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Determination of in situ-generated dimethyldioxirane from an aqueous matrix using selected ion monitoring

Carrie A. Delcomyn [a,*], H. Scott MacLean [a], Michael V. Henley [b], Jean J. Renard [a]

[a] *Applied Research Associates Inc., Air Force Research Laboratory, 139 Barnes Drive, Tyndall AFB, FL 32403, USA*
[b] *Air Force Research Laboratory, Materials & Manufacturing Directorate, 139 Barnes Drive, Tyndall Air Force Base, FL 32403, USA*

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Abstract

There is a growing interest in utilizing in situ-generated dimethyldioxirane (DMDO) as an oxidant for synthetic purposes and bleaching and decontamination applications, but the ability to quantify the organic cyclic peroxide species is often complicated by the presence of other reactive components, peroxymonosulfate and acetone, within the solution matrix. This paper is the first to report the use of a MS method for the quantitation of DMDO from these complex matrices by utilizing an isothermal 30 °C GC program in conjunction with selected ion monitoring (SIM). The volatile organic species is sampled from the headspace of closed batch system vials and quantified by measuring the abundance of *m*/*z* 74. The method achieves a practical quantitation limit (PQL) for DMDO of 0.033 mM, and methyl acetate is identified as a minor decomposition product from the aqueous sample matrix, contributing 9% towards the overall DMDO measurements. The spectroscopic method makes use of common analytical instrumentation and is capable of measuring other in situ-generated dioxiranes, such as those generated from 2-butanone and [$^2H_6$]acetone.

Keywords: Dioxiranes; Selected ion monitoring (SIM); Quantitation; Oxidant; In situ; Headspace sampling; Dimethyldioxirane; Methyl acetate

1. Introduction

Dioxiranes are highly reactive oxidative species that can be generated in situ by the addition of a ketone to a neutral buffered aqueous solution containing a peroxymonosulfate anion [1]. Dimethyldioxirane (DMDO), generated from the addition of acetone to the system, has been proposed as a sterilization agent for the disinfection of medical equipment [2], as well as evaluated as a chlorine-free process for bleaching kraft pulp by the paper industry [3–5]. DMDO has also historically been used for synthetic purposes to facilitate oxygen transfer reactions that result in high yield conversion of olefins to epoxides [6,7]. Based on its reactivity for the lone pair oxidation of organic sulfides and amine compounds [8,9], recent examination of DMDO as a potential decontaminant for chemical warfare agents [10] has prompted the need for a method to directly measure the concentration of oxidant generated from aqueous matrices. Large-scale utilization of dioxiranes (i.e., bleaching, decontamination, or disinfection) employ in situ-generated dioxiranes for practical and economic reasons, thus an unambiguous method is required to identify the presence of these compounds in the media in which they are generated.

The properties of the in situ aqueous system are dynamic, involving decomposition and oxidation reactions occurring simultaneously between peroxymonosulfate and dioxirane. A schematic representation is shown in Fig. 1 in which acetone is placed into a bicarbonate-buffered aqueous system to generate DMDO. Experiments using ^{18}O-labeled reagents have elucidated the mechanistic behavior of the ketone, showing that it behaves as a catalyst and is recycled within the system [11]. The regenerated acetone will continue to react as long as active oxygen is available from the peroxymonosulfate anion. Active oxygen content of the peroxymonosulfate will decrease over time due to auto decomposition, evolving

* Corresponding author. Tel. +1 850 283 6198; fax: +1 850 286 6979.
E-mail address: carrie.delcomyn.ctr@tyndall.af.mil (C.A. Delcomyn).

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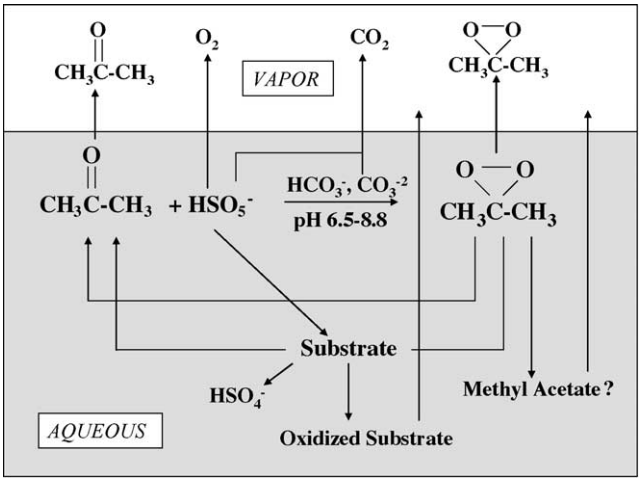


Fig. 1. Schematic representing the partitioning behavior of components between aqueous and vapor phases from an in situ-generated DMDO system. Reaction occurs by the addition of acetone (CH_3COCH_3) with peroxymonosulfate anion (HSO_5^-) in the presence of a carbonate buffer system (HCO_3^-/CO_3^{-2}) within a neutral pH range to generate the cyclic peroxide of DMDO ($CH_3C(OO)CH_3$).

