Method number:	PV2321
Version:	1.0
Target concentration:	0.4 ppm
OSHA PEL: ACGIH TLV:	None 0.4 ppm (1.24 mg/m^3) TLV-STEL, inhalable fraction and vapor
Procedure:	Collect air samples by drawing workplace air through a cassette containing one 25-mm quartz fiber filter, coated with titanium oxysulfate, followed by an impinger containing methyl p-tolyl sulfide (MTS) and 4-chlorophenyl methyl sulfone in acetonitrile (ACN). Samples are analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Recommended sampling time and sampling rate:	15 min at 1 L/min (15 L)
Reliable quantitation limit:	0.04 ppm
Status of method:	Partially validated method. This method has been subjected to the established validation procedures of the Methods Development Team and is presented for information and trial use.

November 2019 Michael Simmons

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Sandy UT 84070-6406

1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact OSHA Salt Lake Technical Center (SLTC) at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

Peracetic acid (PAA) is used occupationally to sterilize medical devices and as a disinfectant in food production.[1] Commercial solutions of PAA contain hydrogen peroxide (H_2O_2), acetic acid, and water in equilibrium ($CH_3CO_2H + H_2O_2 \leftrightarrow CH_3CO_3H + H_2O$). Due to the unstable and reactive nature of PAA, use of a derivatizing agent is necessary when performing air monitoring with a sampling medium.

In 1984, Di Furia et al. described the use of MTS to quantitatively evaluate peracids in solution. The oxidation of MTS by PAA was shown to be fast, resulting in the formation of methyl p-tolyl sulfoxide (MTSO), with a negligible amount of MTSO formed from oxidation with H_2O_2.[2] The first air monitoring of PAA was described in 1999 by Effkemann et al. using impingers and reagent coated solid sorbent tubes.[3] MTS and 2-([3-{2-[4-amino-2-(methylsulfanyl)phenyl]-1-diazenyl}phenyl]sulfonyl)-1-ethanol (ADS) were tested as derivatizing agents that were oxidized to the sulfoxides (MTSO and ADSO) by PAA. The impinger solution consisted of 35 mL of 50:50 ACN / water with either 2 mL of 1 mM MTS or ADS added. Acetic acid was added to the MTS impinger solution to adjust the pH to 3-4. The sampling tubes consisted of 500 mg of Chromabond C18f ec coated with MTS or ADS. During initial testing it was found that MTS was too volatile and stripped off the coated sorbent tubes. The ADS impinger was recommended for use because of its lower LOD and larger analytical linear range. Effkemann et al. also described the use of 2,2´-azino-bis(3-ethyl-benzothiazoline)-6-sulfonate (ABTS) as a derivative in impingers and coated on silica gel.[4] The technique is based on the oxidation of ABTS by PAA, resulting in the formation of a radical cation $ABTS^+$ with analysis by spectrophotometry. The coated silica gel was found to have a high cross selectivity towards H_2O_2.

In 2002, Hecht and Hery described the use of bubblers containing 2.7 mM MTS in 15 mL of 75/25 ethanol/water.[5] Recovery of vapor spiking was 97% compared to the same quantity of PAA spiked directly into the MTS bubbler solution. Fifty microliters of 0.1 M H_2O_2 solution spiked directly into the MTS bubbler solution showed <1% reactivity with MTS after 3 days. Two years later Hecht et al. described the use of a two-piece sampler for simultaneous sampling of H_2O_2 and PAA.[6] The sampler consists of two 25-mm quartz fiber filters coated with titanium oxysulfate, followed by a 3-mL glass solid-phase extraction tube containing 600 mg of silica gel coated with sodium carbonate and MTSO.

[1] American Conference of Governmental Industrial Hygienists (ACGIH). *Documentation of the Threshold Limit Values and Biological Exposure Indices*; Cincinnati, OH, 2014; pp. Peracetic Acid - 1 through Peracetic Acid - 5.

[2] Di Furia, F.; Prato, M.; Quintily, U.; Salvagno, S.; Scorrano, G. Gas - liquid chromatographic method for the determination of peracids in the presence of a large excess of hydrogen peroxide. *Analyst,* **1984**, *109*, pp 985-987.

