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Gas chromatographic–mass spectrometric determination of sulfolane in wetland vegetation exposed to sour gas-contaminated groundwater

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Abstract

Described is a GC–MS method for the determination of the levels of sulfolane (tetrahydrothiophene 1,1-dioxide, $C_4H_8O_2S$; a water miscible chemical used in the sweetening of sour gas) in wetland vegetation (roots, shoots, berries, seeds, grasses, and leaves). The technique was developed to provide positive detection of sulfolane in a variety of wetland vegetation and to determine the extent to which sulfolane may translocate within the plants. Vegetation samples collected at a sour gas processing facility were extracted using a two-stage process which utilized a back extraction of a water extract with toluene. The main advantages of this procedure were: good extraction efficiency (recovery of 80±12%), exclusion of most of the highly polar co-extractives during the toluene back extraction step, and a final extract well suited to routine GC–MS selected ion monitoring of sulfolane with a detection limit of 90 ng g^{-1} (wet mass). In general, the method was rugged, based on a study period of 18 months in which over 175 runs were conducted.

Keywords: Plant materials; Environmental analysis; Sulfolane

1. Introduction

Sulfolane (tetrahydrothiophene 1,1-dioxide, $C_4H_8O_2S$) is a liquid, completely miscible in water at 30°C, with a boiling point of 285°C [1] and is considered weakly to moderately basic (structure is shown in Fig. 1, associated with molecular ion at m/z 120). Sulfolane is commonly used in combination with diisopropanolamine (DIPA) in the Sulfinol process to remove toxic levels of sour gases such as hydrogen sulphide and carbonyl sulphide from raw natural gas condensate [2]. The wastes associated with the acid-gas removal process include spent Sulfinol, sludges, and industrial filters. These wastes are often stored in surface retention pits or landfills, leakage from which has inadvertently contaminated subsurface soils, groundwater and wetland ecosystems to varying degrees over the years of operation of the sour gas processing facilities (SGPFs).

Based on its complete miscibility in water, sulfolane is expected to be mobile in the aqueous phase. Little has been established on its cosolvency effects under field conditions and the extent to which it may mobilize other co-contaminants in groundwater [3,4].

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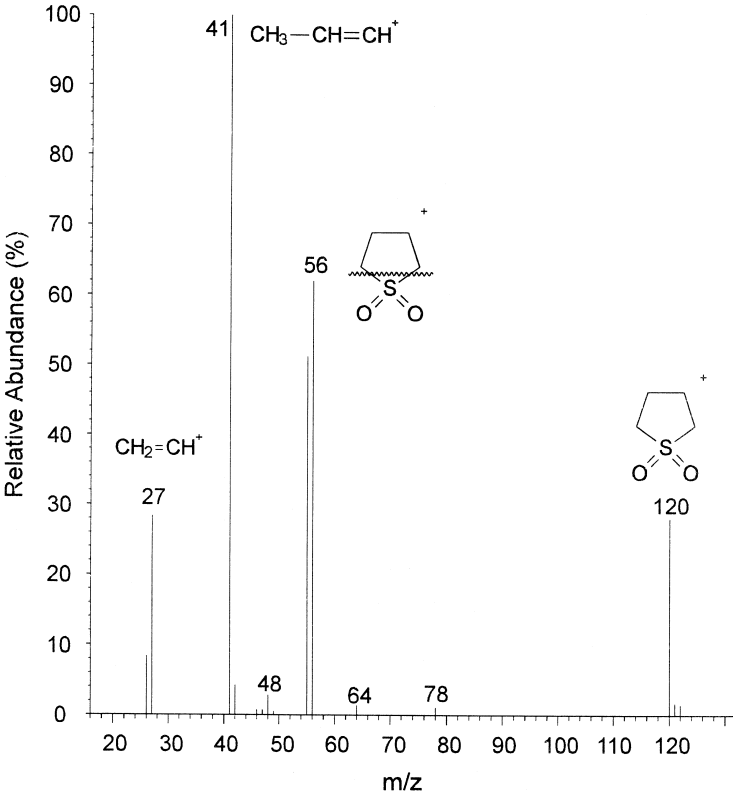

Fig. 1. Electron impact mass spectrum of sulfolane.

