2-BUTANONE (MEK)
HEXONE (MIBK)

Method number: 1004

MEK:
Target concentration: 200 ppm (590 mg/m^3) TWA
OSHA PEL: 200 ppm (590 mg/m^3) TWA
ACGIH TLV: 200 ppm TWA
300 ppm STEL/C

MIBK:
Target concentration: 100 ppm (410 mg/m^3) TWA
OSHA PEL: 100 ppm (410 mg/m^3) TWA
ACGIH TLV: 50 ppm TWA
75 ppm STEL/C

Procedure: Active samples are collected by drawing workplace air through SKC Anasorb CMS (carbon molecular sieves) sampling tubes with personal sampling pumps. Diffusive samples are collected by exposing either SKC 575-002 Passive Samplers or 3M 3520 OVMs to workplace air. Samples are extracted with carbon disulfide containing 1% *N,N*-dimethylformamide and analyzed by GC using a flame ionization detector.

Recommended sampling time and sampling rate:
SKC CMS sampling tube: 240 min at 50 mL/min (12 L)
SKC 575-002 Passive Sampler: 240 min
3M 3520 OVM: 240 min

Reliable quantitation limit (RQL) and standard error of estimate (SEE):

	MEK			MIBK		
	RQL		SEE	RQL		SEE
	(ppb)	(µg/m^3)	(%)	(ppb)	(µg/m^3)	(%)
SKC CMS sampling tubes	23	68	6.0	9	36	5.9
SKC 575-002 Passive Sampler	109	320	9.1*	94	384	9.1*
3M 3520 OVM	33	98	8.3*	35	144	8.0*

*For samples where sampling site atmospheric pressure and temperature are known. When either or both of these values are unknown, see Section 4.4 for applicable standard errors of estimate.

Special requirements: Report sampling site pressure and temperature when using diffusive samplers. Refrigerate samples for MEK and MIBK upon receipt at laboratory.

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team.

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1. General Discussion

1.1 Background

1.1.1 History

Workplace determination of 2-butanone (methyl ethyl ketone, MEK) and of hexone (methyl isobutyl ketone, MIBK) is of considerable interest to OSHA. Both MEK and MIBK rank in the top 15 most requested organic solvent analytes for samples received at SLTC. This work was performed to provide OSHA with convenient active and diffusive sampling methods to monitor workplace air for these chemical hazards. The two chemicals were evaluated simultaneously to conserve SLTC resources. Evaluation of MEK revealed certain sampling and analytical problems, such as storage instability and sample extraction difficulties, that are addressed in this method. Evaluation of MIBK was straightforward and uneventful.

Current active sampling methods for MEK specify use of one of the following three sampling media and techniques: 1) two silica gel sampling tubes connected in-series (both tubes150/75 mg sections, 3-L air sample); 2) Carboseive S-III sampling tubes (130/65 mg sections, 3-L air sample); or 3) Anasorb 747 sampling tubes (140/70 mg sections, 12-L air sample).[1] The present sampling method for MIBK requires the use of charcoal tubes (100/50 mg sections, 25-L air sample).[2]

The active sampling medium evaluated in this work (SKC Anasorb CMS) permits collection of a four-hour (12-L) sample for both MEK and MIBK on the same sampling tube. Anasorb CMS is a proprietary carbon molecular sieve that may be similar to Carbosieve S-III carbon molecular sieve marketed by Supelco. Diffusive sampling methods allow a 4-hour sample to be collected on either SKC 575-002 Passive Samplers or on 3M 3520 Organic Vapor Monitors (OVMs). Storage stability tests showed that MEK is more stable on 3M 3520 OVMs than on SKC 575-002 Passive Samplers. The method requires refrigerated storage of samples upon laboratory receipt. Refrigerated storage is precautionary for SKC CMS sampling tubes and for 3M 3520 OVMs, but is obligatory for SKC 575-002 Passive Samplers. Refrigerated sample shipment for SKC 575-002 Passive Samplers is unnecessary, unless sample shipment is anticipated to be delayed for more than three days.

Anasorb 747 sampling tubes were tested, but were found to be unsatisfactory for use in this method. Small Anasorb 747 (140/70 mg sections) sampling tubes did not have sufficient capacity to permit a four-hour MEK sample in the presence of MIBK. Large Anasorb 747 (400/200 mg sections) sampling tubes have sufficient capacity, but ambient MEK storage stability was poor. Anasorb 747 is the sorbent contained in SKC 575-002 Passive Samplers, and MEK storage stability data for active and for diffusive samplers employing this sorbent were comparable. Tests showed that Anasorb 747 does have adequate sampling capacity for MIBK in the presence of MEK, and that ambient storage stability was satisfactory. Some of the Anasorb 747 sampling tube evaluation data is included in this report for the preceding reasons, but it is for information only, and the use Anasorb 747 sampling tubes is not recommended for this application.

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[1] OSHA Salt Lake Technical Center, Chemical Sampling Information, http://www.osha-slc.gov/ChemSamp_data/CH_222300.html (accessed Feb 2000).

[2] OSHA Salt Lake Technical Center, Chemical Sampling Information, http://www.osha-slc.gov/ChemSamp_data/CH_245600.html (accessed Feb 2000).

1.1.2 Toxic effects [3] (This section is for information only and should not be taken as the basis of OSHA policy.)

MEK

ACGIH's Documentation of the TLVs reports mild eye, nose, and throat irritation from exposure to MEK at 100 to 200 ppm. Low-grade intoxication has occurred at 300 to 600 ppm. The 100% response odor threshold was 10 ppm. Central nervous system effects were noted following exposures to mixtures of organic chemicals including MEK. There was no excess cancer risk reported.

MIBK

ACGIH reports that MIBK is an irritant to the eyes, nose, throat, and skin. An odor threshold of 0.3 to 0.7 ppm has been reported. Headache and nausea are common complaints of MIBK exposure. Exposure to high concentrations could result in death because of its narcotic effects. Liver and kidney effects have been reported.

ACGIH, in the 1996 supplement to the Documentation of the TLVs [4], stated that dermal and gastrointestinal absorption of MIBK could be significant. The BEI Committee recommended monitoring of MIBK in urine at the end of the work shift as an indicator of recent exposure to MIBK. The recommended BEI value is 2 mg/L MIBK in urine. Adjustment for creatinine is inappropriate.

1.1.3 Workplace exposure [5]

MEK

MEK is used as a solvent in the surface coating industry and in dewaxing of lubricating oils. It is used in the manufacture of colorless synthetic resins, artificial leather, rubbers, varnishes and glues. It is commonly used with other solvents such as acetone, ethyl acetate, hexane, toluene, and alcohols.

MIBK

MIBK is used as a solvent in synthetic resinous paints, lacquers, aircraft dopes, and varnishes. It is also a solvent for adhesives and rubber cement. It is used as a denaturant for ethyl alcohol, and to extract pharmaceuticals and uranium fission products.

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[3] *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed., American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, vol. II, pp.1002-1004 and 1019-1021.

[4] Supplements (1996) to the 6th Edition of: *Documentation of the Threshold Limit Values and Biological Exposure Indices, 6th ed., American Conference of Governmental Industrial Hygienists, Inc.*: Cincinnati, OH, 1991, vol. II, pp. Supplement: Methyl Isobutyl Ketone (MIBK)- BEI 1-3.

[5] *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed., American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, vol. II, pp.1002-1004 and 1019-1021.

1.1.4 Physical properties and descriptive information [6, 7]

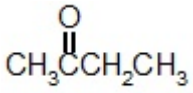
MEK

CAS number:	78-93-3	vapor pressure:	10.3 kPa at 20 °C
IMIS number:	0430	flash point:	-4 °C (closed cup)
molecular weight:	72.10	odor:	acetone-like
boiling point:	79.6 °C	lower explosive limit:	1.8% (by volume)
melting point:	-86 °C	synonyms:	butan-2-one; MEK
appearance:	colorless liquid	solubility:	water, all common industrial organic solvents
specific gravity:	0.805 at 20 °C		
molecular formula:	C_4H_8O		

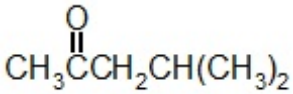
MIBK

CAS number:	108-10-1	vapor pressure:	2.0 kPa at 25 °C
IMIS number:	1385	flash point:	18 °C (closed cup)
molecular weight:	100.16	odor:	pleasant, sweet
boiling point:	115.8 °C	lower explosive limit:	1.4% (by volume)
freezing point:	-84.7 °C	synonyms:	4-methyl-2-pentanone; MIBK
appearance:	colorless liquid		
specific gravity:	0.8017 at 20 °C	solubility:	1.91 g/mL in water, miscible with many many organic solvents
molecular formula:	$C_6H_{12}O$		

structural formulas:



MEK



MIBK

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[8]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25 °C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limits of the analytical procedure are 4.90 pg for MEK and 3.13 pg for MIBK. These are the amounts of analyte that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1)

[6] *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed., American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, vol. II, pp.1002-1004 and 1019-1021.