[3] Effkemann, S.; Brødsgaard, S.; Mortensen, P.; Linde, SA.; Karst, U. Determination of gas phase peroxyacetic acid using pre-column derivatization with organic sulfide reagents and liquid chromatography. *J. Chromatogr. A*. **1999**, *855*, pp 551-561.

[4] Effkemann, S.; Brødsgaard, S.; Mortensen, P.; Linde, SA.; Karst, U. Spectrophotometric and direct-reading methods for the analysis of gas phase peroxyacetic acid. *Fresenius J. Anal*. Chem. **2000**, *366*, pp 361-364.

[5] Hecht, G.; Hery, M. Generation of controlled atmospheres for the determination of the irritant potency of peroxyacetic acid. *Ann. occup. Hyg.,* **2002**, *46*(1), pp 89-96.

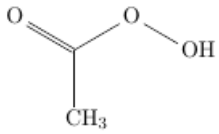
[6] Hecht, G.; Hery, M.; Hubert, G.; Subra, I. Simultaneous sampling of peroxyacetic acid and hydrogen peroxide in workplace atmospheres. *Ann. occup. Hyg.,* **2004**, *48*(8). pp 715-721.

H_2O_2 reacts with the titanium oxysulfate on the front filter, and PAA oxidizes the MTSO on the silica gel to form methyl p-tolyl sulfone.

Nordling et al. later improved the impinger technique using 15 mL of ACN containing 0.02 mg/mL MTS and 0.002 mg/mL triphenylphosphine oxide (TPPO).[7] Following sampling any remaining oxidizers are eliminated by addition of 4-6 mL of a stabilizer solution consisting of 1% sodium thiosulfate in 18.0 MΩ water. The TPPO is added as an internal standard eliminating the need to measure impinger solution volume prior to sample analysis.

Of the derivatives discussed above, only MTS and MTSO were considered as the others were not available commercially, or easily obtained at the time method validation work began. Vapor spike testing by OSHA of a commercially available sampler, based on the two-piece sampler described above by Hecht et al.[6], did not meet OSHA's >75% recovery requirement. To facilitate sampling until a solid sorbent sampler method is validated, OSHA decided to issue this impinger based method. This method uses 15 mL of ACN with MTS and an internal standard, similar to the technique described above by Nordling et al.[7] However, instead of using a post sampling stabilization solution, a 25-mm quartz fiber filter, coated with titanium oxysulfate, is placed upstream of the impinger to scrub H_2O_2. The internal standard, 4-chlorophenyl methyl sulfone, was selected based on its previous use by Di Furia et al. [8]

1.1.2 Physical properties and other descriptive information[1]

synonyms:	peroxyacetic acid, acetic peroxide, acetyl hydroperoxide
IMIS[9]:	P230
CAS number:	79-21-0
boiling point:	110 °C
melting point:	-0.2 °C
specific gravity:	1.228
molecular weight:	76.051
appearance:	clear liquid
solubility:	soluble in water
vapor pressure:	14.5 torr at 25 °C
molecular formula:	$C_2H_4O_3$
structural formula:	

[7] Nordling, J; Kinsky, O. R.; Osorio, M.; Pechacek, N. Description and evaluation of a peracetic acid air sampling and analysis method. *Toxicol Ind Health,* **2017**, *33(*12*)*, pp 922-929.

[8] Di Furia, F.; Prato, M.; Scorrano, G.; Stivanello, M. Gas – liquid chromatographic method for the determination of peracids in the presence of a large excess of hydrogen peroxide. Part 2. Determination in alkaline solutions. *Analyst,* **1988**, *113*, pp 793-795.

[9] Peracetic Acid (OSHA Occupational Chemical Database). United States Department of Labor, Occupational Safety and Health Administration Web site. http://www.osha.gov/dts/chemicalsampling/data/CH_246600.html (accessed August 2019).

This method was validated according to the OSHA SLTC "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[10]. The Guideline defines analytical parameters, specifies required laboratory tests, statistical calculations, and acceptance criteria. Air concentrations listed in ppm are referenced to 25 °C and 760 mmHg (101.3 kPa).

