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Note

Determination of dimethylsulphoxide using ion-exclusion chromatography with ultraviolet absorption detection

J. P. IVEY and P. R. HADDAD*
Department of Analytical Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)
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Dimethylsulphoxide (DMSO) has been found to occur in rain and aerosol/gas phases as a probable oxidation product of dimethylsulphide (DMS) gas of marine origin[1,2]. Its presence has also been reported in the productive upper zone of ocean waters[2]. In natural water samples, DMSO has been determined by reduction to DMS followed by gas chromatographic (GC) analysis with flame photometric detection[1], or by direct analysis using sample preconcentration followed by GC with electrolytic conductivity detection[3]. Krull and Friedman[4] have reported a liquid chromatographic (LC) method using an ion-exchange column with water as eluent, however this approach is not applicable to the low levels of DMSO found in precipitation and marine samples.

In this study we report an ion-exclusion method for the determination of DMSO, using a polymeric cation-exchange column and UV absorption detection. This method is applied to the determination of DMSO in rain and sea-water.

EXPERIMENTAL

The liquid chromatograph consisted of a Waters Assoc. (Milford, MA, U.S.A.) Model 510 pump, Model U6K injector and Model M481 variable-wavelength UV detector. Chromatograms were recorded on an Omniscribe (Houston Instruments, Austin, TX, U.S.A.) chart recorder or an LDC/Milton Roy (FL, U.S.A.) model C1-10 integrator. Studies with amperometric detection were performed using a Bio-Analytical Systems (Lafayette, IN, U.S.A.) Model BAS-4B amperometric detector fitted with a glassy carbon working electrode.

The columns used in this study were a Bio-Rad (Richmond, CA, U.S.A.) HPX-87H organic acid analysis column (300 × 4.6 mm I.D.) and a Waters Assoc. SCX Rad-Pak cartridge used in conjunction with a Z Module radial compression unit. The eluent was a 0.005 *M* solution of analytical reagent-grade orthophosphoric acid, filtered through a 0.45-μm membrane filter and degassed in an ultrasonic bath before use.

A stock solution of DMSO containing 1000 ppm sulphur was prepared from first grade reagent obtained from Sigma (St. Louis, MO, U.S.A.). This solution was diluted as required.

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RESULTS AND DISCUSSION

Detection of DMSO

The sulphoxide functional group present in DMSO provides two potential avenues for detection of this species; UV absorption at low wavelengths and electrochemical detection through oxidation to the sulphone. Both of these approaches were evaluated.

The UV absorbance spectrum of a 100 ppm (as S) solution of DMSO was recorded and it was found that strong absorbance was evident at wavelengths below 200 nm. When 0.005 *M* orthophosphoric acid was employed as eluent in the subsequent chromatographic studies, the optimal signal-to-noise ratio was observed at a wavelength of 195 nm, where the molar extinction coefficient was measured to be 9300 l/mol/cm. At lower wavelengths, excessive baseline noise was observed.

Krull and Friedman[4] reported the determination of DMSO using oxidation with permanganate, suggesting that oxidative amperometric detection was possible for this species. This approach was investigated by conducting flow-injection experiments in which DMSO solution was injected into a flowing stream of 0.005 *M* orthophosphoric acid passing directly into the cell of the electrochemical detector. When glassy carbon was used as the working electrode, no detectable oxidative current for DMSO was observed in the potential range 0–1.3 V (with respect to the standard calomel electrode). It is interesting to note that Krull and Friedman[4] found that DMSO did not react with ceric ion (E^0 1.61 V), but did with permananage (E^0 1.7 V).

Chromatographic behaviour of DMSO

The retardation of low-molecular-weight polar compounds such as DMSO presents a difficult problem when contained in an aqueous solvent. Affinity with bonded non-polar stationary phases is minimal and the aqueous solvent precludes use of normal-phase chromatography using a silica column. Krull and Friedman[4] found that DMSO was retarded on Dowex 50 cation-exchange resin using water as eluent and proposed that retention was due to a dipole–dipole interaction between the partial positive charge on the sulphur atom of DMSO and the negatively charged sulphonic acid functionality of the resin.