[7] OSHA Salt Lake Technical Center, Chemical Sampling Information, http://www.osha-slc.gov/ChemSamp_data/CH.html (Accessed Jan 2000).

[8] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are shown in Table 1.2.2. These are the amounts of analytes spiked on the respective sampler that will give detector responses that are significantly different from the responses of respective sampler blanks. (Section 4.2)

Table 1.2.2
Detection Limits of the Overall Procedure

	MEK			MIBK		
sampler	ng	ppb	µg/m^3	ng	ppb	µg/m^3
SKC CMS	244	7	20	129	3	11
SKC 575-002	388	33	96	376	28	115
3M 3520	230	10	29	281	11	43

1.2.3 Reliable quantitation limit

The reliable quantitation limits are shown in Table 1.2.3. These are the amounts of analytes spiked on the respective samplers that will give detector responses that are considered the lower limits for precise quantitative measurements.(Section 4.2)

Table 1.2.3
Reliable Quantitation Limits

	MEK				MIBK			
sampler	ng	ppb	µg/m^3	E_E	ng	ppb	µg/m^3	E_E
SKC CMS	813	23	68	98.5	430	9	36	111.7
SKC 575-002	1295	109	320	90.4	1255	94	384	81.0
3M 3520	766	33	98	105.3	937	35	144	86.4

E_E is extraction efficiency

1.2.4 Instrument calibration

The standard errors of estimate are 64 µg/sample for MEK and 47 µg/sample for MIBK over the range of 1900 to 14250 µg/sample for MEK and 1300 to 9753 µg/sample for MIBK. This range corresponds to 0.25 to 2 times the target concentration for SKC CMS sampling tubes. This is the sampler with the highest mass loading. (Section 4.3)

1.2.5 Precision (Section 4.4)

SKC CMS sampling tubes

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 15-day storage test (at the target concentration) for SKC CMS tubes are ±11.7% for MEK, and ±11.5% for MIBK. These precisions each include an additional 5% for sampling pump variability.

Diffusive samplers

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 15-day storage tests (at the target concentration) are shown in Table 1.2.5. There are different values given, depending on whether both, either, or neither temperature (*T*) or atmospheric pressure (*P*) at the sampling site are known. If the sampling site temperature is unknown, it is assumed to be 22.2 ± 15 °C (72 ± 27 °F) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included. Each 3M precision

value includes an additional 7.4% for sampling rate variation, and each SKC value an additional 8.7% also for sampling rate variation[9].

Table 1.2.5
Precision of the Overall Procedure for Diffusive Samplers

known condition	SKC 575-002 Passive Sampler		3M 3520 OVM	
	MEK precision (±%)	MIBK precision (±%)	MEK precision (±%)	MIBK precision (±%)
both *T* & *P*	17.9	17.7	16.3	15.7
only *T*	18.8	18.7	17.3	16.8
only *P*	23.4	23.3	22.2	21.8
neither *T* nor *P*	24.1	24.0	23.0	22.6

1.2.6 Recovery

The recovery of MEK and of MIBK from samples used in 15-day storage tests remained above those shown in Table 1.2.6. (Section 4.5)

Table 1.2.6
Recovery (%)

sampler	storage temp	MEK	MIBK
SKC Anasorb CMS tubes	ambient	84.9	93.2
SKC 575-002	refrigerated	91.3	88.1
3M 3520	ambient	96.4	102.6

1.2.7 Reproducibility

Six samples for each of the three samplers evaluated in this method were collected from a controlled test atmosphere and were submitted to OSHA SLTC for analysis. The samples were analyzed utilizing a draft copy of this procedure for instruction. They were analyzed following 2 days of storage at 4 °C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.6)

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

2.1.1 SKC Anasorb CMS sampling tubes

Samples are collected with 7-cm × 4-mm i.d. × 6-mm o.d. glass sampling tubes packed with two sections of SKC Anasorb CMS. The front section contains 150 mg and the back section contains 75 mg of CMS. The sections are held in place with glass wool plugs. For this evaluation, commercially prepared Anasorb CMS sampling tubes were purchased from SKC Inc. (catalog no. 226-121).

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

[9] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

2.1.2 SKC 575-002 Passive Samplers and 3M 3520 OVMs

Samples are collected with either SKC 575-002 Passive Samplers, or with 3M 3520 OVMs. Samplers were purchased from SKC, Inc. (catalog no. 575-002, contains one 500-mg section of Anasorb 747), or from 3M (catalog no. 3520, contains two-sections with charcoal adsorbent pads).

A thermometer and a barometer are used to determine the sampling site air temperature and atmospheric pressure.

2.2 Reagents

None required.

2.3 Technique

2.3.1 SKC Anasorb CMS sampling tubes

Break off the ends of the flame-sealed sampling tube, to provide an opening approximately half the internal diameter of the tube, immediately before sampling. Wear eye protection when breaking tube ends. Use sampling-tube holders to reduce the hazard of broken sampling-tube ends to the employee. All tubes should be from the same lot.

The smaller section of the sampling tube is used as a back-up and it is positioned nearest the sampling pump. Attach the tube holder to the sampling pump with flexible non-crimping tubing. Position the sampler in the worker's breathing zone so that the sampling tube is in an approximately vertical position with the inlet facing down during sampling. Position the sampling pump, tube holder and tubing so they do not impede work performance or safety.

Draw air to be sampled directly through the inlet of the tube holder. The air being sampled should not pass through any hose or tubing before entering the sampling tube.

After sampling for the appropriate time, remove the sampling tube and seal it with plastic end caps. Seal each sample end-to-end with an OSHA-21 form as soon as possible.

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

Record sample air volume (liters), sampling time (minutes) and sampling rate (mL/min) for each sample, along with any potential interferences on the OSHA-91A form.

Submit the samples to the laboratory for analysis as soon as possible after sampling. Store the samples in a refrigerator if a delay is unavoidable. Ship any bulk samples separate from the air samples.

2.3.2 SKC 575-002 Passive Samplers (In general, follow the manufacturer's instructions.)

Remove the sampler from the clear, air-tight bag just before sampling is to begin. **CAUTION - The monitor begins to sample immediately when it is removed from this bag.** Keep the O-ring, press-on cover, cover retainer, port plugs and PTFE tube for later use.

Record the **start time** on the sampler label and on the Form OSHA-91A.

Attach the sampler to the worker near his/her breathing zone with the perforations in the sampler facing forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period.

At the end of the sampling period, immediately detach the sampler from the worker and attach the cover with the O-ring in place onto the sampler using the cover retainer. Visually inspect the O-ring to be sure it is forming a proper seal around the entire circumference of the sampler. Record the **stop time** on sampler label and on OSHA-91A form.

Prepare a blank by removing an unused sampler from its clear package and immediately attaching a cover with the O-ring in place onto it.

Seal each sampler with an OSHA-21 form.

Verify that the sampling times are properly recorded on the OSHA-91A form for each sample. Also, identify blank samples on this form.

Record the **sampling site temperature and atmospheric pressure** on the Form OSHA-91A.

List any compounds that could be considered potential interferences, especially solvents, that are being used in the sampling area.

Submit the samples to the laboratory for analysis as soon as possible after sampling. Store the samples in a refrigerator if a delay is unavoidable. Include all port plugs and PTFE tubes as they are used in the laboratory analyses. Ship any bulk sample(s) in a container separate from the air samples.

2.3.3 3M OVMs (In general, follow the manufacture's instructions supplied with the samplers.)

The monitors come individually sealed in small metal cans. Just before sampling is to begin, remove the plastic lid from the can and lift up on the revealed ring. Pull back on the ring to open the can. Discard the metal top of the can and remove the monitor. **CAUTION - The monitor begins to sample immediately when the can is unsealed.**

Keep the two closure caps with attached port plugs, cup and PTFE tubes in the can for later use. Close the can with the plastic lid.

Record the **start time** on the back of the monitor and on the OSHA-91A form.

Attach the monitor to the worker near his/her breathing zone with the white face forward. Assure that the area directly in front of the sampler is unobstructed throughout the sampling period. Do not remove the white film and ring from the monitor until the sampling period is terminated.

