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Trace analysis of total naphthenic acids in aqueous environmental matrices by liquid chromatography/mass spectrometry-quadrupole time of flight mass spectrometry direct injection

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ABSTRACT

A rapid and sensitive liquid chromatography quadrupole time of flight method has been established for the determination of total naphthenic acid concentrations in aqueous samples. This is the first methodology that has been adopted for routine, high resolution, high throughput analysis of total naphthenic acids at trace levels in unprocessed samples. A calibration range from 0.02 to 1.0 μg mL^{-1} total Merichem naphthenic acids was validated and demonstrated excellent accuracy (97–111% recovery) and precision (1.9% RSD at 0.02 μg mL^{-1}). Quantitative validation was also demonstrated in a non-commercial oil sands process water (OSPW) acid extractable organics (AEOs) fraction containing a higher percentage of polycarboxylic acid isomers than the Merichem technical mix. The chromatographic method showed good calibration linearity of ≥0.999 RSQ to 0.005 μg mL^{-1} total naphthenic acids with a precision <3.1% RSD and a calculated detection limit of 0.0004 μg mL^{-1} employing Merichem technical mix reference material. The method is well suited to monitoring naturally occurring and industrially derived naphthenic acids (and other AEOs) present in surface and ground waters in the vicinity of mining developments. The advantage of the current method is its direct application to unprocessed environmental samples and to examine natural naphthenic acid isomer profiles. It is noted that where the isomer profile of samples differs from that of the reference material, results should be considered semi-quantitative due to the lack of matching isomer content. The fingerprint profile of naphthenic acids is known to be transitory during aging and the present method has the ability to adapt to monitoring of these changes in naphthenic acid content. The method's total ion scan approach allows for data previously collected to be examined retrospectively for specific analyte mass ions of interest. A list of potential naphthenic acid isomers that decrease in response with aging is proposed and a quantitative assay of an adamantane carboxylic acid is reported.

1. Introduction

Naphthenic acids (NAs) occur naturally at low levels in regional ground waters but their industrial extraction from petroleum, shale oil, oil sands, and coal tar deposits has driven the analysis of these compounds to the forefront over the last decades [1–3]. Crude NAs extracted from alkaline sludges are contributors to the reported toxicity of oil sands process water (OSPW) [4,5]. Despite their prevalence and toxicity, quantitative analysis of NAs has been slow to evolve as a result of a number of challenges. One major factor is the complex array of acid extractable organics (AEOs) that have been recognized as components of oil sands process waters (OSPW) [6]. Classic NAs are generally defined as carboxylic acids with one or more saturated ring structures. The acids are predominantly fused rings of alkyl substituted cyclo-aliphatic carboxylic acids with smaller acyclic aliphatic (paraffinic or fatty) acids. Within the classic formula $C_nH_{2n+Z}O_2$, n represents carbon number and Z an even, negative integer corresponding to hydrogen deficiency by loss due

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to ring formation. The original classification of NAs was recently recognized as insufficient to include other components of OSPW acids, including more oxygenated polycarboxylic acid species and additionally NAs with the heteroatom components nitrogen and sulfur atoms [5–8].

In addition to the sheer complexities described above, analysis of NAs in contaminated waters has hitherto been hampered by an inadequate match between commercially available standard reference materials and the varying NA components of OSPW and natural waters. The diversity of NA isomers in OSPW water is additionally complicated by the changes that occur to the NA profile over time due to natural aging processes (often termed weathering). Researchers have reported that the less cyclized NAs (Z −0 or −2) are those more subject to biodegradation [9,10]. It is therefore expected that the profile, or fingerprint, of the NAs from a specific location is dynamic and dependent upon a number of factors. Based on fingerprint profiling, Frank et al. have recently emphasized several parameters, including the O2:O4 ratio within AEOs, as being relevant in identifying the difference between natural ground waters and oil sands process waters (OSPW) [11].