Sulfolane readily undergoes biodegradation under laboratory conditions [5,6]; however, little is known of its biodegradation under field conditions and even less is established about the degree to which it is taken up by wetland vegetation. It is not known whether the latter is a significant process in the possible transmission of sulfolane in the food chain.

These knowledge gaps have hampered a full assessment of the fate of sulfolane in subsurface environments and wetland ecosystems. Furthermore, as sulfolane is miscible with water, extraction from vegetation tissue can lead to excessive levels of co-extractives as polar solvents are required for effective extraction. Selective and sensitive analytical methods are thus a prerequisite for the quantification of sulfolane in vegetation samples.

Preliminary work was conducted using LC–MS of water extracts of the vegetation with positive ion and negative ion electrospray ionization. This approach has been shown to be well suited to the determination of other process chemicals, for example alkanolamines such as DIPA, in wetland vegetation [7]. However, electrospray ionization resulted in very poor sensitivity for the detection of sulfolane. While other modes of ionization, such as atmospheric pressure chemical ionization [8] with LC separation, may potentially prove to be successful, we opted to pursue the development of a conventional GC–MS approach. The latter, to date, has been limited to applications of sulfolane in water and soil samples [2].

In this work, we describe a GC–MS application for the determination of the levels of sulfolane in wetland vegetation (roots, shoots, berries, seeds, grasses, and leaves), which was developed to provide positive detection of sulfolane in a variety of wetland vegetation growing near SGPFs and to determine the extent to which sulfolane may translocate within these plants. Extraction of tissue was performed using a two-stage process which utilized a back extraction of a water extract with toluene. It is demonstrated that the main advantages of this pro-

cedure are: good extraction efficiency (recovery of 80±12%), exclusion of most of the highly polar co-extractives during the toluene back extraction step, and a final extract well suited to routine GC–MS selected ion monitoring of sulfolane at the ng g^{-1} level (all concentrations given on a wet mass tissue basis).

2. Experimental

2.1. Materials

Analytical-grade sulfolane was obtained commercially from Sigma–Aldrich (Oakville, Canada). A stock solution (1000 mg l^{-1}) was prepared by accurately weighing approximately 25 mg of the analytical grade standard into a 25-ml volumetric flask and bringing to volume with toluene. Working standard solutions were prepared by transferring appropriate volumes of the stock solution to 50-ml volumetric flasks and diluting to volume with toluene. The solutions were stored at 4°C, and replaced after 6 months, or sooner as required. All glassware was washed with hot soapy water, hot water rinsed, followed by multiple rinses with Milli-Q water and dried in an oven at 100°C. All glassware was further rinsed with toluene prior to use.

2.2. Sampling

Sampling of vegetation was conducted by Komex International (Calgary, Canada) at a wetland near an industrial gas processing facility in Western Canada. Sampling was performed during the growing season of the summer months to coincide with possible maximum rates of uptake of contaminants from the wetland soil and water. The selection of vegetation was based on two factors: whether the plant was palatable to the area's wildlife, and the number of animals that inhabit the wetland area and consume the vegetation.

Samples of plant tissues, including roots, leaves, berries (or seeds) and flowers, were collected in triplicate from five different plant species. In addition, samples of plant tissues of similar or the same species were collected from an uncontaminated site (South Saskatchewan River at Saskatoon, Canada) and used as controls. Over two growing seasons (1997 and 1998), 147 wetland plant tissue samples and 66 control plant tissue samples were collected. All samples were stored in clean plastic bags or glass jars which were maintained at −40°C until extracted.