At the end of the sampling period, detach the monitor from the worker and remove the white film and retaining ring. Immediately snap a closure cap onto the primary (top) section of the monitor (where the white film and ring were removed). It is critical that this step be done as quickly as possible because the sampling rate is more than five times greater without the white film in place. This can be an important consideration, especially for short-term sampling. Assure that the attached port plugs are placed firmly into the port holes. The white film and ring can be discarded. Record the **stop time** on the back of the monitor and on the OSHA-91A form.

The following steps should be performed in a low background (uncontaminated) area for a set of monitors as soon as possible after sampling.

Prepare a blank by removing a new sampler from its can. Immediately remove the white film and ring and then immediately attach a closure cap onto the unused monitor.

For each monitor (one at a time), separate the primary (top) and secondary (bottom) sections of the monitor using the edge of a coin as a pry.

Securely snap a cup onto the bottom of the primary section.

Snap a closure cap onto the secondary section of the monitor and assure that the attached port plugs are placed firmly into the port holes.

Return the sampler sections with closure caps and cup in place to the metal can containing the PTFE tubes (which will be used by the laboratory). Close the can with the plastic lid, and seal it with an OSHA-21 form.

Verify that the sampling times are properly recorded on OSHA-91A form for each sample. Also, identify blank samples on this form.

Record the **sampling site temperature and atmospheric pressure** on the OSHA-91A form.

List any compounds that could be considered potential interferences, especially solvents, that are being used in the sampling area.

Submit the samples to the laboratory for analysis as soon as possible after sampling. Store the samples in a refrigerator if a delay is unavoidable. Ship any bulk sample separate from the air samples.

2.4 Sampler capacity (Section 4.7)

2.4.1 The sampling capacity of the front sections of SKC Anasorb CMS sampling tubes was tested by sampling a dynamically generated test atmosphere of MEK and MIBK (1131 mg/m^3 or 384 ppm MEK, and 774 mg/m^3, or 189 ppm MIBK) at an absolute humidity of 13.9 milligrams of water per liter of air (74% relative humidity at 22 °C). The samples were collected at 50 mL/min. The 5% breakthrough sampling time for MEK was determined to be 300 min. No breakthrough of MIBK was observed, even after samples were collected for 600 min.

2.4.2 The sampling rate and capacity of SKC 575-002 Passive Samplers and of 3M 3520 OVMs were determined by sampling from atmospheres of MEK and MIBK at about two times their respective target concentrations and at an absolute humidity of 16.4 milligrams of water per liter of air (about 80% relative humidity at 23 °C) for increasing time intervals. The sampling rates are shown in Table 2.4.2. A recommenced sampling time of 240 min was obtained from this test.

Table 2.4.2
Sampling Rates (mL/min)
at 760 mmHg and 298.2 K

	MEK	MIBK
SKC 575-002	16.88	13.62
3M 3520	32.59	27.00

2.5 Extraction efficiency (Section 4.8)

It is the responsibility of each analytical laboratory to determine extraction efficiency in-house because the adsorbent material, internal standard, reagents and laboratory techniques could be different than those used in this evaluation and they could influence analytical results.

The mean extraction efficiencies of MEK and MIBK from dry media over the range of the RQL to 2 times the target concentrations are shown in Table 2.5. The extraction efficiency for MEK was affected by the presence of water. This effect was caused by the instability of MEK on wet carbon-based sorbents. MIBK was not affected by the presence of water.

Table 2.5
Extraction Efficiency Summary

medium	MEK			MIBK		
	RQL (µg)	2× (µg)	E_E (%)	RQL (µg)	2× (µg)	E_E(%)
Anasorb CMS	0.81	14250	100.3	0.42	9753	102.3
SKC 575-002	1.28	4750	92.2	1.27	2601	92.9
3M 3520 OVM	0.76	9500	98.0	0.94	5201	96.5

Extracted MEK samples with punctured septa gave results more than 10% lower than MEK samples with intact septa upon standing in an autosampler rack for a day. The loss was attributed to volatility of MEK, room temperature, and septa condition rather than chemical reactivity of MEK.

Extracted MEK samples with punctured septa remained stable for 12 h. Extracted MIBK samples with punctured septa remained stable for at least a day. Extracted samples for both MEK and MIBK with intact septa remained stable for at least a day.

2.6 Recommended sampling time and sampling rate

2.6.1 SKC Anasorb CMS sampling tubes

Sample for up to 240 min at 50 mL/min (12 L) when using SKC Anasorb CMS sampling tubes to collect TWA (long-term) samples.

Sample for 5 min at 50 mL/min (0.25 L) when using SKC Anasorb CMS sampling tubes to collect ceiling (short-term) samples.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for SKC Anasorb CMS sampling tubes is 1.1 ppm (3.25 mg/m^3) for MEK when 0.25 L is sampled.

2.6.2 SKC 575-002 Passive Samplers and 3M 3520 OVMs

Sample for up to 240 min when using SKC 575-002 Passive Samplers and 3M 3520 OVMs to collect TWA (long-term) samples.

Sample for 5 min when using SKC 575-002 Passive Samplers and 3M 3520 OVMs to collect ceiling (short-term) samples.

Table 2.6.2
Sampling Rates (mL/min)
at 760 mmHg and 298.2 K

	MEK	MIBK
SKC 575-002	16.88	13.62
3M 3520	32.59	27.00

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for 3M 3520 OVMs is 1.6 ppm (4.70 mg/m^3) for MEK when 0.163 L is sampled.

2.7 Interferences, sampling (Section 4.9)

2.7.1 Active sampler

Retention efficiency

Six SKC Anasorb CMS sampling tubes were used to sample a test atmosphere containing two times the target concentrations of MEK and of MIBK for one hour. Three samples were removed and analyzed after the initial one hour, and the remaining three were used to sample contaminant-free air for an additional three hours (four hours total). The absolute humidity of the test atmosphere was 14.6 milligrams of water per liter of air (77.8% relative humidity at 21.4 °C). The percent of the four-hour sample means relative to the one-hour sample means are shown in Table 2.7.1.1. MEK and MIBK were efficiently retained following collection.

Table 2.7.1.1
Mean Recovery

MEK (%)	MIBK (%)
95.6	97.2

Low humidity

Three SKC Anasorb CMS sampling tubes were used to sample a test atmosphere containing two times the target concentrations of MEK and of MIBK. The absolute humidity of the test atmosphere was 2.7 milligrams of water per liter of air (13.2% relative humidity at 22.6 °C). The recovery for all samples was more than 95.1% of theoretical for MEK and 98.2% of theoretical for MIBK. Low humidity had no significant effect on recovery.

Low concentration

Three SKC Anasorb CMS sampling tubes were used to sample a test atmosphere containing 0.1 times the target concentrations of MEK and of MIBK. The absolute humidity of the test atmosphere was 15.5 milligrams of water per liter of air (79.7% relative humidity at 22.3 °C). The recovery for all samples was more than 94.9% of theoretical for MEK and 101.1% of theoretical for MIBK. Low concentration had no significant effect on recovery.

Sampling interferences

Three Anasorb CMS sampling tubes were used to sample a test atmosphere containing one times the target concentrations of MEK and of MIBK; and 553.3 mg/m^3 of acetone, 253.7 mg/m^3 of isopropyl alcohol, 190.1 mg/m^3 of toluene, 92.5 mg/m^3 of xylene isomers, and 16.3 mg/m^3 of ethyl benzene. The absolute humidity was 15.6 milligrams of water per liter of air (79.0% relative humidity at 22.3 °C). The recovery for all samples was more than 99.0% of theoretical for MEK and 102.2% of theoretical for MIBK. The sampling interferences had no significant effect on recovery.

2.7.2 Diffusive samplers

Reverse diffusion

Six SKC 575-002 and six 3M 3520 samplers were used to test for reverse diffusion by first exposing the samplers to a test atmosphere containing two times the target concentrations of MEK and of MIBK for one hour. Three of each sampler were analyzed after the initial exposure, and the remaining three of each sampler

Table 2.7.2.1
Mean Recovery

SKC 575-002		3M 3520	
MEK (%)	MIBK (%)	MEK (%)	MIBK (%)
99.3	100.0	96.0	98.6

were exposed to contaminant-free air for an additional three hours (four hours total). The absolute humidity of the test atmosphere was 14.6 milligrams of water per liter of air (77.8% relative humidity at 21.4 °C). The percent of the means of the four hour samples relative to the one hour sample means are shown in Table 2.7.2.1. Reverse diffusion was not significant.