O_2 and precipitating sulfate into solution. When the source of peroxymonosulfate is obtained as a salt of a peroxymonosulfuric acid compound (i.e., Oxone®) and added to a bicarbonate buffered solution, CO_2 is also generated. The presence of methyl acetate as a decomposition product is also a possibility within the in situ matrix based on a previous report in which it was observed to slowly form within isolated DMDO-acetone solutions at room temperature [12]. Any methyl acetate generated within the aqueous mixture would therefore be expected to partition into the headspace of the system along with acetone, DMDO, and organic substrate, as described by their respective Henry's constants.

Iodometric titration and oxidation of methyl phenyl sulfide are common analytical techniques that could be utilized for quantitating oxidant concentrations from aqueous matrices. However, the presence of peroxymonosulfate, also an oxidant, would not be differentiated from DMDO in the measurements. Most researchers have opted for using dioxiranes isolated into neat ketone solvent for simplicity to conduct spectroscopic evaluations, thereby eliminating aqueous phase interferences of multiple oxidants, salts and off-gassing that occurs from in situ-generated matrices. Spectroscopic data obtained by microwave, UV, IR, and NMR for numerous dioxiranes has been adequately reviewed by Murray [13]. NMR data for DMDO were found difficult to interpret without the use of isotopically labeled acetone [9], and UV data differed between reported extinction coefficients for the compound [6,14]. A GC method for the separation of fluorinated dioxiranes has also been reported in which cryogenic trapping, followed by flame ionization detection (FID), was employed as a preliminary identification tool prior to confirmatory analysis by ^{19}F NMR [15]. However, no references have been cited in the literature to date that have utilized mass spectrometry for the quantitative measurement of dioxiranes.

The method presented here first demonstrates the separation of dioxiranes from ketones of acetone, [$^2H_6$]acetone (acetone-d_6), and 2-butanone using gas chromatography at near ambient temperatures. Secondly, the method enables the quantitation of DMDO from an in situ aqueous matrix using selected ion monitoring (SIM). Since the parent ion fragment mass of methyl acetate and DMDO are identical (*m*/*z* 74), an oxidant-quenching agent is incorporated into the experimental procedure to account for any possible methyl acetate that may interfere with the DMDO measurement. Headspace is sampled directly from closed batch system vials, requiring no sample cleanup or elaborate extraction procedure. No studies on the measurement of methyl acetate from in situ-generated DMDO systems have been reported in the literature.

2. Experimental

2.1. Reagents

Oxone® (triple salt, 48.5% as potassium peroxymonosulfate), 2-butanone (>99%), [$^2H_6$]acetone (100 at.% ^2H), sodium bicarbonate (>99.7%), and methyl acetate (99%) were all acquired from Sigma–Aldrich, Milwaukee, WI, USA. Ultra-Resi Analyzed acetone was obtained from J.T. Baker, Phillipsburg, NJ, USA and USP/FCC sodium thiosulfate from Fisher Scientific, Fair Lawn, NJ, USA. Deionized water (DI) was collected from a Milli-Q system (Millipore, Molshein, France) at 18 MΩ.

2.2. Analytical instrumentation

Analyses were carried out on a Hewlett-Packard (Palo Alto, CA, US) 5890 GC and 5971 MS operated in electron impact (EI) mode. Oven temperature was maintained isothermally at 30 °C, with an injector temperature of 30 °C and transfer line temperature of 100 °C. Ultra high purity (UHP) helium (Airgas, Radnor, PA, USA) was used as the carrier gas. Detector flow rate was 1.0 mL/min unless specified otherwise. Target groups of ions were selected for each analyte based on the expected fragmentation pattern and elution time range determined from an initial full scan analysis performed for the corresponding ketone. Dwell times for each ion group were 100 ms. A manually adjusted tune file at an electron multiplier voltage of 2080 was used for optimizing mass spectrometer parameters to a tune mass of *m*/*z* 69 to enhance sensitivity towards the targeted low-weight organic analytes.

2.3. Identification of multiple dioxiranes

Batch systems were prepared at pH 7 and 21 °C in DI water, with an initial mixture consisting of 4.2% (w/v) sodium bicarbonate and 10% (w/v) Oxone®. Due to vigorous off gassing during preparation, solid Oxone® reagent was added slowly to bicarbonate in water and allowed to mix

for 10 min. An 18-mL aliquot of the buffered solution was transferred to a 30-mL capacity Wheaton amber serum vial (Fisher Scientific) and acetone, or 2-butanone in combination with deuterated acetone, was injected into the system at 10% (v/v) resulting concentrations. Batch vials were sealed using aluminum crimp tops containing PTFE-lined rubber septum inserts (Supelco, St. Louis, MO, USA). The contents were shaken briefly and allowed to react for at least 1 h. The headspace was manually assayed at a 500 μL volume using a gastight Hamilton syringe (Fisher Scientific). A vacuum was pulled on the syringe to flush residual gas contents between each assay. Control matrices consisted of bicarbonate–acetone (adjusted to pH 7 using sulfuric acid) and bicarbonate–Oxone®, each prepared at the corresponding reagent concentrations.