1.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

The DLOP is measured as mass per sample and expressed as equivalent air concentration based on the recommended sampling parameters. Ten samplers were spiked with approximately equal descending increments of analyte (MTSO), such that the highest sampler loading was equivalent to 0.927 µg/sample of PAA. This is the amount spiked on a sampler that would produce a response approximately 10 times the response of a sample blank. These spiked samplers and a sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 0.212 and 0.011 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 0.16 µg/sample (3.43 ppb).

Table 1.2
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV·s)
0.000	0.012
0.093	0.025
0.185	0.044
0.278	0.073
0.371	0.064
0.464	0.119
0.556	0.138
0.649	0.140
0.742	0.174
0.834	0.184
0.927	0.198

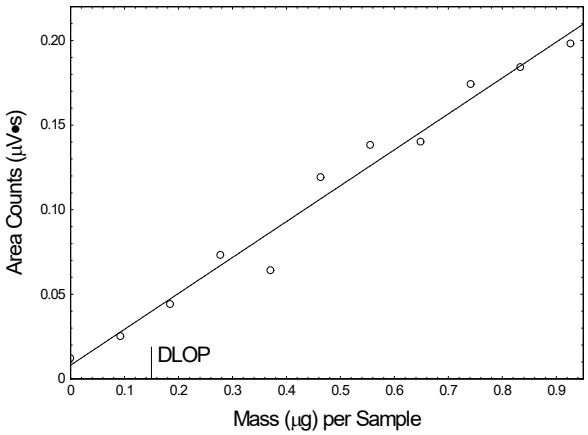


Figure 1.2. Plot of data to determine the DLOP/RQL (y = 0.212x + 0.008).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of the DLOP providing 75% to 125% of the analyte is recovered. The calculated RQL is 0.52 µg/sample (11.1 ppb) with a 110.3% recovery. A vapor spiking study of PAA at the RQL, performed as described in Section 2.4, resulted in recoveries outside the recovery requirement of 75% to 125%; therefore, the RQL was set to 0.1× the target concentration (1.87 µg/sample, 40 ppb). This RQL value is supported by empirical data discussed subsequently in Section 2.4, which demonstrated that vapor spiking recoveries at 1.74 ug/sample (0.037 ppm) met this recovery requirement.

[10] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed March, 2019).

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

Collect samples with a cassette containing one 25-mm quartz fiber filter, coated with titanium oxysulfate, followed by an impinger containing MTS and 4-chlorophenyl methyl sulfone in 15 mL of ACN. For this evaluation, the following commercially available items were used:

- Titanium oxysulfate coated quartz fiber filter preloaded into a 25-mm cassette (SKC, Inc. catalog no. 225-9037).
- Threaded midget impinger, 22-mL (Sigma-Aldrich, catalog no. 64712-U). Replace clear glass 22-mL vial with 22-mL amber vial listed below.
- Amber glass vial, 22-mL with 20-mm thread (Sigma-Aldrich, catalog no. 27073-U).
- Cap, 20-mm thread with PTFE liner (Sigma-Aldrich, catalog no. 27174-U).
- Micro impinger trap (SKC, Inc. catalog no. 225-22-01).
- Silicon tubing, 3/16 in. I.D. × 5/16 in. O.D.
- Replacement micro connectors, 20-mm to 20-mm (Sigma-Aldrich, catalog no. 64700-U).
- Impinger holder (Sigma-Aldrich, catalog no. 20271).

Caution: overtightening of the micro connector can cause the glass or connector to break. It is recommended to have on hand extra 22-mL amber glass vials and micro connectors.

Samples are collected using a personal sampling pump calibrated to within ±5% of the recommended flow rate with the sampling device in-line.