Low humidity

Three SKC and three 3M diffusive samplers were used to sample a test atmosphere containing two times the target concentrations of MEK and of MIBK. The absolute humidity of the test atmosphere was 2.7 milligrams of water per liter of air (13.2% relative humidity at 22.6 °C). The lowest recoveries for all samplers are shown in Table 2.7.2.2. Low humidity had no significant effect on recovery.

Table 2.7.2.2
Low Humidity (% recovery)

analyte	SKC 575-002	3M 3520
MEK	92.2	92.9
MIBK	102.5	101.0

Low concentration

Three SKC and three 3M diffusive samplers were used to sample a test atmosphere containing 0.1 times the target concentrations of MEK and of MIBK. The absolute humidity of the test atmosphere was 15.5 milligrams of water per liter of air (79.7% relative humidity at 22.3 °C). The lowest recoveries for all samplers are shown in Table 2.7.2.3. Low concentration had no significant effect on recovery.

Table 2.7.2.3
Low Concentration (% recovery)

analyte	SKC 575-002	3M 3520
MEK	90.3	89.8
MIBK	96.8	95.0

Sampling interferences

Three SKC and three 3M diffusive samplers were used to sample a test atmosphere containing one times the target concentrations of MEK and of MIBK; and 553.3 mg/m^3 of acetone, 253.7 mg/m^3 of isopropyl alcohol, 190.1 mg/m^3 of toluene, 92.5 mg/m^3 of xylene isomers, and 16.3 mg/m^3 of ethyl benzene. The absolute humidity was 15.6 milligrams of water per liter of air (79.0% relative humidity at 22.3 °C). The lowest recoveries for all samplers are shown in Table 2.7.2.4. The sampling interferences had no significant effect on recovery.

Table 2.7.2.4
Sampling Interferences (% recovery)

analyte	SKC 575-002	3M 3520
MEK	97.6	93.5
MIBK	102.2	101.8

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan[10]. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning this analytical procedure.

3.1 Apparatus

3.1.1 A GC equipped with a flame ionization detector (FID). A Hewlett-Packard Model 5890 Series II GC equipped with a ChemStation, an automatic sample injector, and an FID were used in this evaluation.

[10] Occupational Exposure to Hazardous Chemicals in Laboratories. *Code of Federal Regulations*, Part 1910.1450, Title 29, 1998.

3.1.2 A GC column capable of separating MEK and MIBK from the extraction solvent, internal standards, and potential interferences. A J&W Scientific 60-m × 0.32-mm i.d. DB-Wax (0.5-µm df) capillary column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring GC detector response. A Waters Millennium Chromatography Manager system was used in this evaluation.

3.1.4 Two and four-milliliter glass vials with PTFE-lined septum caps.

3.1.5 One and two-milliliter volumetric pipets.

3.1.6 An SKC Desorption Shaker with rack (226D-03K) was used to extract SKC 575-002 Passive Samplers in this evaluation.

3.2 Reagents

3.2.1 2-Butanone (methyl ethyl ketone, MEK) [CAS no. 78-93-3], reagent grade or better. The MEK used in this evaluation was 99+% A.C.S. Reagent grade (lot no. 11619CX) purchased from Aldrich (Milwaukee, WI).

3.2.2 Hexone (methyl isobutyl ketone, MIBK) [CAS no. 108-10-1], reagent grade or better. The MIBK used in this evaluation was Analytical Reagent grade (lot no. CVT) purchased from Mallinckrodt (St. Louis, MO)

3.2.3 Carbon disulfide (CS_2), [CAS no. 75-15-0], reagent grade or better. The carbon disulfide used in this evaluation was 99.9+% low benzene content grade (lot no. 1054JQ) purchased from Aldrich (Milwaukee, WI).

3.2.4 *N,N*-Dimethyl formamide (DMF) [CAS no. 68-12-2], reagent grade or better. The DMF used in this evaluation was Certified A.C.S. grade (lot no. 902902) purchased from Fisher (Fair Lawn, NJ).

3.2.5 1-Phenylhexane (hexylbenzene) [CAS no. 1077-16-3], reagent grade or better. The 1-phenylhexane used in this evaluation was 97% reagent grade (lot no. 03006PZ) purchased from Aldrich (Milwaukee, WI).

3.2.6 The extraction solvent used for this evaluation consisted of 1% DMF in CS_2. 1-Phenylhexane (1 µL/mL) was added to the solution for use as an internal standard. Other internal standards can be used provided they are fully tested.

3.3 Standard preparation

3.3.1 Prepare concentrated stock standards by weighing 3 mL of MEK and/or 2 mL of MIBK into a 5-mL volumetric flask, and diluting to the mark with CS_2. Obviously, no CS_2 addition is necessary if both MEK and MIBK are added to the same flask. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into vials containing either 1 or 2 mL of extracting solution delivered from the same dispenser used to extract samples. For example, to prepare a target level standard to analyze SKC Anasorb CMS sampling tubes, inject 15 µL of a stock solution containing 480 mg/mL of MEK and 320 mg/mL MIBK into 1 mL of extracting solution.

3.3.2 Bracket sample concentrations with standard concentrations. If, upon analysis, sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with extraction solvent and reanalyze the diluted samples.

3.4 Sample preparation

3.4.1 SKC Anasorb CMS sampling tubes

Remove the plastic end caps from the sample tube and carefully transfer each section of the adsorbent to separate 2-mL vials. Discard the glass tube and glass wool plugs.

Add 1.0 mL of extracting solution to each vial and immediately seal the vials with polytetrafluoroethylene-lined caps.

Shake the vials vigorously several times during the 60 min extraction time.

3.4.2 SKC 575-002 Passive Samplers (In general, follow the manufacturer's instructions.)

Cut off the ends of the two protruding tubes (ports) of each sampler with a razor blade or sharp knife.

Slowly and carefully add 2.0 mL of extraction solvent through the protruding tube (port) nearest the outside edge of the sampler.

Immediately insert plugs into the ports.

Mount the samplers in the sampler rack (SKC Cat. No. 226-04-5) of a specialized shaker (SKC Cat. No. 226D-03-1) and shake the samplers for 1 hour.

Do not leave the extracted sample in the sampler. Transfer each extracted sample by removing the plugs from the sampler ports, firmly inserting the tapered end of a supplied PTFE tube into the outer port, and carefully pouring the solution through the PTFE tube into a labeled autosampler vial. Immediately cap each vial.

3.4.3 3M 3520 OVMs (In general, follow the manufacturer's instructions.)

Remove both sampler sections from the metal cans, along with the sections of PTFE tubing. Assure that the closure caps are firmly snapped to the primary and secondary sections of all the samplers. Also assure that all cap plugs are firmly seated in the cap ports. Any deviations must be noted.

Prepare one section of the sampler at a time by temporarily removing the cap plugs from the ports and adding 2.0 mL of extraction solvent through the center port.

Allow the sampler sections to extract for one hour. Apply gentle agitation to the sampler sections, periodically, during the extraction period.

Do not leave the extracted sample in the sampler. Transfer the solution from each sampler section by removing both plugs from the ports, firmly inserting a decanting spout (a small section of PTFE tubing) into the outer port and carefully pouring the liquid through the spout into a labeled autosampler vial. Immediately cap each vial.

3.5 Analysis

3.5.1 Analytical conditions

GC conditions

column temperature:	initial 40 °C , hold 1 min, program at 4 °C/min to 140 °C, hold until column is clear.
zone temperatures:	220 °C (injector) 220 °C (detector)
run time:	26 min
column gas flow:	4.9 mL/min (hydrogen)
septum purge:	3.3 mL/min (hydrogen)
injection size:	1.0 µL (26:1 split)
column:	60-m × 0.32-mm i.d. capillary J&W DB-Wax (0.5-µm df)
retention times:	4.1 min (MEK) 6.3 min (MIBK) 23.4 min (1-phenylhexane)

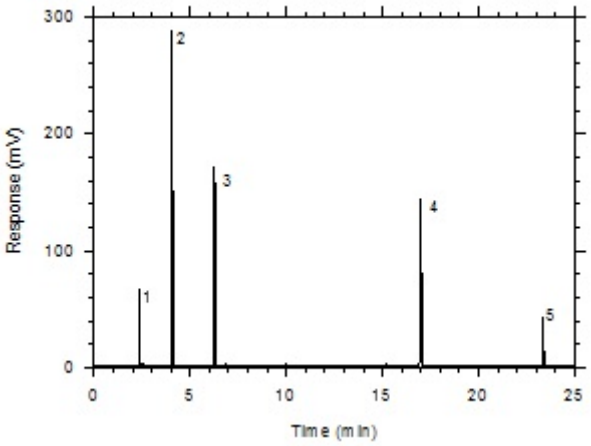


Figure 3.5.1. Chromatogram obtained at the target concentrations with the recommended conditions. (1- CS_2; 2- MEK; 3- MIBK; 4- DMF; 5- 1-phenylhexane)