A 100% dimethyl polysiloxane megabore GC column (Agilent HP-1, 30 m × 0.53 mm, 1.5 μm) was used for separation of the dioxiranes and ketones. A splitter was placed immediately prior to the MS transfer line to reduce the flow rate to 0.5 mL/min. Groups of ions targeted from [$^2H_6$]acetone system were within a 0–30 min range and consisted of *m*/*z* 80, 64, and 46; ions from 30 to 50 min for 2-butanone and its dioxirane were *m*/*z* 88 and 72. The ion group for analysis of DMDO consisted of *m*/*z* 43, 58, and 74. DMDO was prepared and injected as an individual batch system to avoid co-elution with [$^2H_6$]DMDO (DMDO-d_6) on the GC column.

2.4. Quantitation of in situ-generated DMDO

Formulations were prepared at 0.8% (w/v) sodium bicarbonate, 0.8% (w/v) Oxone®, and 4.6% (v/v) acetone in DI water. The mixture was transferred to pre-weighed 60-mL amber serum vials, filled to zero-headspace (no headspace), and sealed with a crimp top containing PTFE-lined septa. Each batch solution was prepared fresh immediately prior to analysis to minimize instability and degradation of the oxidant. Sample preparation and mixing times were kept consistent for each batch system vial. The purpose of utilizing zero headspace was to generate the oxidant at a total mass within the batch system so that the equilibrium partitioning between air and water could be accurately represented by the dimensionless Henry's constant. A control batch solution treated by the same zero-headspace experimental procedure consisted of 0.7% (w/v) sodium bicarbonate, 0.5% (w/v) potassium sulfate, and 4.5% (v/v) acetone based in DI water and adjusted to pH 7 with sulfuric acid.

Separate 15-mL amber serum vials were flushed with argon (99.997%, Airgas), sealed, and weighed. These vials were used as the 'partitioning vials' in which an aqueous aliquot could be transferred to allow for headspace equilibration of the target analyte(s) prior to analysis. A stainless steel cannula was placed into both the partitioning vial and the corresponding zero-headspace sample vial. A gastight syringe filled with 10-mL argon gas was used to displace a corresponding aqueous sample volume into the argon-filled partitioning vial. The same cannula was used (solvent rinsed and dried between each sample) for each batch vial so that consistent aqueous volumes would be transferred. Once an aliquot was transferred, the partitioning vial was inverted to minimize any potential loss of the gaseous analyte through holes in the pierced septum. Each partitioning vial was weighed again and the contents allowed to equilibrate at least 20 min. Headspace was assayed from the partitioning vial and GC analysis performed using a diphenyl dimethyl polysiloxane-based column (Restek RTX 502.2, 30 m × 0.25 mm, 1.4 μm). Targeted SIM ions consisted of *m*/*z* 74, 59, 43, 41, 34, 33, and 58. The area count of the *m*/*z* 74 fragment was used for quantitation against the corresponding calibration curve.

2.5. Standardization of DMDO

No commercial standards exist for dioxiranes; therefore, DMDO was isolated from an in situ-generated aqueous solution by collecting the reactive volatile component as a condensate in acetone under slight vacuum at −70 °C [16]. Isolated solutions were stored at −20 °C and quantified by iodometric titration [17] immediately prior to each use. Yields of DMDO isolated into acetone solvent range from 0.04 M to a maximum of 0.18 M under optimized experimental conditions.

To construct a calibration curve for the method, varied aliquots of DMDO isolate were placed in a control matrix solution consisting of sodium bicarbonate (0.7%, w/v) and potassium sulfate (0.5%, w/v) in DI water (adjusted to pH 7 with sulfuric acid) and sealed into vials to zero-headspace volumes. The calibration levels ranged from 0.05 mM (near a 5:1 signal to noise ratio) to 1.3 mM. The experimental procedure for assaying from the corresponding partitioning vials was performed as previously described, and the resulting linear curve produced a regression coefficient of 0.9867. A separate experiment (results not shown) indicated that no DMDO degradation was observed from zero-headspace batch systems in which isolated DMDO was injected into a sulfate-containing matrix and allowed to sit up to 1 h.

