+Z}O_2$ where n = number of carbons, Z = hydrogen deficiency, by formation of rings), but in light of recent studies [13–15], the definition has been expanded to include compounds with sulfur and/or nitrogen heteroatoms, mono- and polyoxygenated species, and a variety of mixed oxygen-/nitrogen-/sulfur-containing species (e.g. NO_x, SO_x). For each chemical class, a range of double bond equivalents (DBEs) and car-

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bon numbers (degree of alkylation) exist [16], in addition to a large number of structural isomers for each n- and Z-values [17–20]. In order to accommodate this broader definition of NAs, the mixture of chemicals present in the acidified fraction of OSPW is generally referred to as acid extractable organics (AEOs), or, more commonly, naphthenic acid fraction compounds (NAFCs) [12].

Advances in analytical techniques, such as ultrahigh resolution mass spectrometry, have greatly improved our ability to detect and characterize NAFCs in environmental samples. Fourier transform ion cyclotron mass spectrometry (FTICR MS) coupled to negative electrospray ionization (ESI) [13,15,21,22] has contributed to the unambiguous assignment of elemental compositions to thousands of features in OSPW due to its ultrahigh mass resolution (~500,000 resolution at m/z 400) and high mass accuracy (<1 ppm) [23,24]. Direct infusion FTICR MS has also been coupled with atmospheric pressure photoionization (APPI) [15] to provide complementary data for nonpolar compounds with poor ESI efficiencies. However, direct infusion does not allow the distinction of structural isomers, which have been shown to be useful in NA fingerprinting applications [25–28]. Derivatized extracts containing NAFCs have been analyzed by gas chromatography (GC) coupled to FTICR MS with electron ionization (EI), chemical ionization with methane (CI-CH_4) and ammonia (CI-NH_3) [17], and atmospheric pressure chemical ionization (APCI). [18] The mass resolution of FTICR MS is sufficient to resolve multiple heteroatom classes, but the selected ion chromatograms (SICs) were consistent with an unresolved complex mixture of structural isomers [17]. When NAFCs are separated by high performance liquid chromatography (HPLC), structural isomers also typically co-elute as one peak [29]. The chromatographic resolution of NAFCs has been significantly improved by packed column supercritical fluid chromatography (SFC), where the authors showed that the technique could partially and fully resolve many isobaric naphthenic acids [29].

Comprehensive two-dimensional gas chromatography mass spectrometry (GC × GC/MS) has also significantly improved the chromatographic resolution of NAFCs, and allowed the separation of structural isomers. The structures of individual naphthenic acids with cyclohexane [19], alicyclic bicyclic [20,30], adamantane [19,31], diamantane- [32], indane- [19,33], tetralin- [19,33], and naphthalene- [33] chemical moieties ("O_2" class) have been firmly identified in previous studies by comparison to reference standards. In addition, the structures of a few naphthenic acids from "non-traditional" chemical classes have been confirmed with reference standards, such as thiophene carboxylic acids [19] ("SO_2" class) and diamondoid dicarboxylic acids [34] ("O_4" class). However, a large proportion of the chemical species within naphthenic acid mixtures still remain unidentified. The structural elucidation of unknown NAFCs by GC × GC is challenging due to the extreme complexity of NA mixtures, lack of available standards and absence of NAFC mass spectra in mass spectral libraries. Complete chromatographic separation of NAFCs has yet to be achieved, especially in the latter part of the chromatogram. Coupling GC × GC with a high resolution mass spectrometer has been shown to significantly improve the non-targeted analysis of complex environmental mixtures [35–42]. Such techniques are advantageous since they can not only resolve structural isomers and produce isomer profiles, but also provide information on chemical classes, double bond equivalents, and carbon numbers based on mass accuracy.