FID conditions

hydrogen flow:	35 mL/min
air flow:	450 mL/min
nitrogen makeup flow:	37 mL/min

3.5.2 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting ISTD-corrected response of standard injections versus micrograms of analyte per sample. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

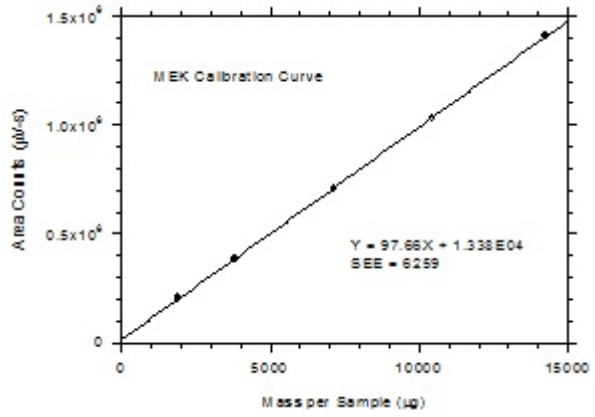


Figure 3.5.2.1. Calibration curve for MEK.

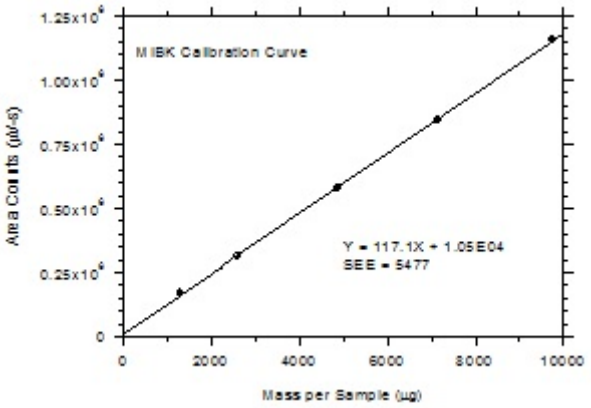


Figure 3.5.2.2. Calibration curve for MIBK.

3.6 Interferences (analytical)

3.6.1 Any compound that produces an FID response and has a similar retention time as the analyte or internal standard is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity of an analyte peak can be confirmed with additional analytical data (Section 4.9).

3.7 Calculations

3.7.1 SKC Anasorb CMS sampling tubes

The amount of MEK and/or MIBK per sample is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. The back section is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, it is added to the amount on the front section. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

$$C_M = \frac{M}{VE_E}$$

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample
V is liters of air sampled
E_E is extraction efficiency, in decimal form

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

where C_V is concentration by volume (ppm) V_M is molar volume at 25 °C and 760 mmHg (NTP)
C_M is concentration by weight
M_r is molecular weight (MEK = 72.10, MIBK = 100.16)

3.7.2 Diffusive samplers

The amount of MEK and/or MIBK for the samples is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for extraction efficiency. The 3M 3520 is a two-section sampler and the back section is analyzed primarily to determine the extent of sampler saturation. If any analyte is found on the back section, the amount is multiplied by 2.2 (as per manufacturer's instructions) and then added to the amount on the front section. The total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulas.

Table 3.7.2
Sampling Rates (mL/min)
at 760 mmHg and 298.2 K (NTP)

	MEK	MIBK
SKC 575-002	16.88	13.62
3M 3520	32.59	27.00

$$R_{SS} = R_{NTP}\left(\frac{T_{SS}}{T_{NTP}}\right)^{\frac{3}{2}}\left(\frac{P_{NTP}}{P_{SS}}\right)$$

where R_{SS} is the sampling rate at sampling site
R_{NTP} is the sampling rate at NTP
T_{SS} is the sampling site temperature in K
T_{NTP} is 298.2 K
P_{SS} is the sampling site pressure in mmHg
P_{NTP} is 760 mmHg

$$C_M = \frac{10^3\ M}{tR_{SS}E_E}$$

where C_M is concentration by weight (mg/m^3)
M is micrograms per sample
R_{SS} is the sampling rate at the sampling site
t is the sampling time

E_E is extraction efficiency, in decimal form

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

where C_V is concentration by volume (ppm)
V_M is molar volume at NTP
C_M is concentration by weight
M_r is molecular weight (MEK = 72.10, MIBK = 100.16)

If the sampling site temperature is not provided, assume that it is 22.2 °C. If the sampling site atmospheric pressure is not given, calculate an approximate value based on the sampling site elevation from the following equation.

$$P_{SS} = AE^2 - BE + 760.0$$

where P_{SS} is the approximate atmospheric pressure
E is the sampling site elevation, ft
A is 3.887×10^{-7} mmHg/ft^2
B is 0.02748 mmHg/ft

4. Backup Data

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatography Analysis"[11]. The Guidelines define analytical parameters, specific laboratory tests, statistical calculations and acceptance criteria.

4.1 Detection limit of the analytical procedure (DLAP)

DLAP is measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equal increments with the highest standard containing 475 ng/mL of MEK and 553 ng/mL of MIBK. These are concentrations that would produce peaks approximately 10 times the response of a reagent blank near the elution times of the analytes. These standards, and the reagent blank were analyzed with the recommended analytical parameters (1-µL injection with a 26:1 split), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. The DLAP for MEK was 4.90 pg and it was 3.13 pg for MIBK.

[11] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

Table 4.1.1
Detection Limit
of the Analytical Procedure for MEK

concentration (ng/mL)	mass on column (pg)	area counts (µV-s)
0	0	0
48	1.8	16
95	3.6	28
142	5.5	35
190	7.3	43
238	9.2	60
285	11.0	40
332	12.8	70
380	14.6	74
428	16.5	83
475	18.3	96

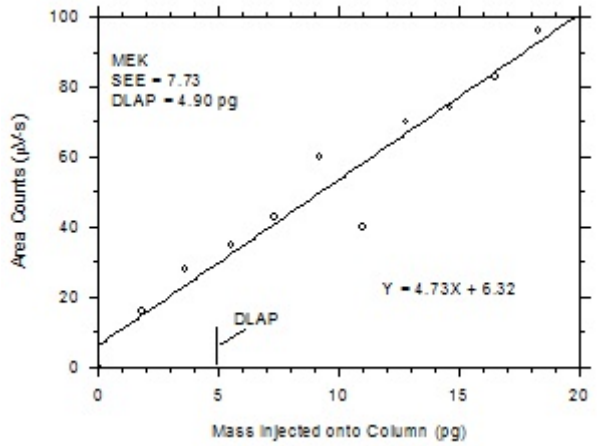


Figure 4.1.1. Plot of data used to determine the DLAP for MEK.

Table 4.1.2
Detection Limit
of the Analytical Procedure for MIBK

concentration (ng/mL)	mass on column (pg)	area counts (µV-s)
0	0	0
33	1.3	12
98	3.8	23
163	6.3	45
228	8.8	55
293	11.3	68
358	13.8	90
390	15.0	90
423	16.3	92
488	18.8	99
553	21.3	132

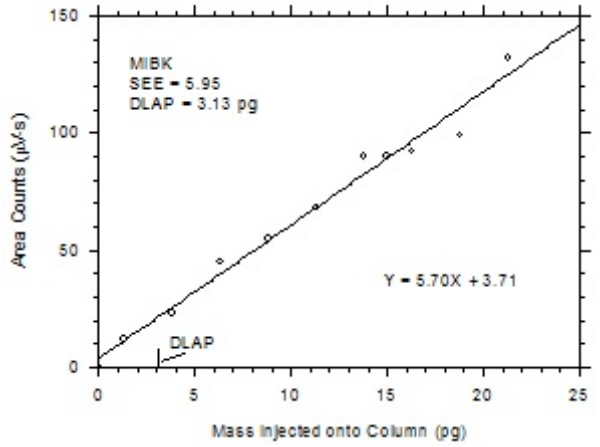


Figure 4.1.2. Plot of data used to determine the DLAP for MIBK.

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

DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with descending increments of analyte. The highest amount shown in the following tables is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank. These spiked samplers, and the sample blanks 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.