2.2 Reagents

Impinger solution (see Section 3.2)

2.3 Technique

Caution: overtightening of the impinger 20-mm to 20-mm micro connector can cause the glass sampler or connector to break**.**

Remove the plastic end plugs from the filter cassette immediately before sampling. Using a 1.5-cm length of tubing connect the bottom of the filter cassette to the top port of the impinger. The connection should be tight so the bottom connector of the cassette tightly abuts the impinger port. The tubing serves to hold the cassette tightly against the impinge port, but the air stream passes directly from the cassette outlet into the impinger port and does not contact the tubing. Remove the cap from the 22-mL sampling vial containing 15 mL of impinger solution and connect the impinger to the vial using a 20-mm to 20-mm micro connector. Connect the sampling pump to the side port of the impinger using an appropriate length of tubing. Use of a micro impinger trap between the pump and impinger is recommended.

Position the sampling pump, sampler, and tubing so it does not impede work performance or safety.

Draw the air to be sampled directly into the inlet of the cassette. The air being sampled is not to be passed through any hose or tubing before entering the cassette.

Sample for 15 min at 1 L/min (15 L) to collect samples.

After sampling, disconnect the impinger from the 22-mL sampling vial. Cap and seal the vial with a Form OSHA-21. Return the cassette and impinger trap to the laboratory for proper disposal.

Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.

Record sample air volume (liters), sampling time (min), and sampling rate (L/min) for each sample, along with any potential interference on the Form OSHA-91A.

Submit the samples to the laboratory for analysis as soon as possible after sampling.

2.4 Recovery and stability

All vapor spiking for this study was performed by spiking 2 - 5 µL of a PAA solution, diluted in ACN, onto the internal wall of a 9-cm (6-mm i.d.) long glass tube placed directly upstream of the sampler. Unless noted, after spiking the glass tube 15 L (15 min @ 1 L/min) of humid air (80% relative humidity at 21 °C) was drawn through the sampling train. For each test the same amount of PAA spiking solution was spiked directly into three separate vials containing 15 mL of the impinger solution. These three solutions were analyzed, along with the samples, and the mean concentration was used as the reference concentration in determining sample recovery. The PAA spiking solution was prepared from a solution of approximately 32% PAA diluted in acetic acid [Peracetic Acid Solution, Sigma-Aldrich, product no. 269336].

Recovery

A sampler recovery study was performed by vapor-spiking four samplers at each concentration level. The overall mean recovery over the range of 0.1 to 2 times the target concentration was 96.79%. For the single wet test, humid air (80% relative humidity at 21 °C) was drawn through four cassettes, each containing a 25-mm coated quartz fiber filter for 15 min at 1 L/min prior to vapor spiking. Recoveries, as compared to the mean concentration of the three prepared reference standards, are shown in Table 2.4.1.

Table 2.4.1
Recovery of PAA Measured as MTSO (PAA Oxidation Product)

level		sample number recovery (%)				
× target concn	reference solution - µg/sample (%CV, n=3)	1	2	3	4	mean (%CV)
0.09	1.74 (10.7%)	86.00	107.3	103.9	89.85	96.76 (10.8%)
0.25	4.59 (6.8%)	94.14	97.50	98.80	93.71	96.04 (2.6%)
0.44	8.29 (2.2%)	100.31	98.13	98.14	96.88	98.37 (1.4%)
0.94	17.5 (2.2%)	96.59	95.37	98.81	94.93	96.43 (1.8%)
1.43	26.8 (0.3%)	95.72	95.89	94.83	96.31	95.69 (0.6%)
1.96	36.5 (1.3%)	95.82	98.82	97.24	97.92	97.45 (1.3%)
0.92 (wet)	17.2 (1.6%)	96.38	96.47	96.74	97.10	96.67 (0.3%)

Stability

The stability of samples was examined by reanalyzing the 0.94× target concentration samples from the recovery study 24, 48, and 72 hours after the initial analysis. Following the initial analysis, two vials were recapped with new septa which were replaced after each reanalysis. The remaining two vials retained their punctured septa throughout the test. All samples were stored at room temperature in the autosampler tray used for analysis. Reanalysis was completed using freshly prepared standards, and each septum was punctured four times for each injection.

The data obtained are shown in Table 2.4.2.