2.3. Extraction

Tissues were prepared and extracted using two different methods: (a) an approximately 1-g subsample of soil-free plant tissue was thawed in a 150-ml centrifuge tube to which 10.0 ml of organic-free Milli-Q water was added. The tissues were homogenized using a Polytron tissue homogenizer (Brinkmann Instruments Canada, Mississauga, Canada). (b) An approximately 1-g subsample of plant tissue was ground under liquid nitrogen to a fine powder using a mortar and pestle, then the powder was transferred to a 150-ml centrifuge tube and allowed to warm to room temperature before the addition of Milli-Q water to avoid ice formation in the following extraction step. The tissue was allowed to soak in the water for 40 min with intermittent swirling every 10 min. In both methods, the tissue–water mixture was subsequently centrifuged for 45 min at 2500 rpm (1400 *g*) to remove large debris. The supernatant was filtered using a 0.20-μm surfactant-free cellulose acetate membrane filter and 1.00 ml of aqueous plant extract transferred to a 15-ml graduated conical-bottomed centrifuge tube equipped with a ground-glass stopper. This extract was back extracted serially with 3×5 ml of water-saturated toluene by mixing the phases in the stoppered tube for 1 min using a Vortex mixer. The phases were allowed to separate and the upper toluene layer transferred to a second graduated centrifuge tube via a disposable pipette. The combined toluene extracts were concentrated under a gentle flow of nitrogen at 50°C to approximately 0.8–0.9 ml, followed by the addition of toluene to bring the volume to 1.00 ml. Following this step, no further cleanup was required and the toluene extract was transferred to a crimp-top vial for GC–MS analysis. Sample extraction was completed in triplicate and in addition, matrix spikes and glassware blanks were analysed for quality assurance and quality control. Quantification of sulfolane was based on the external standard method.

2.4. Instrumental analysis

The vegetation extracts were analyzed using a Hewlett-Packard (HP Canada, Mississauga, Canada) Model 5890 GC system which was equipped with an HP Model 7673 injector and an HP 5970 mass-selective detector. The GC system was fitted with a 25-m×0.25-mm I.D. DB5-MS (0.25-μm film thickness) fused-silica open tubular (FSOT) column (Chromatographic Specialties, Brockville, Canada). The GC operating conditions were: split-splitless injector, 250°C; helium carrier gas head pressure, 72 kPa (10.5 p.s.i.), giving a linear flow-rate of 25 cm s^{-1}; oven temperature program: initial temperature, 80°C (held for 2 min), followed by an increase to 160°C at a rate of 10°C min^{-1} with a second temperature increase to 280°C (held for 5 min) at a rate of 20°C min^{-1} for a total run time of 21 min. The MS operating conditions were: ion source temperature, 280°C; electron impact ionization at 70 eV electron energy; electron multiplier voltage, 2200 V; mass analyser operated in the selected ion-monitoring (SIM) mode; solvent delay time of 6 min; dwell time 50 ms per ion for ions at m/z 120, 56, 41 (at unit mass resolution). Mass calibration was accomplished using perfluorotributylamine (PFTBA). Quantification was based on the integrated area of the ion at m/z 41 (corresponding to $M^+-SO_2CH_3$) and using an external standard method for calibration. For the latter, duplicate runs were performed to check the reproducibility and possible drift in calibration at the beginning, middle and end of each batch of six to 10 samples. A within-batch variability of <10% (median value 6.7%) of the expected value was routinely attainable using the m/z 41 ion for quantification. Positive identification was based on a combination of three diagnostic features: nominal mass of the M^+ ion (m/z 120) at a retention time of 7.79 min, and abundance ratios for ions m/z 41/120 (4.89) and m/z 56/120 (2.34) being within a ±25% window of the respective ion abundance ratio determined by analyses of authentic standards. Values in parenthesis are the mean of relative ion abundances with respect to the abundance of the molecular ion for 30 analyses of authentic standards of sulfolane. The relative standard deviations of the relative ion abundances were 6.0 and 7.2% for m/z 41/120 and m/z 56/120 ratios, respectively, leading to the establishment of the 25% window at approximately three times the relative standard deviation.