2.6. Methyl acetate determination

The same experimental procedure was performed as described for DMDO with the exception of injecting 5-mL volumes of 1 M sodium thiosulfate (calculated in excess to oxidant) into the zero-headspace vials to quench DMDO and/or peroxymonosulfate oxidant. A syringe needle placed through the septa towards the bottom of the vial allowed for overflow of liquid during displacement by the quenching agent. The calibration curve was prepared by injecting neat methyl acetate into the zero headspace vials (0.05–0.24 mM), adding quenching agent, and then transferring aqueous aliquots into corresponding partitioning serum vials with the cannula. The same GC-SIM method used for the quantitation of DMDO was used for methyl acetate analysis. The linear curve resulted in a regression coefficient of 0.9866.

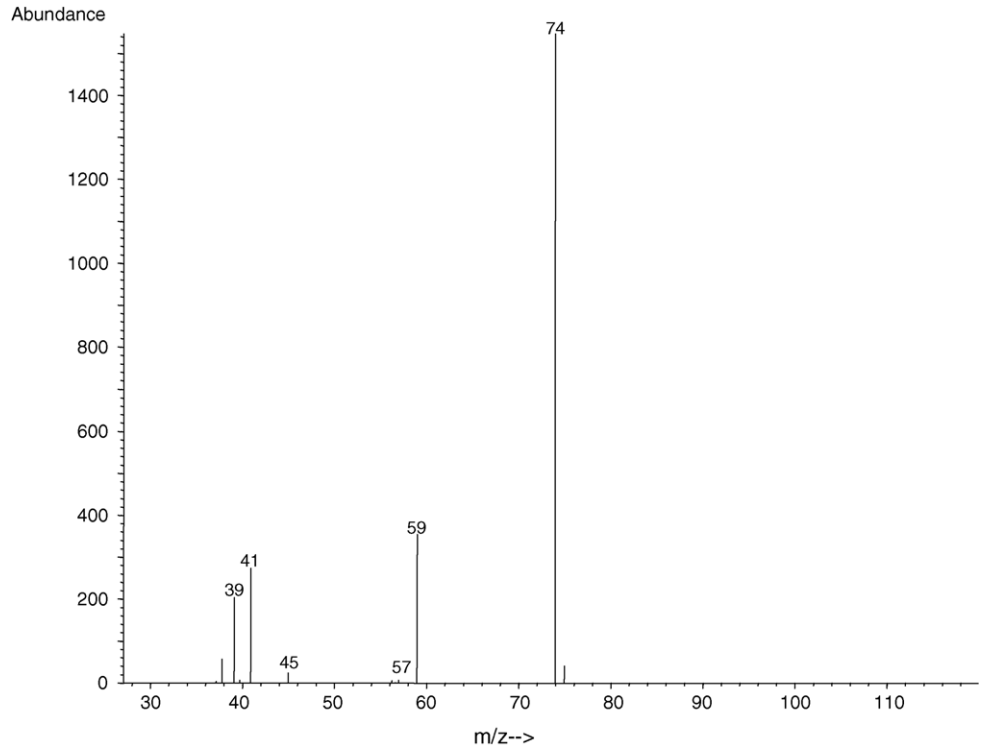


Fig. 2. Full scan mass spectrum with background subtraction obtained from analysis of DMDO isolated into neat acetone.