To examine this hypothesis, a silica-based bonded cation-exchange column containing a sulphonic acid functionality was employed with either water or dilute phosphoric acid as eluents. No retention of DMSO was observed, which suggested that the retention mechanism operating with the Dowex 50 ion-exchange resin was ion-exclusion and that modern ion-exclusion columns could prove suitable for chromatography of DMSO. When the Bio-Rad HPX-87H column packed with a sulphonated styrene divinylbenzene resin was used with 0.005 *M* phosphoric acid as eluent, the chromatogram shown in Fig. 1 was obtained. The peak identity was confirmed in the following manner. The volume of eluent corresponding to the peak was collected and titrated with dilute potassium permanganate solution. The permanganate was decolorised on contact with the solution until added in excess. The amount of permanganate consumed in this reaction corresponded stoichiometrically with the amount of DMSO initially injected.

Variation of the eluent concentration over the range 0–0.01 *M* phosphoric acid

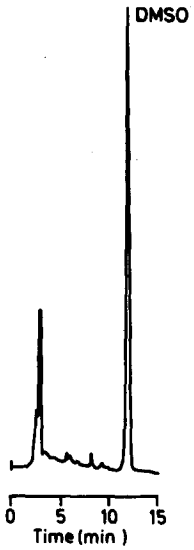

Fig. 1. Chromatogram of DMSO using ion-exclusion chromatography. Conditions: column, Bio-Rad Aminex HPX-87H (300 × 4.6 mm I.D.); eluent, 0.005 *M* orthophosphoric acid; flow-rate, 1.2 ml/min; detection, UV absorption at 195 nm; detector sensitivity, 0.05 a.u.f.s.; sample, 200 μl of a 5-ppm DMSO solution.

had negligible effect on the retention of DMSO since the pK_a of DMSO precluded any appreciable change in the degree of protonation at these acid concentrations. On the other hand, the retention behaviour of potentially interfering species having pK_a values of 3–5 could be expected to change using eluents within the pH range used above. An optimal eluent concentration of 0.005 *M* was therefore selected on the basis of elimination of co-elution by species which could be expected to occur in the water samples to be analysed. In natural waters, nitrite, nitrate, acetate, formate and sulphide are the main trace ions present which show absorbance at 195 nm and Table I shows the retention times of these species and other low-molecular-weight organic acids at the optimal eluent concentration. Nitrite and nitrate were unretained and

TABLE I

RETENTION TIMES FOR POTENTIAL INTERFERING SPECIES

Chromatographic conditions as for Fig. 1.

Species	*Retention time (min)*	*Species*	*Retention time (min)*
Nitrite	<4	Acetate	8.68
Nitrate	<4	Propionate	9.80
Succinate	4.27	Butyrate	12.14
Tartrate	6.13	DMSO	13.07
Lactate	6.62	Carbonate	–*
Formate	7.96		

* No observable peak.

none of the retained species showed interference with DMSO. The only possible exception to this would be when butyrate was present at high concentrations relative to DMSO and this situation is unlikely to occur in environmental water samples.

The effect on peak shape of variation in the sample injection volume was investigated and the results are presented in Fig. 2 which depicts the chromatographic peaks obtained with a range of injection volumes, each containing the same absolute amount of DMSO (1 μg S). It can be seen that peak width increased progressively with injection volume and peak height was progressively reduced. Peak area was constant within the precision limits of the manual injection technique used. These results show that large injection volumes were possible with the method, provided peak area measurements were emplolyed and no sample component eluted close to DMSO. Nevertheless, we have adopted 200 μl as the optimal injection volume so that adequate sensitivity may be obtained with peak height measurements. Under these conditions, linear calibration plots for DMSO were obtained over the concentration range 0.01–5.0 ppm sulphur (correlation coefficients 0.9994 and 0.9999 for peak height and area measurements, respectively), giving an absolute detection limit of 2 ng S (twice baseline noise).

