

ABATEMENT OF POLAR ORGANICS IN NATURAL WETLANDS AND RIVERS – ANALYTICAL METHODS *

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Abstract

Described are three innovative and complementary methods for the characterization of polar organics in natural waters. A simple and rugged GC/MS procedure is shown to be well suited for the determination of sulfolane, (tetrahydrothiophene 1,1 - dioxide, C₄H₈O₂S; a water miscible chemical used in the sweetening of sour – gas) a compound that is known to be readily sequestered by wetland vegetation. In contrast, LC/MS employing electrospray ionization is ideal for the quantification of two other classes of polar chemicals, namely (a) alkanolamines in vegetation and (b) mixtures of naphthenic acids in natural waters in oilsands regions of Northern Alberta, Canada. The modern techniques take advantage of quite simple extraction procedures, with no need for derivatization steps and exploit the polar nature of the chemicals to separate the analytes from high back ground non – polar components. For the alkanolamines, MS/MS is a prerequisite for obtaining diagnostic product ion scans of the molecular ion formed under soft – ionization conditions.

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Introduction

The analytical methods described herein share a common theme in that the analytical procedures are needed to support water quality monitoring and research in the Environment and Energy Sector. In the first case described, the methods for the analysis of sulfolane and alkanolamines were used for monitoring the concentrations of chemicals in natural wetlands at a number of oil – and – gas plants in Alberta, Canada. In the second application, the method for the determination of toxic naphthenic acids was used to help establish base – line data for decision making on future development of oilsands refining in the Fort McMurray region of Northern Alberta, Canada.

In the case of the oil – and gas operations, there are questions and concerns pertaining to the remediation of sulfolane and alkanolamines in groundwater and wetlands discharging to localized surface waters. Sulfiol, a mixture of sulfolane and diisopropanolamines (DIPA), is sometimes used for the processing of natural gas to remove toxic levels of acidic sour gases, such as hydrogen sulfide and carbonyl sulfide, from the raw gas – condensate (Merck Index 1983; RAO et al, 1990; RAO et al, 1991). Waste associated with the acid – gas removal process include spent sulfinol, sludges, and industrial filters (GREENE et al. 1998). These wastes are often stored in surface retention pits or landfills. Leakage from these sources has inadvertently contaminated subsurface soils, ground water and surface water to varying degrees at some sour gas processing facilities (GREENE et al. 1998a; GREENE et al. 1998b). An investigation was thus initiated to evaluate the impact of releases of these process chemicals on a natural wetland adjoining a gas processing facility and to assess the viability of natural attenuation as a passive long – term treatment solution for contaminated wetlands (HEADELY et al. 1999).

Likewise, the interest in naphthenic acids centers around their corrosive and toxic properties in aquatic ecosystems. Naphthenic acids or petroleum acids occur naturally in petroleum deposits, but their concentration is elevated in effluent water resulting from the bitumen extraction process used at the Athabasca Oilsands in Fort McMurray, Alberta, Canada. This process produces large amounts of effluent water containing naphthenic acids, components of which are acutely toxic to aquatic species. According to MacKinnon et al. (1986), the toxicity of the oilsands wastewater appears to be due primarily to polar organic carboxylic acids. However, it is not established to what degree natural seepage of such polar chemicals from oilsands deposits in Northern Alberta, Canada, migrate to natural surface waters. Background base-line data is needed for relatively pristine locations to assess the level of industrial development the region can sustain.

Experimental

The gas chromatography/mass spectrometry (GC/MS) method and liquid chromatography methods (LC/MS) adopted are suitable for the determination of the levels of sulfolane and alkanolamines in water and associated wetland vegetation (roots, shoots, berries, seeds, grasses, and leaves). Full details of the procedures are reported in the literature (HEADELY, et al. 1999 a,b).