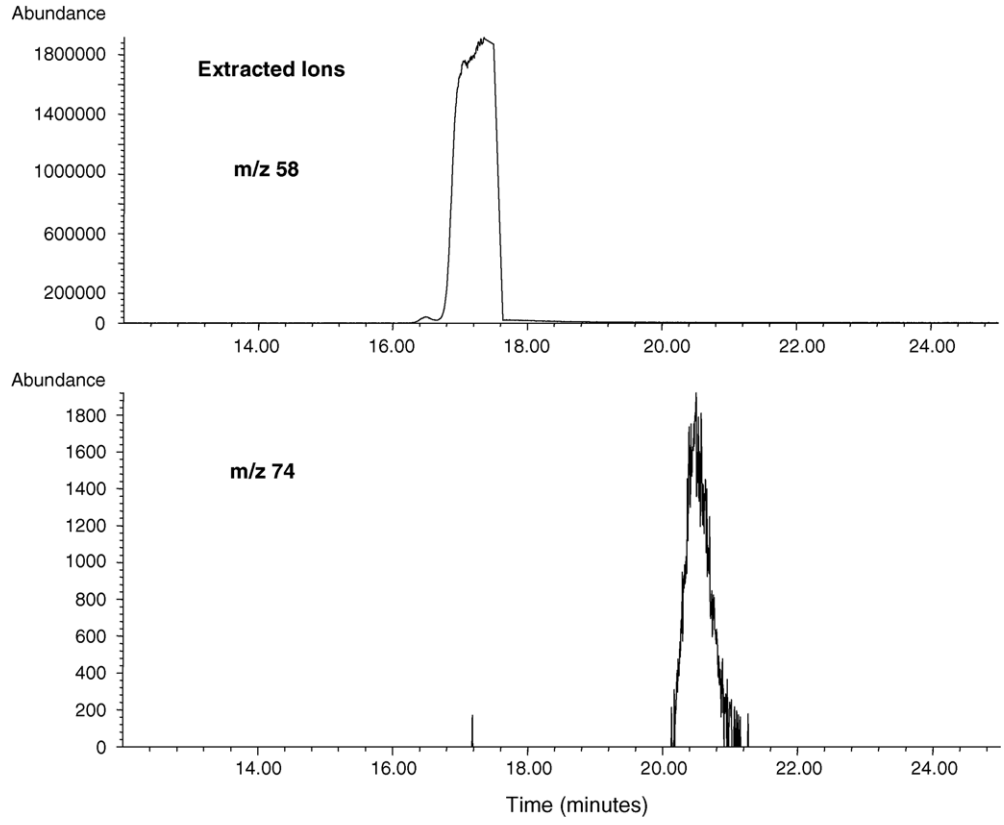


Fig. 3. Extracted ion profiles for acetone (*m*/*z* 58, top) and DMDO (*m*/*z* 74, bottom) obtained from the full scan mass spectrum of DMDO isolated into neat acetone.

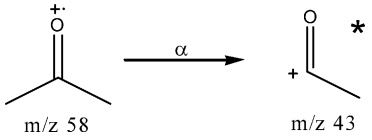
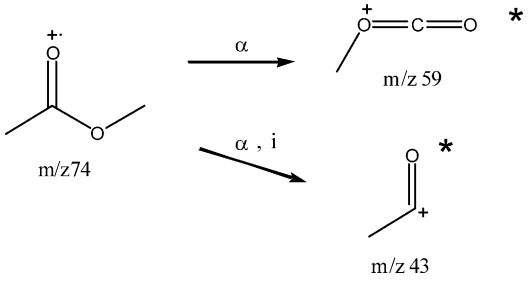
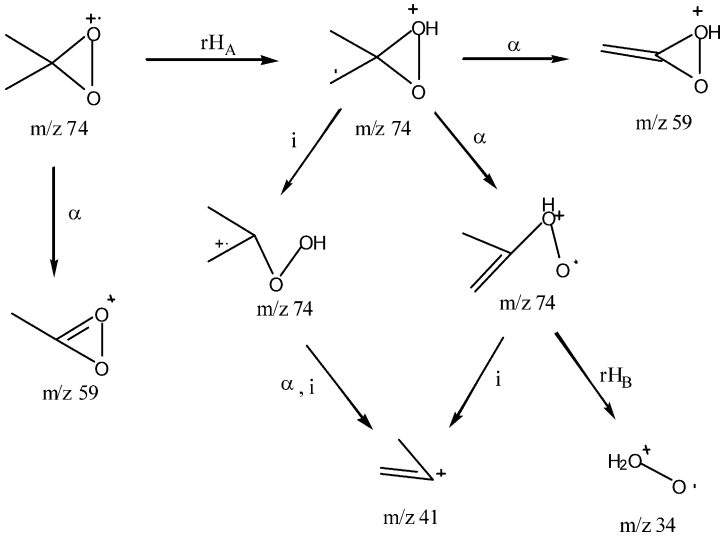
3. Results and discussion

3.1. Identification of dioxiranes

The initial screening was performed by analyzing the headspace above an isolated DMDO stock solution. Using the low temperature program but in full scan mode with a standard autotune file, an EI mass spectrum was obtained for DMDO as shown in Fig. 2. Key fragments of *m*/*z* 74, 59, and 41 were observed, as well as an isotope ion of *m*/*z* 75. The spectrum shown was obtained by performing a background subtraction of a significant level of adjacent ketone ions; however, the presence of these fragments concurs with the predicted pattern outlined in Table 1. Extraction of *m*/*z* 74 from the total ion chromatogram (TIC) indicated that DMDO elutes shortly after the acetone peak (Fig. 3). The sensitivity and abundance of DMDO represented by *m*/*z* 74 was considerably lower than expected for the given high level of DMDO obtained from neat ketone solvent (i.e., approximately 0.06 M). A 100 or 1000-fold decrease in DMDO mass analyzed from an in situ-generated aqueous solution would therefore not be detected by the MS in full scan mode. The SIM mode was utilized to enhance this sensitivity and expand the range of DMDO that could be measured.