Table 2.4.2
Stability of MTSO (PAA Oxidation Product)

	punctured septa replaced recovery (%)		punctured septa retained recovery (%)	
time (days)	1	2	1	2
0	96.60	95.37	98.81	94.93
1	94.76	95.02	98.28	95.00
2	94.22	95.94	99.97	95.73
3	93.57	93.02	99.20	96.19

2.5 Retention efficiency

Retention efficiency samples for MTSO (PAA oxidation product) were prepared by vapor spiking three samplers at approximately twice the target concentration (0.73 ppb) with 15 L of humid air (79.5% relative humidity at 21.0 °C) drawn through each. An additional three samplers were vapor spiked at approximately twice the target concentration (0.77 ppb) with 18.75 L of humid air (78.9% relative humidity at 21.0 °C) drawn through each. A second impinger was placed behind each sample to measure analyte retention in each impinger. The data obtained are shown in Tables 2.5.1 and 2.5.2.

Table 2.5.1
Retention Efficiency of MTSO (PAA Oxidation Product, 15 L)

	sample number recovery (%)			
section	1	2	3	mean
front	95.99	95.48	97.27	96.25
rear	2.83	2.48	2.91	2.74
total	98.82	97.96	100.18	98.99

Table 2.5.2
Retention Efficiency of MTSO (PAA Oxidation Product, 18.75 L)

	sample number recovery (%)			
section	1	2	3	mean
front	94.13	94.83	95.59	94.85
rear	3.45	3.70	4.89	4.01
total	97.58	98.53	100.48	98.86

2.6 Storage stability

Storage samples for MTSO (PAA oxidation product) were prepared by vapor spiking twelve samplers at approximately the target concentration (0.36 ppm) at a relative humidity of 79.2% and a temperature of 20.6 °C. Three samples were analyzed on the day of generation. Nine samples were stored on a bench top, laid sideways, at ambient temperature (about 21 °C). At 4-5 day intervals three samples from those remaining were selected and analyzed. Results are shown in Table 2.6 and plotted in Figure 2.6. The recovery of MTSO (PAA oxidation product) from samples used in a 15-day storage test remained above 91.98% when stored at 21 °C.

Table 2.6
Ambient Storage Test for MTSO (PAA Oxidation Product)

time (days)	storage recovery (%)		
0	97.50	96.23	94.55
4	95.13	93.07	93.57
10	95.70	95.42	93.45
15	91.48	91.63	90.45

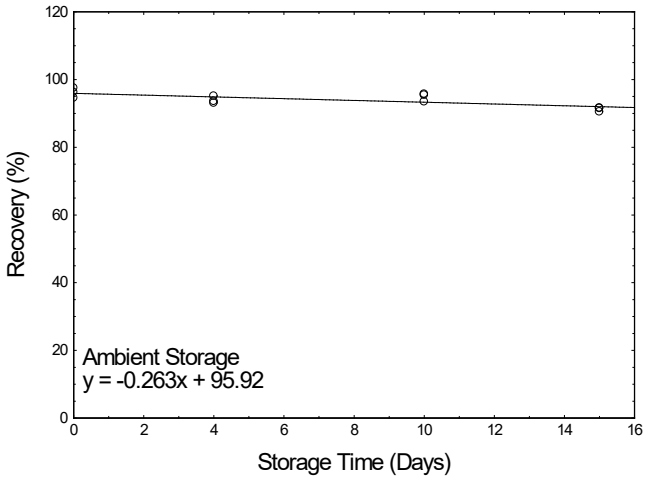


Figure 2.6. Ambient storage stability for MTSO (PAA oxidation product).

3. Analytical Procedure

3.1 Apparatus

GC equipped with an FID. An Agilent Model 7890 GC equipped with an automatic sample injector was used in this validation.

A GC column capable of separating MTS, MTSO, ACN, and the internal standard. An Agilent J&W HP-5, 30-m × 0.25-mm i.d., (1-µm d_f) capillary column (part no. 19091J-233) was used in this validation.

GC inlet liner. A Restek 4.0 mm ID Low Pressure Drop Precision Inlet Liner w/wool (catalog no. 23309) was used in this validation.

An electronic integrator or other suitable means of measuring and integrating GC detector response. Waters Empower 3 Data System was used in this validation.

Two-milliliter amber GC glass vials with PTFE-lined screw caps.

Dispenser or pipettes capable of delivering 15 mL of impinger solution to prepare standards and samples.