Table 4.2
Detection Limits of the Overall Procedure

	MEK			MIBK		
sampler	ng	ppb	µg/m^3	ng	ppb	µg/m^3
SKC CMS	244	7	20	129	3	11
SKC Anasorb 747	291	8	24	329	7	27
SKC 575-002	388	33	96	376	28	115
3M 3520	230	10	29	281	11	43

Table 4.2.1
DLOP/RQL for MEK Collected
on SKC CMS Sampling Tubes

mass per sample (ng)	area counts (µV-s)
0	0
48	26
142	14
238	31
332	44
428	47
522	54
570	58
618	66
713	66
808	94

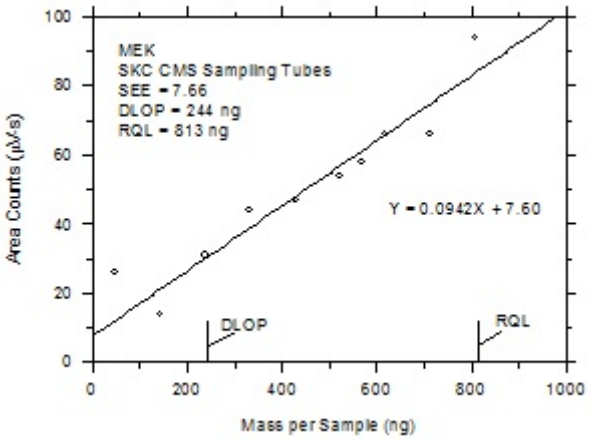


Figure 4.2.1. Plot of data to determine the DLOP/RQL for MEK collected on SKC CMS sampling tubes.

Table 4.2.2
DLOP/RQL for MIBK Collected
on SKC CMS Sampling Tubes

mass per sample (ng)	area counts (µV-s)
0	0
65	0
130	16
195	22
260	28
325	32
358	40
390	43
455	66
520	64
553	61

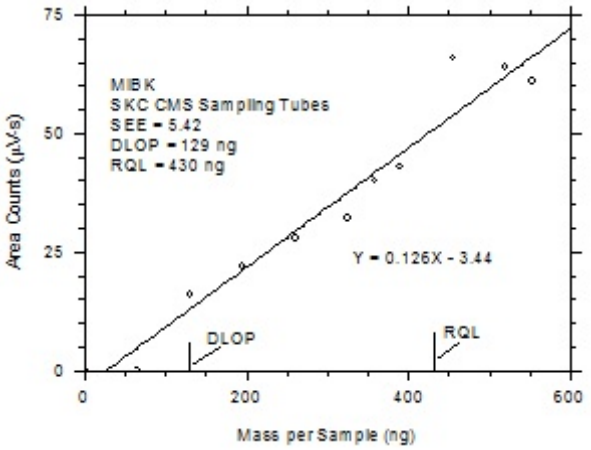


Figure 4.2.2. Plot of data to determine the DLOP/RQL for MIBK collected on SKC CMS sampling tubes.

Table 4.2.3
DLOP/RQL for MEK Collected
on SKC Anasorb 747 Sampling Tubes

mass per sample (ng)	area counts (µV-s)
0	0
190	11
380	18
570	25
665	31
760	36
855	42
1045	46
1235	57
1425	68
1615	93

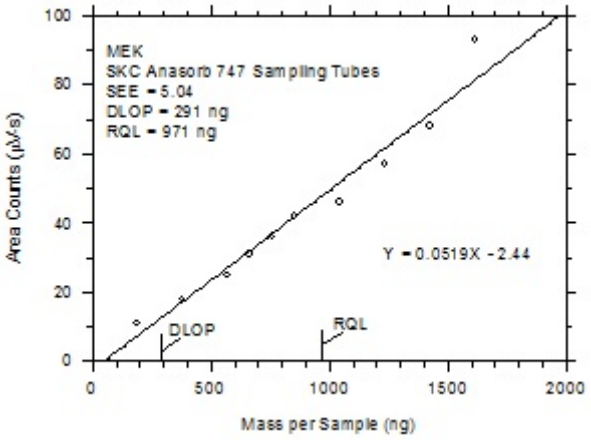


Figure 4.2.3. Plot of data to determine the DLOP/RQL for MEK collected on SKC Anasorb 747 sampling tubes.

Table 4.2.4
DLOP/RQL for MIBK Collected
on SKC Anasorb 747 Sampling Tubes

mass per sample (ng)	area counts (µV-s)
0	0
130	13
260	24
390	40
455	33
520	35
585	42
715	53
845	57
975	76
1105	110

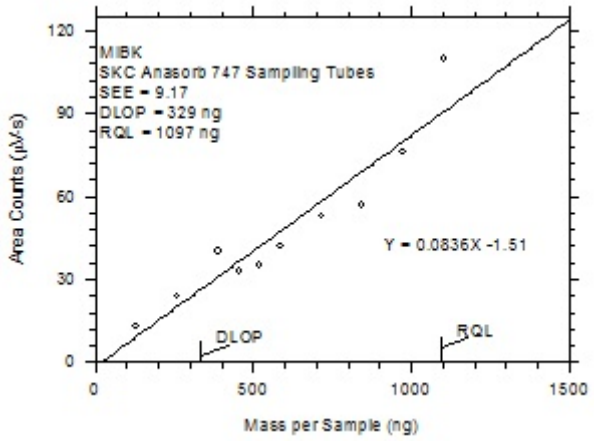


Figure 4.2.4. Plot of data to determine the DLOP/RQL for MIBK collected on SKC Anasorb 747 sampling tubes.

Table 4.2.5
DLOP/RQL for MEK Collected
on SKC 575-002 Passive Samplers

mass per sample (ng)	area counts (µV-s)
0	0
190	24
380	34
570	40
665	47
760	46
855	46
1045	59
1235	70
1425	90
1615	82

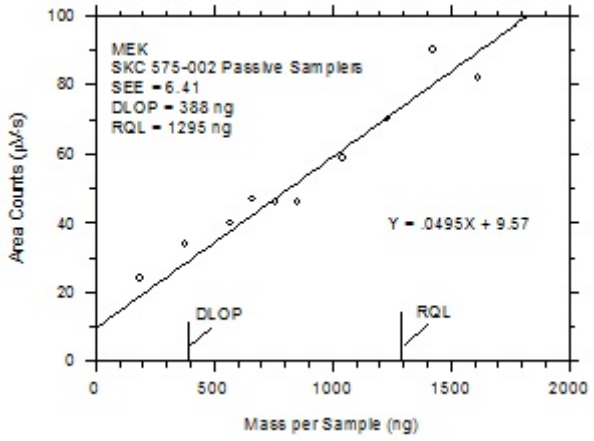


Figure 4.2.5. Plot of data to determine the DLOP/RQL for MEK collected on SKC 575-002 Passive Samplers.

Table 4.2.6
DLOP/RQL for MIBK Collected
on SKC 575-002 Passive Samplers

mass per sample (ng)	area counts (µV-s)
0	0
130	11
260	21
390	28
455	29
520	40
585	39
715	66
845	77
975	55
1105	79

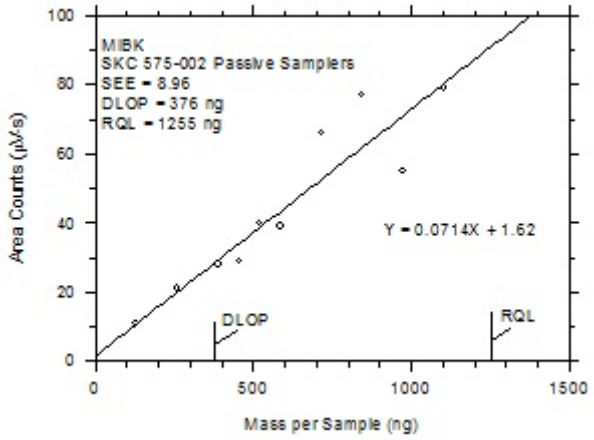


Figure 4.2.6. Plot of data to determine the DLOP/RQL for MIBK collected on SKC 575-002 Passive Samplers.

Table 4.2.7
DLOP/RQL for MEK
Collected on 3M 3520 OVMs

mass per sample (ng)	area counts (µV-s)
0	0
95	6
285	24
475	29
665	42
855	49
1045	58
1140	65
1235	79
1425	80
1615	86

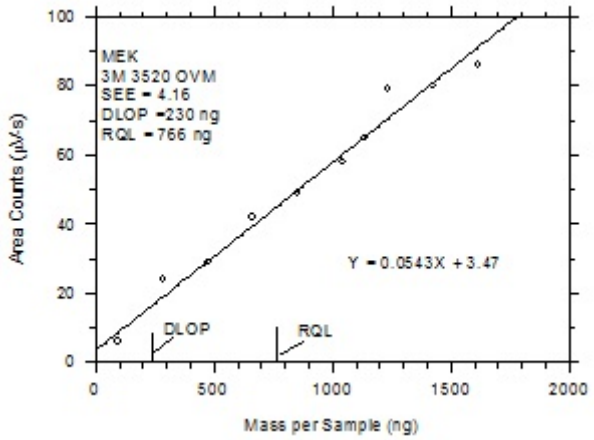


Figure 4.2.7. Plot of data to determine the DLOP/RQL for MEK collected on 3M 3520 OVMs.