Headspace from an in situ-generated system was analyzed in SIM mode using the ion group of *m*/*z* 43, 58, and 74. The ions targeted for acetone identification included its molecular ion of 58 and a fragment ion resulting from the loss of a methyl group (via alpha cleavage) to create the *m*/*z* 43 fragment (Table 1). The first peak observed in the total SIM chromatogram (Fig. 4) is attributed to CO_2 generated within the batch system vial containing the mixture of bicarbon-

Table 1
Fragmentation patterns predicted for target analytes by EI mass spectrometry [20]

Analyte	Fragmentation
Acetone	
Methyl acetate	
DMDO	

Electron loss of non-fragmented parent compound produces the cation radical that proceeds through alpha cleavage (α), inductive cleavage (i), or radical alpha or beta charge site rearrangement (rH$_A$, rH$_B$). Asterisk (*) depicts a resonance structure. For *m*/*z* 41 an allyl cation could also envisaged. For *m*/*z* 34 the hydrogen peroxide radical cation HO$^{\bullet+}$—OH is an alternative candidate.

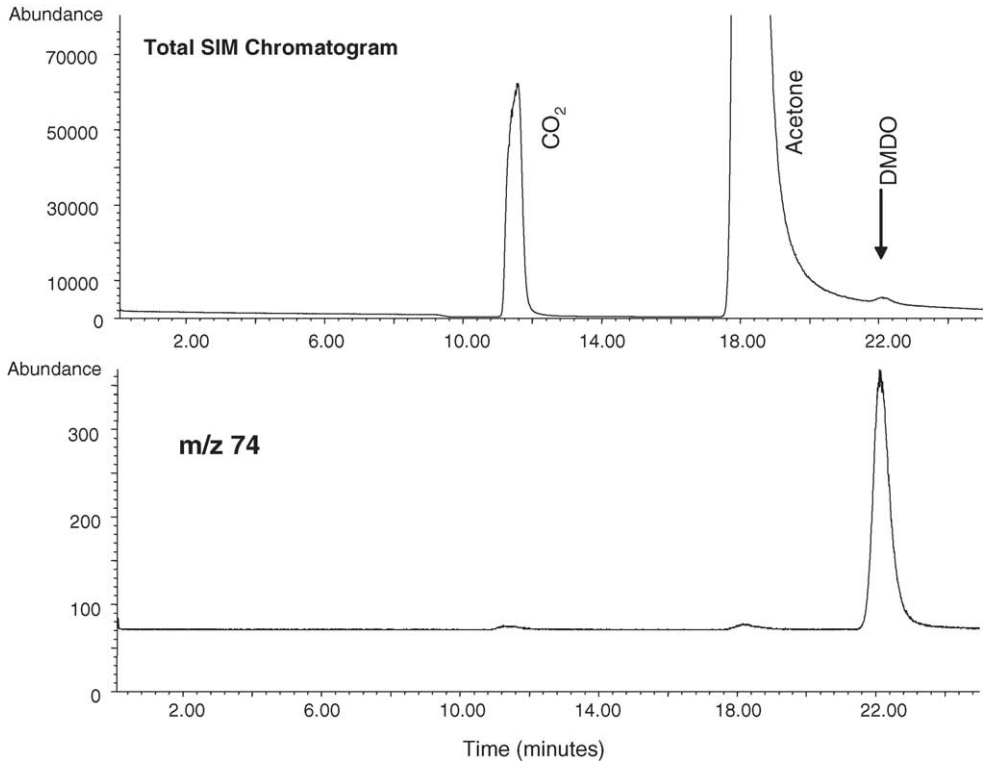


Fig. 4. Total SIM chromatogram of headspace analysis from an in situ-generated DMDO system (top) and extracted ion profile (*m*/*z* 74) for DMDO identification (bottom).

ate with acidic Oxone®. This peak appeared consistently in chromatograms for all batch system vials that contained the combination of these reagents. DMDO eluted as a small peak within the tailing of the parent acetone peak. Extraction of *m*/*z* 74 via SIM demonstrated enhanced resolution for the analyte obtained from the less concentrated aqueous system matrix. Analyses from control batch systems which consisted of buffered Oxone® and bicarbonate–acetone, did not indicate any *m*/*z* 74 peak at the corresponding retention time of DMDO.

To further support the detection technique, additional dioxiranes from [$^2H_6$]acetone and 2-butanone were generated in situ and analyzed by the GC-SIM method. Both dioxiranes eluted as small peaks off their parent ketone (Fig. 5), with a stronger response observed for 2-methylethyldioxirane represented by *m*/*z* 88. Although qualitative, the observed response differences between these dioxiranes are likely due to a difference in either the rate of equilibration within the batch vial, rate formation of the dioxirane oxidants, or 2-methylethyldioxirane possessing a higher Henry's constant compared to [$^2H_6$]DMDO (*m*/*z* 80).