As both sulfolane and DIPA are miscible with water, selective and sensitive analytical methods are required for their analysis in vegetation samples. The analysis of DIPA was performed using water extracts of the vegetation and an ion chromatography-electrospray ionization – tandem mass spectrometry (ESI/LC/MS/MS) procedure, full details of which are

described elsewhere {2}. In brief: About 1 g of thawed tissue was ground under liquid nitrogen to a fine powder using a mortar and pestle. The dry powder was transferred to a centrifuge tube, and 10 mL of organic free Milli – Q water was added. After mixing and centrifugation, the supernatant was filtered using a 0.20 μ m surfactant – free cellulose acetate membrane filter. No further cleanup steps were performed before ESI/ LC/MS/MS determination. Sulfolane was extracted from the water extracts of the vegetation using toluene. The toluene back – extraction served as a clean – up step prior to gas chromatography – mass spectrometry (GC/MS) determination of sulfolane in the toluene extract, details of which are described elsewhere {13}. The main advantages of this two – stage procedure are: (a) good extraction efficiency (recovery of $80\% \pm 12\%$), (b) exclusion of most of the highly polar co – extractives during the toluene back extraction step and (c) a final extract well suited to routine GC/MS selected ion monitoring of sulfolane with a detection limit of 20 ng/g (dry weight).

In addition to the wetland vegetation, soils and water were also analyzed to gain some insight on the partitioning of the chemicals from the wetland soil and water to the vegetation. Soil samples were sieved to remove matter larger than 2 mm in diameter, then extracted with water and analyzed for DIPA and sulfolane as described above for plant tissues. Water samples were filtered before analysis for DIPA, and extracted with toluene for analysis of sulfolane, as described above. Some of the water samples collected early in the study were screened using Dionex 4000 ion chromatograph equipped with Autoion 400 software. For instrumental analysis, a sample loop of 50 μ l was utilized with guard and analytical OmniPac PAX – 500 columns connected to a PAD-2, gold working electrode. Ag/AgCl was used as the reference electrode. In contrast to the

ESI studies, analytes were present in their neutral form and separation was based on the reverse phase properties of the column. The eluent was: 10g of NaOH + 30ml of acetonitrile/2 litre of milli-Q water at a flow of 1ml /min.

Assessment of the fate and transport of naphthenic acids in the environment has been hampered by a void of published analytical methods. To date, methods have been limited to infrared detection and qualitative analysis by fast atom bombardment mass spectrometry. To help address this void, a recent application has been developed for the determination of dissolved naphthenic acids in natural waters using negative-ion electrospray mass spectrometry (HEADELY et al. 2001). Concentrated water samples are introduced into an electrospray ionization source of a Micromass AutoSpec Q by loop injection. Acetonitrile: water (50:50) plus 0.4% NH_4OH are used as the eluent at a flow rate of 30 $\mu\text{l}/\text{min}$. Concentration of the pH adjusted water sample is accomplished by a solid phase extraction procedure utilizing a highly crosslinked polystyrene based polymer with elution using acetonitrile. The extraction and analytical procedure have been shown to be fast and efficient for the recovery and detection of naphthenic acids.

The method provides a 1000 fold enrichment of the sample based on solid phase extraction of one litre samples. In addition, the extraction procedure is efficient in the desalting of the extract prior to mass spectrometry analysis leading to less interference contribution by inorganic ions.

Results and Discussion

The recovery of sulfolane and DIPA from the range of vegetation fortified at 0.98 mg kg^{-1} (all concentrations given on a wet mass tissue basis), were $80\% \pm 12\%$ r.s.d.; and $90\% \pm 25\%$ r.s.d.; respectively for a total of 15 determinations. Detection limits for sulfolane and DIPA in the various plant tissues were 0.09 mg kg^{-1} and 0.02 mg kg^{-1} , respectively. As the same procedures were used for soils as the vegetation, it was assumed that the method performance was the same for soil samples. The recovery for a soil matrix spike was, however, 126% and 55% for sulfolane and DIPA respectively. For soils, there may thus be some interference for sulfolane while the strong sorption of DIPA to soils (LUTHER et al 1998) may result in a non – extractable portion. Likewise, for a water matrix spike, the recovery was 127% and 100% for sulfolane and DIPA with corresponding detection limits of 0.001 and 0.005 mg/L respectively.