Syringes, 10 and 25-µL.

Small glass transfer pipettes.

Volumetric flasks, class A 5-mL, 15-mL, and 500-mL.

Analytical balance capable of weighing at least 0.01 mg.

3.2 Reagents

Methyl p-tolyl sulfide (MTS), [CAS no. 623-13-2]. The MTS used in this evaluation was purchased from Sigma-Aldrich with a listed purity of 99%.

4-chlorophenyl methyl sulfone, [CAS no. 98-57-7]. The 4-chlorophenyl methyl sulfone used in this evaluation was purchased from Sigma-Aldrich with a listed purity of 98%.

(R)-(+)-Methyl p-tolyl sulfoxide (MTSO), [CAS no. 1519-39-7]. The MTSO used in this evaluation was purchased from Sigma-Aldrich with a listed purity of 99%.

Acetonitrile (ACN), [CAS no. 75-05-8]. The ACN used in this evaluation was HPLC grade purchased from Fisher Chemical with a listed purity of 99.9%.

Impinger solution. The same impinger solution used to collect samples should also be used to prepare analytical standards. To prepare 500 mL of impinger solution add approximately 2 mg of 4-chlorophenyl methyl sulfone, used as the internal standard (ISTD), to a 500 mL volumetric flask. Next add 400 mL of ACN, followed by 10 µL of MTS. Fill to the mark with ACN and mix well.

3.3 Standard preparation

Prepare a 1.87 µg/uL equivalent PAA stock standard by placing 19.0 mg of MTSO into a 5-mL volumetric flask and dilute to mark with ACN. Correct for purity if necessary. For example:

$$\frac{19.0\text{ mg MTSO} \times \dfrac{76.05\ \left(\frac{g}{mol}\right)\text{PAA}}{154.23\ \left(\frac{g}{mol}\right)\text{MTSO}}}{5\text{ mL}} \times \frac{1000\text{ ug}}{1\text{ mg}} \times \frac{1\text{ mL}}{1000\text{ uL}} = 1.87\ \frac{ug}{uL}\text{PAA}$$

Prepare a new stock standard monthly and store in an air-tight amber vial when not in use.

Immediately before analysis, prepare calibration standards by injecting microliter amounts of the stock standard into 15-mL volumetric flasks and diluting to mark with impinger solution. For example, to prepare a target level standard of 18.7 µg/sample PAA equivalent, inject 10 µL of stock standard into a 15-mL volumetric and dilute to mark with impinger solution.

Transfer approximately 1.5 mL of each calibration standard to a 2-mL autosampler vial. Cap and analyze as described in Section 3.5.

Bracket sample concentrations with standard concentrations. If sample concentration is above the range of prepared calibration standards, dilute with ACN and repeat analysis. Do not dilute with impinger solution.

3.4 Sample preparation

It is not necessary to measure the returned sample solution volume as the internal standard in the impinger solution will correct for solvent loss during sampling.

For each sample, carefully open the shipping vial and transfer approximately 1.5 mL of the impinger solution to a 2-mL autosampler vial. Cap and analyze as described in Section 3.5.

3.5 Analysis

It is recommended that the GC inlet septum be replaced daily, and the GC inlet liner weekly or sooner if degradation in chromatography is seen. A chromatogram obtained at the target concentration is shown in Figure 3.5.1.

3.5.1 Analytical conditions

GC conditions

column:	Agilent J&W HP-5 capillary column, 30-m × 0.25-mm i.d., d_f = 1.0-µm, or equivalent
inlet liner:	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Restek catalog no. 23309, or equivalent)
carrier:	hydrogen, 1.4 mL/min, constant flow mode
septum purge:	hydrogen, 3.0 mL/min
injection:	0.8 µL, split injection (5:1 ratio)
inlet temperature:	275 °C
oven temperature:	60 °C (hold 0 min), ramp to 195 °C at 20 °C/min (hold 0 min), ramp to 211 °C at 5 °C/min (hold 0 min), ramp to 325 °C at 35 °C/min (hold 0.75 min)
run time:	13.96 min
retention times:	6.44 min - MTS 8.64 min - MTSO (PAA oxidation product) 9.63 min - ISTD