3.2. Quantitation of DMDO and methyl acetate

The GC-SIM method was utilized to determine the potential formation of methyl acetate within in situ-generated DMDO solutions by using the difference of *m*/*z* 74 measured between oxidant-quenched and unquenched system batch vials. The fragmentation patterns described in Table 1 suggest that *m*/*z* 43 may have been ideal for differentiation between DMDO and methyl acetate. It is the base peak fragment for methyl acetate and not postulated as being created from the DMDO molecule. However, *m*/*z* 43 is also the base peak for the closely eluting acetone and would therefore mask any presence of methyl acetate. Also, differentiation using proposed fragment *m*/*z* 34 created from the DMDO molecule would likely be at too low a response for obtaining a reproducible measurement. Performing a separate experiment that incorporates the use of an oxidant quenching agent and eliminates *m*/*z* 74 contributions from DMDO allows for methyl acetate production to be monitored from an in situ system. Fragmentation abundances of *m*/*z* 74 between DMDO and methyl acetate would also be expected to be reflected in the response factors determined from each of their respective standards due to differences in their dimensionless Henry's constants (i.e., abundance of this fragment to differences in vapor phase concentrations).

The generation of methyl acetate was confirmed to occur upon mixture of the system reagents within solution. Taking into account the corrected amount of DMDO by subtracting the contribution of methyl acetate, the production level of each compound was determined from the headspace of batch systems over time (Fig. 6). The corrected concentration due to the original dilution of thiosulfate quenching agent in the methyl acetate measurements was also taken into account.

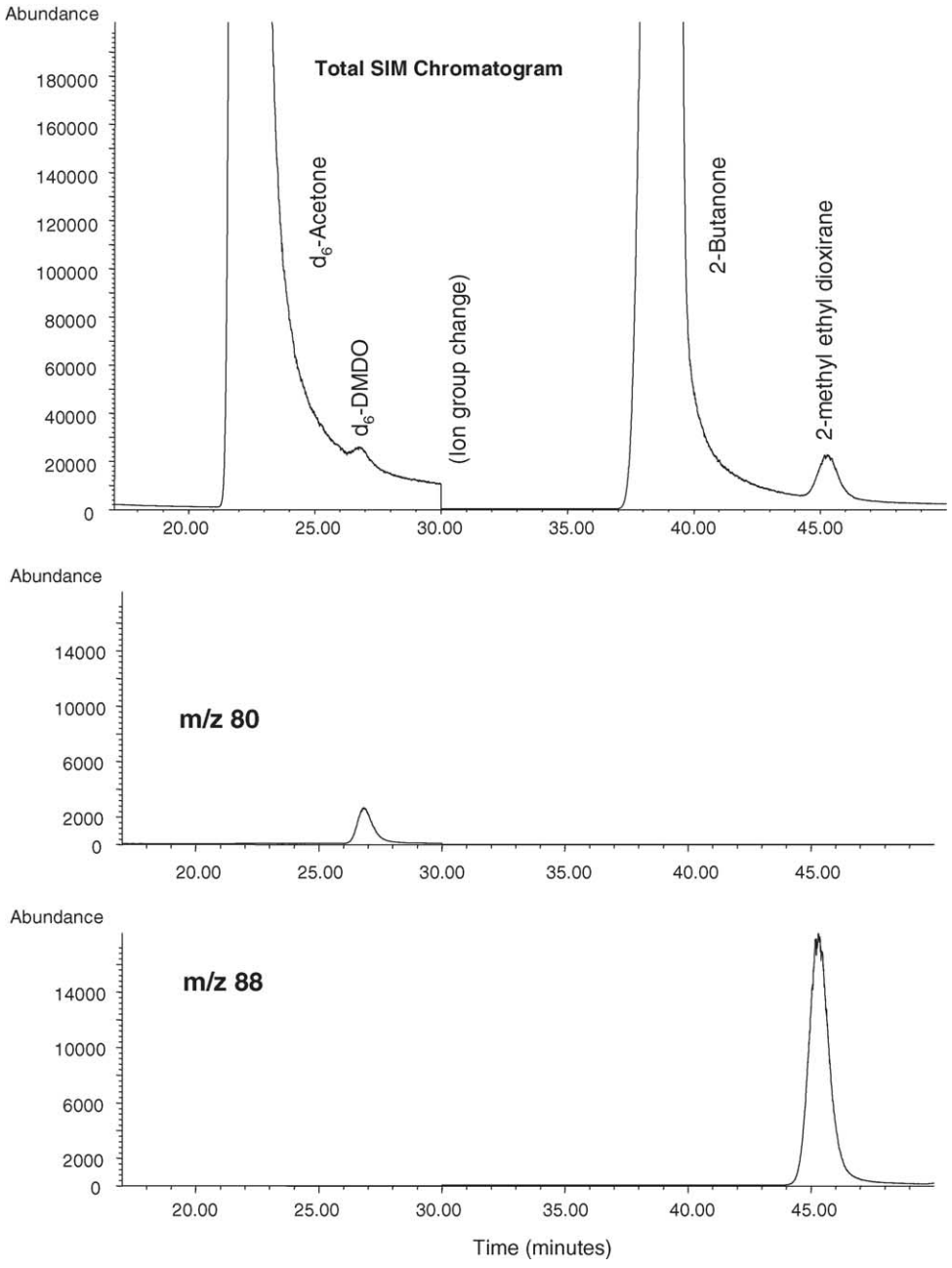


Fig. 5. Total SIM chromatogram of headspace analysis from an in situ mixture containing [$^2H_6$]acetone and 2-butanone in a buffered Oxone® solution (top). Extracted ion profiles represented as *m*/*z* 80 for [$^2H_6$]DMDO (top), and *m*/*z* 88 for 2-methylethyldioxirane (bottom).