Table 4.2.8
DLOP/RQL for MIBK
Collected on 3M 3520 OVMs

mass per sample (ng)	area counts (µV-s)
0	0
65	4
195	14
325	18
455	24
585	44
715	43
780	48
845	54
975	81
1105	70

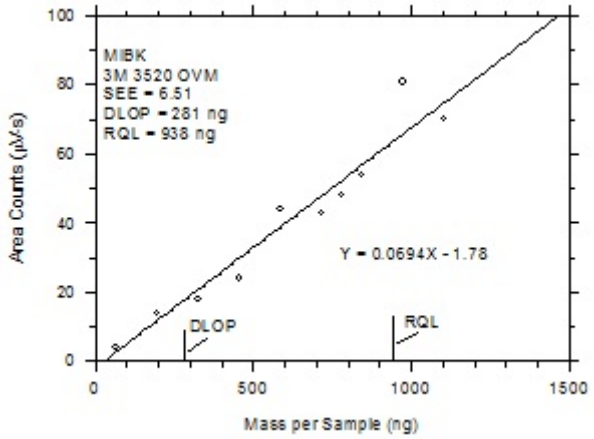


Figure 4.2.8. Plot of data to determine the DLOP/RQL for MIBK collected on 3M 3520 OVMs.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for calculation of the DLOP, providing the extraction efficiency (*EE*) is 75% to 125%.

Table 4.2.9
Reliable Quantitation Limits

	MEK				MIBK			
sampler	ng	ppb	µg/m^3	*EE*	ng	ppb	µg/m^3	*EE*
SKC CMS	813	23	68	98.5	430	9	36	111.7
SKC Anasorb 747	971	27	81	101.5	1097	22	91	98.2
SKC 575-002	1295	109	320	90.4	1255	94	384	81.0
3M 3520	766	33	98	105.3	937	35	144	86.4

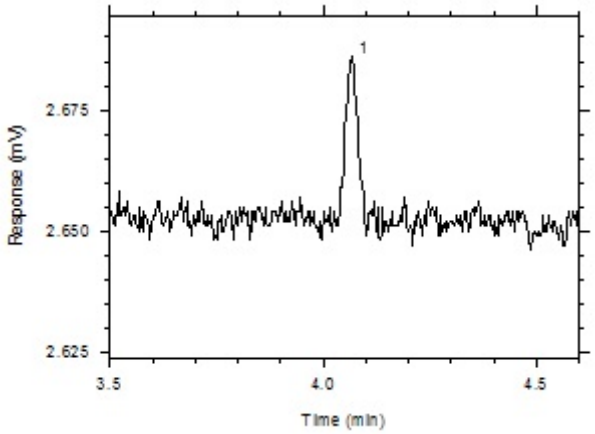


Figure 4.2.9. Chromatogram of the RQL for MEK extracted from SKC Anasorb CMS sampling tubes. Peak 1 is MEK.

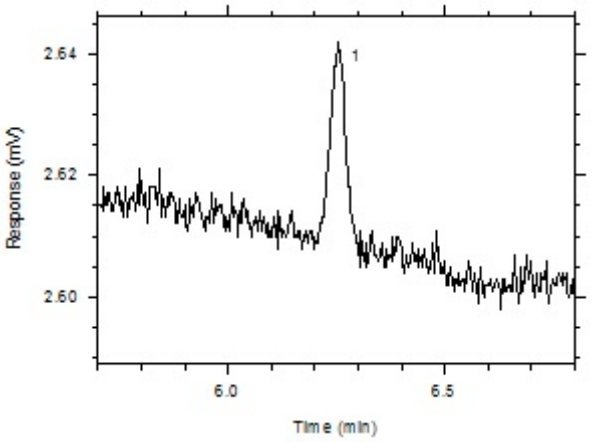


Figure 4.2.10. Chromatogram of the RQL for MIBK extracted from SKC Anasorb CMS sampling tubes. Peak 1 is MIBK.

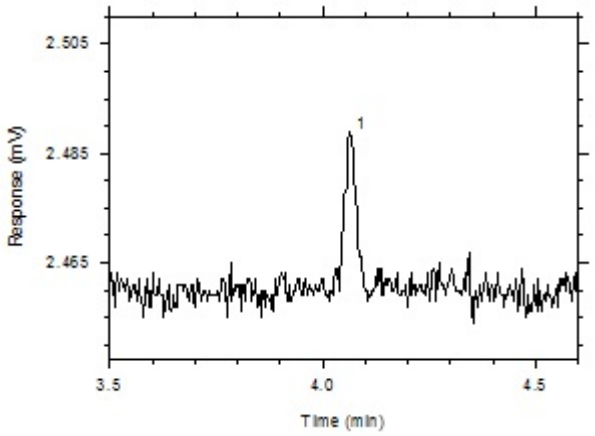


Figure 4.2.11. Chromatogram of the RQL for MEK extracted from SKC Anasorb 747 sampling tubes. Peak 1 is MEK.

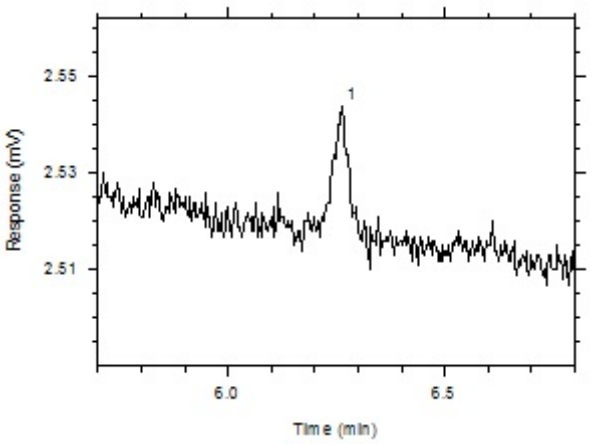


Figure 4.2.12. Chromatogram of the RQL for MIBK extracted from SKC Anasorb 747 sampling tubes. Peak 1 is MIBK.

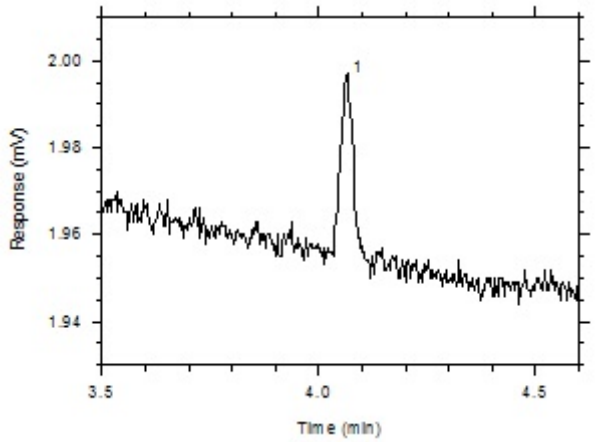


Figure 4.2.13. Chromatogram of the RQL for MEK extracted from SKC 575-002 Passive Samplers. Peak 1 is MEK.

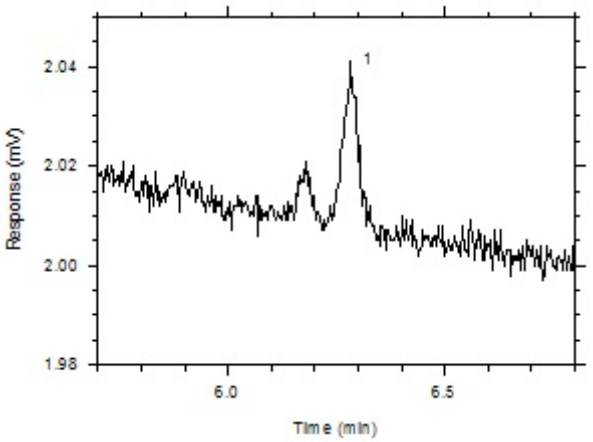


Figure 4.2.14. Chromatogram of the RQL for MIBK extracted from SKC 575-002 Passive Samplers. Peak 1 is MIBK.