3. Results and discussion

The full scan electron impact mass spectrum of sulfolane (Fig. 1) contains an intense ion at m/z 41. Although an ion at this low mass is not normally the best choice for quantification, in this application the ion at m/z 41 was preferred to the molecular ion due to its intensity. In addition, the two-step extraction procedure provided a very clean extract with no detectable compounds with an ion at m/z 41 co-eluting with the analyte. Diagnostic ions at m/z 56 (corresponding to the loss of SO_2) and the molecular ion at m/z 120 were monitored for confirmation purposes as described above. In our laboratory, linear calibration curves were obtained for sulfolane standards (no matrix present) in the range 0.15–4.0 ng μl^{-1} (Fig. 2).

A SIM mass chromatogram for the determination of sulfolane in a toluene extract of plant tissue from representative wetland vegetation is illustrated in Fig. 3, showing the low chemical background noise present in the GC–MS chromatograms. Sulfolane was generally well resolved from co-extractives in the plant tissue as illustrated in Fig. 3. For the latter, the level of native sulfolane was 1.4 μg g^{-1} in the vegetation.

The recovery of sulfolane from the range of vegetation investigated, fortified at 0.98 μg g^{-1}, was 80.3±11.6% R.S.D. for a total of 15 determinations. This recovery was considered satisfactory to meet the stated data quality objective in this investigation, namely the confirmation of the absence or presence of sulfolane at low (w/w) ppm levels in a variety of plant tissues. Detection and quantification limits using m/z 41 for quantification were estimated to be 90 ng g^{-1} ($S/N=3$) and 300 ng g^{-1} ($S/N=10$), respectively. For comparison, the detection and quantification limits using the molecular ion at m/z 120 were estimated to be 445 and 1480 ng g^{-1}, respectively. This performance was maintained over an 18-month period, illustrating the ruggedness of the technique. These performance parameters were considered acceptable to meet the data quality objectives.

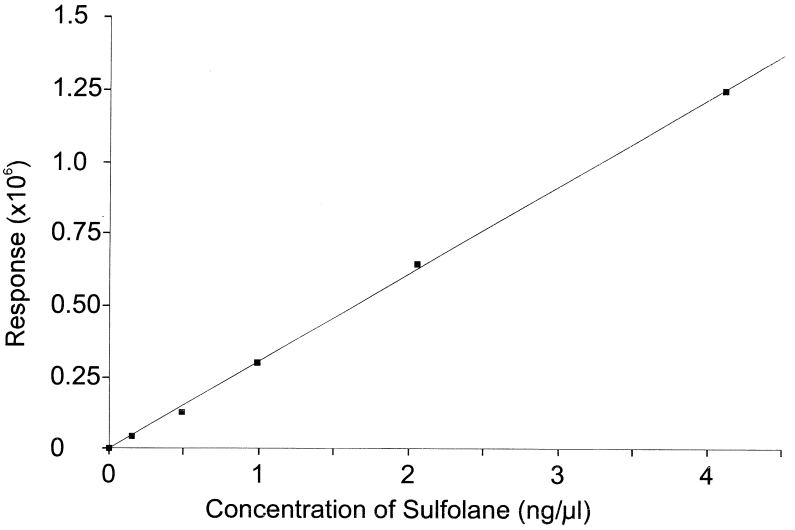

Fig. 2. GC–MS-SIM calibration curve for sulfolane (with no vegetation matrix).

An added advantage of this methodology is that DIPA, used in combination with sulfolane in the Sulfinol process, can be determined by LC–MS in a second aliquot of the same aqueous extract [7]. Therefore, this methodology allows for the determination of two common sour gas processing chemicals using only one extraction step, decreasing processing time and analytical costs.

A summary of the results obtained for the determination of sulfolane in wetland vegetation sam-