Apart from the heterogeneity of the NA analytes, there have also been concerns regarding the accuracy and specificity of instrumentation. Emphasis is shifting from traditional instrumentation, including Fourier transform infrared spectroscopy (FTIR), gas chromatography mass spectrometry (GC/MS) and liquid chromatography mass spectrometry (LC/MS), in favor of high and ultra-high resolution mass spectrometry (reviewed by Zhao et al. [12]). Early liquid chromatography based mass spectrometry procedures for the analysis of total NAs employed single quadrupole instruments [13], while recent advances in high resolution instrumentation now offer a greater mass accuracy, thus improving the specificity of NA analysis. In this regard, quadrupole time of flight mass spectrometry (QToF), Orbitrap, and Fourier transform ion cyclotron resonance (FTICR) have been applied to the analysis of OSPW, although their application to routine quantitative monitoring has yet to be fully demonstrated [6]. In addition to high mass resolution applications, recent progress has been reported on the identification of several new classes of NAs (diamondoid adamantanes, diamantanes, monoaromatic acids) using comprehensive two dimensional GC/GC-ToF/MS by Rowland et al. [14,15]. More recently, differential ion mobility spectrometry in combination with quadrupole time of flight mass spectrometry [16] and supercritical fluid/Orbitrap mass spectrometry [17] have also been employed by other authors for NA fingerprinting. Both techniques offer the improved separation of multiple peaks but have limitations with respect to routine quantitative analysis. For example, despite lengthy separation on a 75 min chromatographic gradient, a significant number of polar polyoxy $O_{\geq 3}$ NA species eluted at the same retention time at the end of the gradient and the complexity of different OSPW sources required optimized elution conditions [17]. The observed chromatography of multiple adjacent and overlapping isomeric peaks, while offering interesting and informative insights into the NA homolog profiles, made SFC/Orbitrap application to routine quantitative analysis of total NAs limited.

Limitations of the high resolution fingerprinting techniques to high throughput total NA analyses are partially due to instrumentation costs but also due to the need for sample clean-up, lack of routine sampling abilities, relevant standards, and the quantity and complexity of produced data. A further consideration with respect to NA analysis is the observation that the clean-up procedure (including solvents, acidification, ion exchange) employed can be selective with respect to the compounds extracted [18–22]. It is therefore apparent that not only will the observed NA profile vary depending upon both the source and age of the sample, but also upon sample preparation and instrument conditions used. Considering the uncertainties with respect to compositional changes during sample processing, the aim of the present study was to develop a much needed practical method for the high throughput determination of total polyoxy-NAs that requires minimal handling. The method had to be demonstrated as applicable to the monitoring of a range of environmental and industrial NA isomer profiles, including application to routine water quality monitoring and toxicological investigations.

2. Materials and methods

2.1. Reagents and supplies

Aqueous reagents were prepared in ultra-high purity water supplied by a MilliQ Plus system. Ammonium hydroxide (≥99.99% purity), acetic acid and ammonium fluoride (≥98% purity) were all supplied by Sigma–Aldrich (Oakville, Ontario, Canada). Formaldehyde (37% by weight stabilized with methanol) was sourced from Fisher Scientific, Canada. Adamantane-1-carboxylic acid was obtained from Alfa Aesar, Canada. Acetonitrile at LCMS grade was purchased from Fisher Scientific, Canada. HPLC grade 2-propanol was purchased from Caledon Lab. Chemicals (Georgetown, ON).

In this study, method parameters were developed, optimized and validated using a variety of matrices and sources of NAs relevant to the Athabasca region of Canada. This included raw oil sands process affected water (OSPW), acid extractable organics (AEOs) from fresh and aged OSPW and commercially available NAs. Merichem technical mixture of naphthenic acids were obtained from Merichem Company (Houston, Texas, USA). Additional naphthenic acids were also sourced from Sigma–Aldrich Canada, Acros (Fisher Scientific, Canada), and Kodak Chemicals. Decanoic-d3 acid was purchased from CDN Isotopes, Canada.

Surface water samples from the Athabasca River region were collected during routine water quality monitoring by Environment Canada staff during 2014. Samples were collected in glass bottles, filled to eliminate headspace, and immediately stored on ice until refrigeration for storage. All surface water samples were stored refrigerated at $4 \pm 2\,^{\circ}C$ prior to analysis without additional preservation. Refer to Section 3.1 for recommended future storage conditions.

Raw OSPW from an undisclosed source in the Athabasca oil sands region was collected in a steel drum and filtered (0.7 μm glass fiber filter followed by a 0.45 μm filter) prior to refrigerated storage in Teflon lined container.

Acid extracted organics (AEOs) were isolated from OSPW collected from the discharge into the West In Pit settling basin at Syncrude Canada Ltd. in the summer of 2009. The AEOs were extracted by Environment Canada (Burlington, Ontario) using a previously described method [23], resulting in a 2600 $\mu g\,mL^{-1}$ solution of total naphthenic acids in 0.1 M sodium hydroxide, the concentration being previously determined by high resolution mass spectrometry [19]. Acid extractable organics were also isolated [23] from an "aged" source of OSPW (Test Pond 9, Syncrude Canada Ltd.) created in 1993 by transferring 6000 L surface OSPW from an active tailings pond, with no subsequent modification other than natural precipitation and evaporation.

All glassware employed was routinely cleaned with FL-70 detergent, thoroughly rinsed with solvent and ultrapure water, and heat treated at >300 °C for more than 12 h before use.

2.2. Sample preparation

To allow for a rapid high throughput analytical procedure, sample preparation was kept to a minimum. Immediately prior to analysis, samples were made alkaline using minimal volume of concentrated ammonium hydroxide to obtain a sample pH ≥10.