FID conditions

detector temperature:	275 °C
hydrogen flow:	40 mL/min
air flow:	450 mL/min
nitrogen make up flow:	45 mL/min

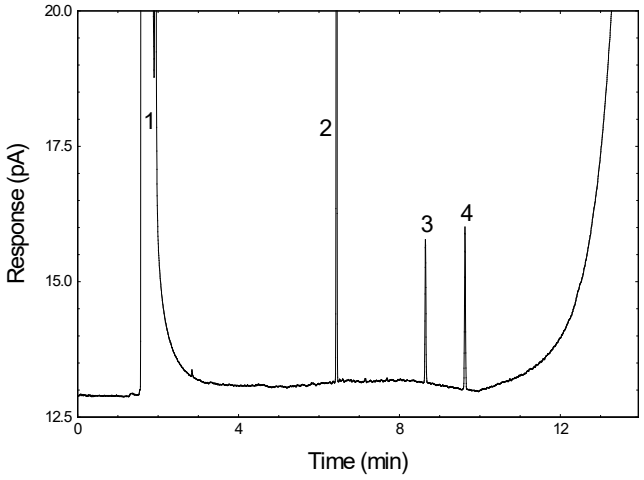


Figure 3.5.1. Chromatogram obtained at the target concentration. Peak labels: 1: ACN, 2: MTS, 3: MTSO (PAA oxidation product), 4: ISTD.

3.5.2 Use an ISTD calibration method. Construct a weighted least-squares linear regression curve by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. A weight of $1/x$ is recommended. An example of a calibration curve is shown in figure 3.5.2.

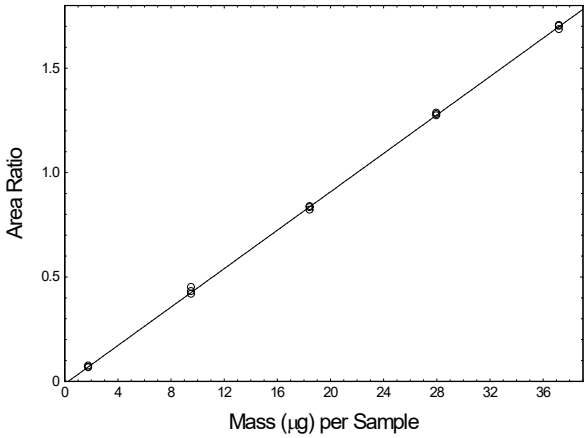


Figure 3.5.2. Calibration curve for MTSO (in terms of equivalent µg per sample PAA, y = 0.046x - 0.012, w_i = 1/x).

3.6 Sampling Interferences

Any compound that produces an FID response and has a similar retention time as MTSO or the internal standard is a potential interference. If any potential interferences were reported, they should be considered before samples are analyzed. Generally, chromatographic conditions can be altered to separate interferences from the analyte. When necessary, the identity of the PAA oxidation product MTSO can be confirmed with additional analytical data or procedures (Section 3.8).

Low humidity

The effect of low humidity was tested by vapor spiking three samplers at the target concentration (0.36 ppm). The air drawn through the samplers at 1 L/min for 15 min had a relative humidity of 21.0% and a temperature of 21.0 °C. Recovery results were 93.69%, 100.34%, and 97.48%.

Hydrogen peroxide

The potential interference of H_2O_2 was tested by vapor spiking three samplers with 41.3 µg of H_2O_2. This is the amount that would be collected from sampling 1.98 ppm H_2O_2 for 15 min at 25 °C and 760 mmHg. The air drawn through the samplers at 1 L/min for 15 min had a relative humidity of 20.5% and a temperature of 21.0 °C. The three samples were analyzed on the same day as collection. The presence of an interfering peak was not detected.