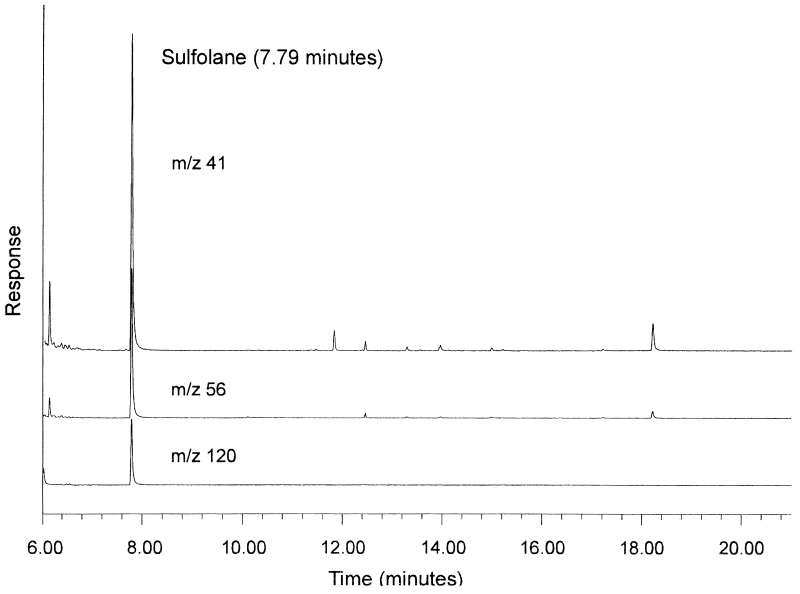

Fig. 3. GC–MS-SIM chromatograms of native sulfolane (1.5 µg g^{-1} wet mass).

pled in the 1997 season is given in Table 1. The levels of sulfolane in control samples collected at a remote site (referred to as off site background in Table 1) near the University of Saskatchewan along the banks of the South Saskatchewan River are also given. The latter location had no reported history of contamination by the compound of interest. The results provide evidence for the uptake of sulfolane at ppm levels in the wetland vegetation and at a location which was originally thought to be a non-contaminated site ('site background' in Table 1) near the wetland. This evidence is considered to be conclusive based on the reproducibility of the results over the period investigated. Sulfolane was detectable in most of the vegetation collected at the exposed sites, with the highest values observed for carex flower heads. Since the most probable source of sulfolane amenable to uptake is ground water and run off, the data suggests that sulfolane translocates to the flower heads and does not bio-accumulate in the root systems. Subsequently, due to its high boiling point (285°C) and a log K_{ow} (octanol–water partition coefficient) of –0.77, accumulation in the vegetation's flowers or top portions of the plant is not likely due to atmospheric deposition. In contrast, highest concentrations of DIPA [7] and a primary metabolite monoisopropanolamine (MIPA) [9] in vegetation samples collected from the same wetland site were found in roots.

Table 1
Levels of sulfolane in wetland vegetation sampled near a gas processing plant

Sample name	Sulfolane concentration (ng/mg wet mass)	S.D.	*n*
Cattail heads	1.2	0.29	3
Cattail roots	5.9	0.35	2
Salix leaves (a)[a]	ND		2
Salix leaves (b)	17	1.9	3
Salix buds (a)	0.61	0.070	3
Salix roots (a)	ND		2
Salix roots (b)	tr		2
Grass heads (a)	1.8		1
Grass heads (b)	25	1.6	2
Carex flower heads (a)	73	4.5	3
Carex flower heads (b)	1.9		1
Carex roots (a)	2.6	0.18	2
Carex roots (b)	ND		1
Dogwood roots (a)	ND		3
Dogwood roots (b)	0.89	0.030	2
Dogwood leaves	ND		2
Grass roots (a)	tr		3
Grass roots (b)	ND		2
Cattail heads[b]	16	2.5	2
Cattail roots[b]	0.71	0.074	3
Grass[c]	ND		2
Rosehip[c]	ND		2
Roots[c]	ND		1
Leaves[c]	ND		1
Seeds[c]	ND		2
Cattail heads	ND		2

[a] Tissue samples indicated by (a) or (b) were obtained from different sampling locations at the wetland. ND, <0.09 ng/mg wet mass; tr, <0.30 ng/mg wet mass.
[b] Denotes site background.
[c] Denotes off site background.

4. Conclusions

The GC–MS procedure described was rugged, based on a study period of 18 months in which over 175 runs were conducted and provided conclusive evidence of the uptake of sulfolane in a variety of wetland vegetation at ng g^{-1} levels.

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