For the given system conditions, only 8.7% of methyl acetate (19% RSD) was found to contribute to the unquenched system sample analysis. The amount of DMDO generated in the aqueous solution was considerably lower in concentration, 0.4–1.0 mM, than typically collected 100 times greater in neat acetone during a vacuum isolation procedure. The conversion resulted in 5 mol of $KHSO_5$ being required to generate approximately 1 mol of DMDO within the dilute aqueous system. A control batch solution of bicarbonate-sulfate-acetone did not produce any measurable *m*/*z* 74 fragment over time.

Methyl acetate has been observed to slowly form at room temperature in DMDO isolated into neat acetone solvent, but it has not been previously detected in in situ-generated systems. The ester product formation has been proposed to proceed via hydrogen abstraction from the parent ketone to generate a reactive radical intermediate [12]. Methyl acetate was particularly observed when isolated solutions underwent flash vacuum pyrolysis (150–180 °C) and thermolysis when refluxed over 15 min. No thermal gas phase decomposition of the species has been reported, particularly at brief exposure to 100 °C (the detector temperature used for our method). Similarly, only high temperature pyrolysis and gas and liquid photolysis studies have been reported using methyl(trifluoromethyl) dioxirane in ketone-free solvents to

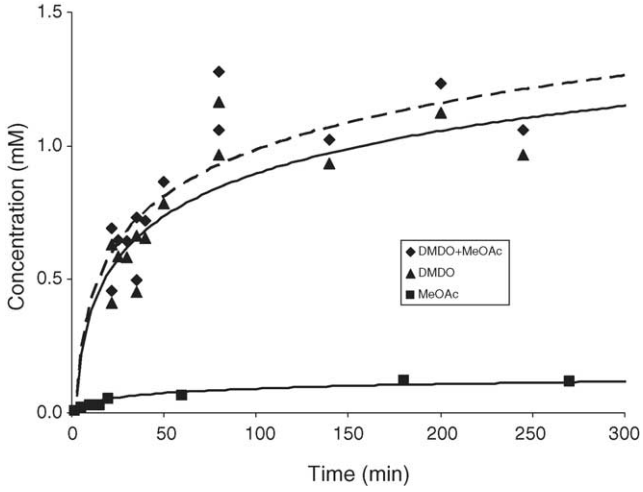


Fig. 6. Quantitation of DMDO and methyl acetate (MeOAc) generated from an in situ aqueous system as measured by the GC-SIM method.

yield acetate products [18]. Using the described GC-SIM method, the decomposition behavior of DMDO was determined by an instrumental technique that does not promote rapid thermal decomposition.

3.3. Quantitation limits

The precision measurements for the experimental procedure and analysis technique were also determined. The total volume capacities of the partitioning serum vials varied by only 2.8%, and the precision of volume transfers via cannula were within 1.2%. The practical quantitation limit (PQL) for DMDO by SIM detection was 0.033 mM based on an extrapolated 5:1 signal to noise ratio from eight individual data points, with a relative standard deviation (RSD) of 19.85%. The slightly elevated RSD is expected, and acceptable, for such low level measurements, particularly since integration was performed for small peaks detected on the tailing of a significantly concentrated ketone peak. The RSD is also based on combined experimental data obtained from two separate experiments. This accounts for the deviation observed for duplicate points at 80 min in Fig. 6. The calculated method detection limit (MDL) at a 99% confidence level was determined as 0.022 mM. Dimensionless Henry's constants reported for DMDO and methyl acetate are 0.0522 and 0.00717, respectively [19]. These dimensionless Henry's constants were predicted based on bond and structural estimation methods.

4. Conclusion

We have developed a method based on GC-SIM that allows for the progress of in situ-generated DMDO reactions to be directly measured from aqueous matrices. Headspace sampling of closed batch system vials eliminates the aqueous phase oxidant interference of peroxymonosulfate, and low temperature GC-SIM analysis allows for separation of DMDO from its parent ketone with improved sensitivity. The performance between different multi-purpose GC columns is consistent and the low temperature program avoids decomposition of the dioxirane during analysis. Methyl acetate is also identified by the method as a minor decomposition product that occurs during the in situ-generation of DMDO. The method is simple and utilizes common analytical instrumentation, with preliminary results suggesting that it could be used to assess the generation of other dioxiranes.

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