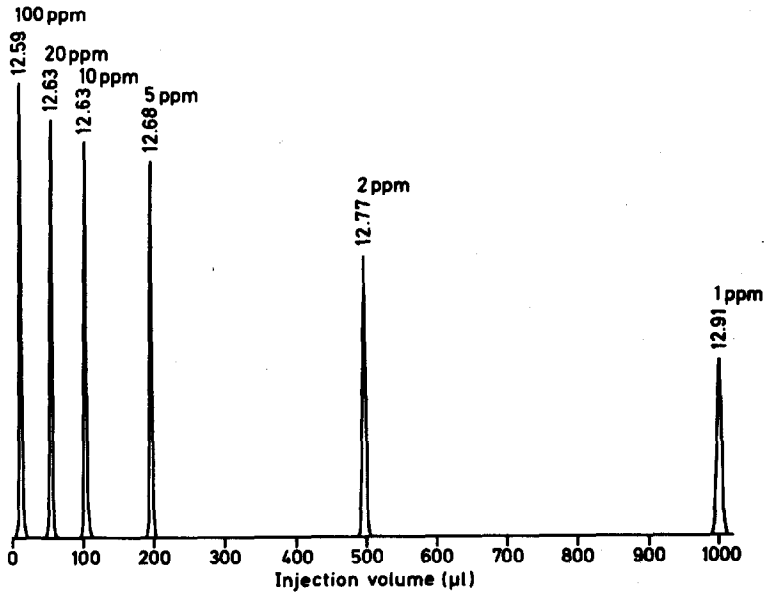

Fig. 2. Effect of increasing injection volume on the DMSO peak shape. In all cases, 1 μg of DMSO was injected. The retention times of the peaks are marked.

Applications

In order to investigate if the proposed method could be applied to the direct analysis of DMSO in sea-water, a standard DMSO solution (1 ppm) was prepared in sea-water. Fig. 3 shows the chromatogram obtained with this sample and it can be seen that the DMSO was eluted as a well resolved peak despite the high ionic

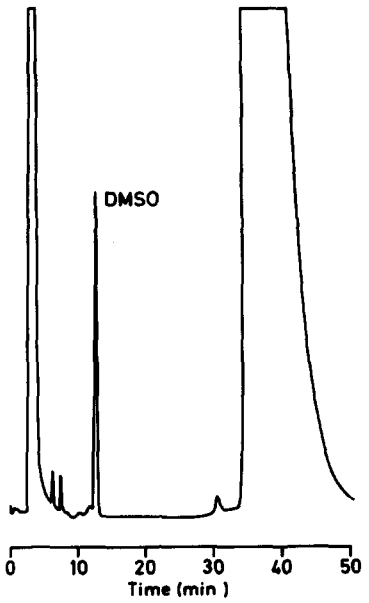

Fig. 3. Chromatogram of DMSO in sea-water. Conditions: as for Fig. 1, except that the sample was 200 μl of a 5-ppm DMSO solution in sea-water containing 0.5% chloroform as a biocide, and the sensitivity was 0.075 a.u.f.s. due to a change in integrator attenuation.

strength of the sample. The large peak in Fig. 3 was attributed to elution of the chloroform added to the sample as a biocide.

The analysis of sulphur compounds considered to be oxidation products of DMS in the maritime atmosphere is of considerable current interest in atmospheric chemistry. Compounds such as DMSO, methanesulphonic acid[5] and dimethylsulphone ($DMSO_2$) are important components in the natural cycling of sulphur in the biosphere. One conclusion from recent work[3] is that DMSO can disproportionate to $DMSO_2$ and DMS in sunlight under aqueous sterile conditions. This reaction was investigated by preparing glass vials containing standard DMSO samples in sea-water and in distilled water, and exposing them to sunlight over a period of one week. No significant decrease in the DMSO peak height was observed and headspace analysis of the sample vials confirmed the absence of DMS which would have been expected to be present had disproportionation occurred.

Harvey and Lang[3] found DMSO to be present in rainwater samples at a concentration of 0.041–2.5 ppb* (S). Our current detection limit precludes direct detection of DMSO in rainwater, however incorporation of a preconcentration step[3] would permit use of the proposed method with these samples.

* Throughout this article, the American billion (10^9) is meant.

CONCLUSIONS

Analysis of DMSO by LC has been achieved using an ion-exclusion column coupled with UV absorption detection. The method has a detection limit of 10 ppb (S) with a 200-μl injection volume, and if peak area measurements are employed, lower detection limits may be obtained with the use of larger injection volumes. When combined with preconcentration techniques, the method has sufficient sensitivity to be applicable to the determination of DMSO in environmental water samples.

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