3.7 Calculations

The amount of PAA sampled is obtained from the appropriate calibration curve for the MTSO (PAA oxidation product) in terms of micrograms PAA per sample. This amount is then corrected by subtracting the total amount (if any) of MTSO found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{m}{V}$$

where C_M is concentration by weight (mg/m^3)
m is micrograms per sample
V is liters of air sampled

$$C_V = \frac{C_M V_M}{M}$$

where C_V is concentration by volume (ppm)
V_M is 24.46 (molar volume at 25 °C & 760 mmHg)
C_M is concentration by weight (mg/m^3)
M is molar mass of PAA (76.051 g/mol)

3.8 Qualitative analysis

When necessary, the identity of MTSO (PAA oxidation product) can be confirmed by gas chromatography - mass spectrometry (GC-MS) using the analytical conditions described below. Confirm the presence of MTSO by matching the retention time and fragmentation pattern of a standard at a similar concentration. The total ion current (TIC) chromatogram obtained at the target concentration is shown in Figure 3.8.1. The mass spectrum obtained for MTSO is shown in Figure 3.8.2.

It is recommended that the GC inlet septum be replaced daily, and the GC inlet liner weekly or sooner if degradation in GC-MS chromatography is seen.

<u>GC conditions</u>

column:	Agilent J&W HP-5 capillary column, 30-m × 0.25-mm i.d., df = 1.0-µm, or equivalent
inlet liner:	Restek Topaz 4.0-mm ID Precision Inlet Liner w/wool (Restek catalog no. 23309, or equivalent)
carrier:	helium, 1.7 mL/min, constant flow mode
septum purge:	helium, 3.0 mL/min
injection:	0.8 µL, split injection (5:1 ratio)
inlet temperature:	275 °C
oven temperature:	60 °C (hold 0 min), ramp to 195 °C at 20 °C/min (hold 0 min), ramp to 211 °C at 5 °C/min (hold 0 min), ramp to 325 °C at 35 °C/min (hold 0.75 min)
run time:	13.96 min
retention times:	6.40 min - MTS 8.67 min - MTSO (PAA oxidation product) 9.68 min - ISTD

<u>mass spectrometer conditions</u>

mode:	electron ionization (EI)
acquisition mode:	scan, *m/z* 30 - 200
solvent delay:	5 min
EMV mode:	gain factor (1)
temperatures:	250 °C (source), 200 °C (quadrupole assembly), 250 °C (transfer line)

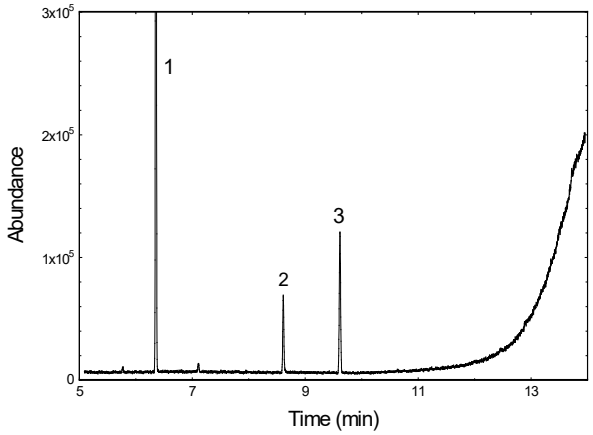


Figure 3.8.1. TIC GC-MS chromatogram obtained at the target concentration. Peak labels: 1: MTS, 2: MTSO (PAA oxidation product), 3: ISTD.

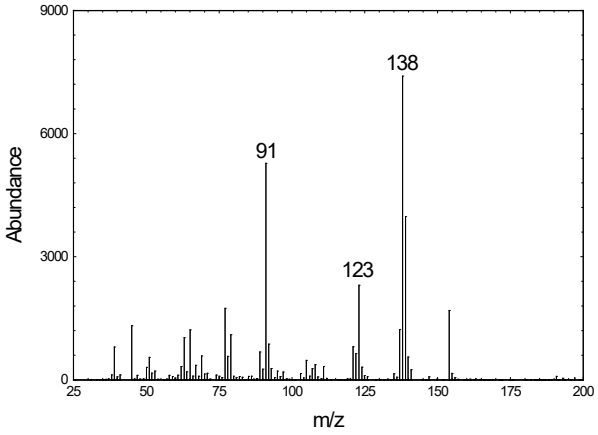


Figure 3.8.2. Mass spectrum of MTSO.