The work described in this study illustrates the application of coupling comprehensive two-dimensional gas chromatography with APCI and a high resolution quadrupole time-of-flight mass spectrometer for the characterization of NAFCs. The combination of multidimensional chromatography and high resolution mass spectrometry was shown to significantly improve NAFC monitoring efforts since it can readily distinguish chemical classes, and also resolve and monitor the presence of individual structural isomers.

2. Experimental

2.1. Sample collection and preparation

The fluid fine tailings (FFT) sample was collected from Base Mine Lake (BML), which is an end pit lake established at the Mildred Lake Mine, located approximately 35 km north of Fort McMurrary, Alberta, Canada. A more in-depth description of the site can be found elsewhere in literature. [43,44] The sample was collected at a depth of 18 m from Platform 2 using a non-commercial pneumatic piston sampling device, as described in a previous study [43]. Following collection, the sample was stored in a pre-cleaned Nalgene plastic bottle (1 L volume) at −20 °C and was thawed prior to extraction.

The FFT sample was centrifuged at 3100 rpm for 60 min and the supernatant was removed. The supernatant was filtered by a 0.45 μm syringe filter (Gelman Sciences, Ann Arbor, MI, USA), acidified to pH 2, and extracted with dichloromethane (4 × 15 mL). The extracts were combined and concentrated to 1 mL by rotary evaporation. The extract was quantitatively transferred to a glass vial and concentrated to 30 μL by blowing gently with nitrogen. The NAFCs with carboxylic acid moieties were converted to methyl ester derivatives by treatment with diazomethane in dichloromethane. Diazomethane was added until the yellow colour persisted, which indicates an excess of derivatizing reagent. Prior to analysis, pyrene-d_{10} dissolved in toluene (final concentration: 1 ppm) was added to the sample as an internal standard. The extraction efficiency of the sample preparation procedure was evaluated by calculating the percent recovery of two recovery surrogate standards (4-tertbutylcyclohexane-1-carboxylic acid, 83% ± 3; 2-hexyldecanoic acid, 87% ± 14), which were added following centrifugation.

2.2. Instrumentation

GC × GC/HRQTOFMS analysis was performed using an Agilent 7890 B gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) fitted with a Zoex ZX2 GC × GC thermal modulator (Zoex, Houston, TX, USA) and interfaced to a Waters Xevo G2-XS quadrupole time-of-flight mass spectrometer (Waters Corporation, Milford, MA, USA). The first-dimension column was a DB–17 ms 30 m × 0.25 mm × 0.15 μm film followed by a Restek Siltek deactivated guard column 1 m × 0.25 mm in the modulator loop. The second-dimension column was a DB–5 ms 1 m × 0.10 mm × 0.10 μm film, and was placed in a secondary oven. The secondary column was then connected to a Custom MXT tubing (sulfinert treated) 0.8 m × 0.18 mm, which was inserted into the transfer line. Helium was used as the carrier gas, and the flow was set at 1 mL/min. The injector temperature was set at 280 °C. The initial oven temperature was held at 40 °C for 1 min, and then ramped at a rate of 3 °C/min to 310 °C, and held for 10 min. The secondary oven was set at a 10 °C offset, relative to the primary oven. The modulator was set at a 15 °C offset, relative to the primary oven, and a modulation period of 3 s was used. The transfer line was set to 340 °C. The cone gas at a flow rate of 100 L/hr and the auxiliary gas flow set at 150 L/hr. The source temperature was 150 °C, with the detector run in TOF mode using an acquisition range of 50–1200 amu with an acquisition rate of 30 Hz. The mass spectrometer was operated at a resolving power of > 20 000 (FWHM), and internal mass calibration was performed by using a lock mass ion (1185.9452) from a reference compound, tris(perfluoroheptyl)-s-triazine. Data processing was conducted using GC Image HRMS R2.5 (Zoex).

A Pegasus 4D system (LECO Corp., St. Joseph, MI, USA) was used to collect nominal mass electron ionization (EI) mass spectra for this study. The system utilized DB–17 ms

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