A detailed discussion of the result obtained for application of the procedures are given in the literature and will not be repeated herein (HEADLY, et al. 1999 a,b). The methods have provided positive detection of polar organic chemicals in a variety of wetland vegetation investigated. In general, the procedures are rugged, based on a study period of 18 months in which over 175 runs were conducted.

For applications of the LC/MS analysis of naphthenic acids in natural waters, extraction recoveries were found to be a function of pH, with 100% at pH 3 but 50% at pH 9 (HEADLY, et al. 2001). This observation appears to be related to differences in the sorption properties of the dissociated naphthenic acids compared with the associated acids. Also, the results indicate that the dissolved fraction of naphthenic acids is

strongly dependent on the pH of the ambient water. In acidic water (pH 3), the composition of the dissolved fraction is dominated by non – cyclic straight – chain and branched – chain fatty acids (C8 to C15). At more basic pH (pH 7.5 – 9), a more typical Z series mass spectrum associated with naphthenic mixtures is evident, indicating that there is more contribution from the ring – type carboxylic acids. This in turn has implications on the bio – availability of these substances to biota and their sorption to river sediments. As the naphthenic acids are a complex mixture, these findings are also critical in the appropriate selection of ions for selected ion monitoring in order to establish detection limits suitable for monitoring naphthenic acids at levels in natural waters. Relying on naphthenic acid standards, even if derived from source material, may lead to false or misleading results if pH is not considered prior to analysis.

References

- MACKINNON, M.D. and BOERGER H. (1986). Description of two treatment methods for detoxifying oil sands tailings pond water. *Water Poll. Res. J. can.* 21: 496-512.
- MERCK INDEX. (1983). An encyclopedia of chemicals, drugs, and biologicals. 10th Edition, Merck & Co., Inc., NJ., USA.
- GREENE, E.A.; GIEG. L.M.; COY, D.L. and FEDORAK, P.M.. (1998). Sulfolane biodegradation potential in aquifer sediments at sour natural gas plant sites. *Water Res.* 32 (12): 3680-3688.
- GREENE, E.A., and FEDORAK, P.M. (1998). A different medium for the isolation and enumeration of sulfolane-degradating bacteria *Journal of Microbiological Methods* 33:255-262..

- HEADELY, J.V.; PERU, K.M.. and DICKSON, L.C.. (1999). Ion-exchange electrospray ionization liquid chromatography mass spectrometry and tandem mass spectrometry of alkanolamines in wetland vegetation exposed to sour-gas contaminated groundwater. *Rapid Communications in Mass Spectrometry* 13 (8): 730-736.
- HEADELY, J.V.; PERU, K.M.. and DICKSON, L.C.. (1999). Gas Chromatographic-mass spectrometric determination of sulfolane in wetland vegetation exposed to sour gas-contaminated groundwater. *Journal of Chromatography A*. 859: 69-75.
- UTHER S.M.; DUDAS M J, AND FEDORAK. PM. (1998). Sorption of Sulfolane and diisopropanolamine by soils, clays and aquifer materials. *J. Contam. Hydrol.* 32: 159-176.
- RAO, S. C., LEE, L.S., and WOOD, A.L. (1991). Solubility, sorption and transport of hydrophobic organic chemicals in complex mixtures. United States Environmental Protection Agency, EPA Environmental Research Brief, Report No. EPA/600/M-91/ 009.
- RAO, S. C., LEE, L.S., and PINAL, R. (1990). Cosolvency and sorption of hydrophobic organic chemicals, *Eviron. Sci. Technol.* 24. 647-654.