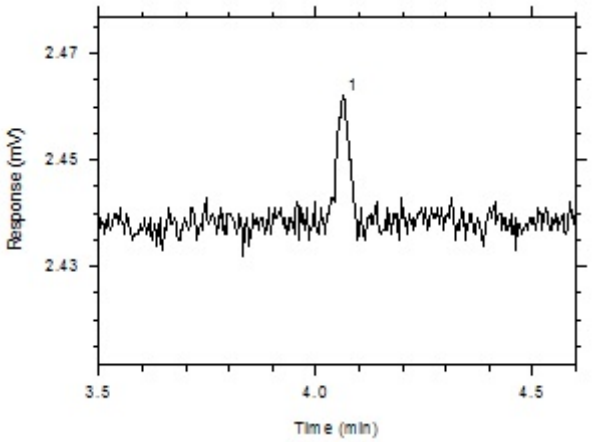


Figure 4.2.15. Chromatogram of the RQL for MEK extracted from 3M 3520 OVM. Peak 1 is MEK.

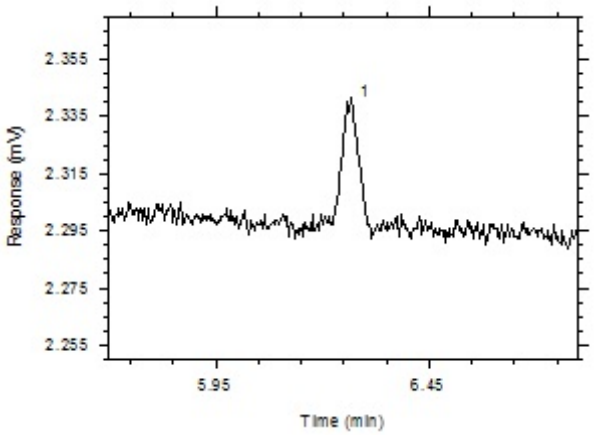


Figure 4.2.16. Chromatogram of the RQL for MIBK extracted from 3M 3520 OVM. Peak 1 is MIBK.

4.3 Instrument calibration

The standard errors of estimate were determined from the linear regressions of data points from standards over a range that covers 0.25 to 2 times the target concentrations for SKC CMS sampling tubes. This was the sampler with the highest mass loadings. Calibration curves were constructed and shown in Section 3.5.2 from the injections of the fifteen standards. The standard errors of estimate are 64 µg/sample for MEK and 47 µg/sample for MIBK.

Table 4.3.1
Instrument Calibration for MEK

standard concn (µg/sample)	area counts (µV•s)		
1900	209059	203442	194603
3800	382186	383631	389559
7125	711627	702855	701446
10450	1030541	1028461	1025964
14250	1410615	1414645	1406129

Table 4.3.2
Instrument Calibration for MIBK

standard concn (µg/sample)	area counts (µV•s)		
1300	171450	166556	158962
2601	313431	313539	319156
4876	584366	57873	576681
7152	845491	842971	839986
9753	1157297	1161587	1153280

4.4 Precision (overall procedure)

4.4.1 SKC CMS sampling tubes

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). In Section 4.5, 95% confidence intervals are drawn about their respective regression lines in the storage graph figures. Each precision includes an additional 5% for sampling error. The precisions of the overall procedure at the 95% confidence interval for the ambient temperature 15-day storage tests (at the target concentration) for MEK and for MIBK were ±11.7% and ±11.5%, respectively. These values are from the standard error of estimates shown in Figures 4.5.1.1 and 4.5.1.3.

4.4.2 Diffusive samplers

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 15-day storage tests (at the target concentration) are shown in Table 4.4.2. There are different values given, depending on whether both, either, or neither temperature (*T*) or atmospheric pressure (*P*) at the sampling site are known. If the

sampling site temperature is unknown, it is assumed to be 22.2 ± 15 °C (72 ± 27 °F) and a variability of ±7.7% is included. If the atmospheric pressure is not known, it is estimated from the sampling site elevation and a variability of ±3% is included. Each 3M precision value includes an additional 7.4% for sampling rate variation, and each SKC value an additional 8.7%, also for sampling rate variation[12].

Table 4.4.2
Standard Error of Estimate and Precision of the Overall Procedure for Diffusive Samplers

known condition	SKC 575-002 Passive Sampler				3M 3520 OVM			
	MEK		MIBK		MEK		MIBK	
	SEE (%)	precision (±%)	SEE (%)	precision (±%)	SEE (%)	precision (±%)	SEE (%)	precision (±%)
both *T* & *P*	9.12	17.8	9.05	17.7	8.32	16.3	8.03	15.7
only *T*	9.60	18.7	9.53	18.7	8.84	17.3	8.57	16.8
only *P*	11.94	23.3	11.88	23.3	11.34	22.2	11.13	21.8
neither *T* nor *P*	12.30	24.1	12.26	24.0	11.73	23.0	11.52	22.6

4.5 Storage tests

4.5.1 Active samples

Storage samples for MEK and MIBK were generated by sampling controlled test atmospheres with SKC CMS and with SKC Anasorb 747 sampling tubes at 50 mL/min for four hours. The analyte concentrations of the test atmospheres were the target concentrations with an absolute humidity of 14.3 milligrams of water per liter of air (77.2% at 21.1 °C). Thirty-three storage samples were collected with each sampler. Three of each sampler were analyzed on the day of generation. Fifteen of each sampler were stored at reduced temperature (about 4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). Three samples were selected from each of the storage sets and analyzed at 2-4 day intervals. Sample results were not corrected for extraction efficiency.

Table 4.5.1.1
Storage Tests for MEK on
SKC CMS Sampling Tubes

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	95.0	94.4	90.8	95.0	94.4	90.8
2	90.7	89.2	96.4	96.3	95.9	96.4
5	88.2	83.7	88.0	93.0	92.7	92.0
8	92.3	89.7	91.5	96.2	94.3	95.1
12	92.2	86.3	87.3	94.0	94.1	93.3
15	85.8	80.4	82.7	92.6	94.2	88.8

Table 4.5.1.2
Storage Tests for MIBK on
SKC CMS Sampling Tubes

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	96.1	95.3	92.6	96.1	95.3	92.6
2	92.7	91.4	97.5	96.3	96.1	95.9
5	91.0	89.7	88.0	95.2	94.6	93.1
8	96.6	94.6	96.5	96.3	96.4	97.0
12	96.7	94.4	95.1	95.3	95.9	96.0
15	95.1	88.5	90.6	95.5	97.2	96.0

[12] Burright, D.; Chan, Y.; Eide, M.; Elskamp, C.; Hendricks, W.; Rose, M. C. *Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 1999.

Table 4.5.1.3
Storage Tests for MEK on
SKC Anasorb 747 Sampling Tubes

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	89.3	90.7	90.8	89.3	90.7	90.8
2	82.8	82.6	84.0	88.9	88.5	87.1
5	75.9	77.1	78.4	86.5	87.1	85.8
8	76.7	76.6	76.9	82.3	81.5	83.1
12	74.2	73.2	70.6	81.2	80.5	78.7
15	73.3	74.0	70.4	79.3	81.1	80.4

Table 4.5.1.4
Storage Tests for MIBK on
SKC Anasorb 747 Sampling Tubes

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	93.6	93.9	94.4	93.6	93.9	94.4
2	93.8	93.4	94.6	93.1	94.5	92.9
5	91.8	93.8	92.9	93.9	91.2	93.0
8	93.4	93.7	93.3	92.4	92.2	91.6
12	92.4	91.5	88.5	92.9	93.1	91.3
15	93.5	93.0	89.2	92.4	93.6	93.8

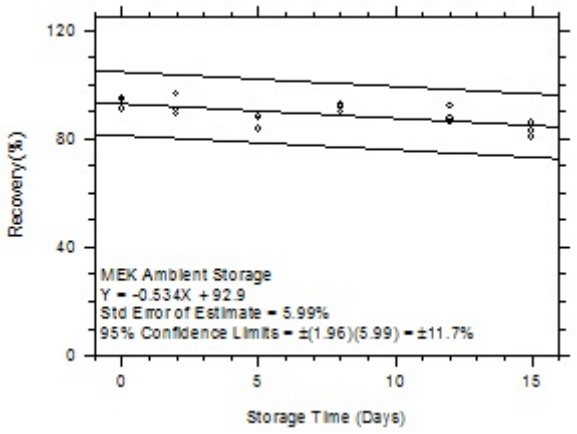


Figure 4.5.1.1. Ambient storage for MEK collected on SKC CMS sampling tubes.

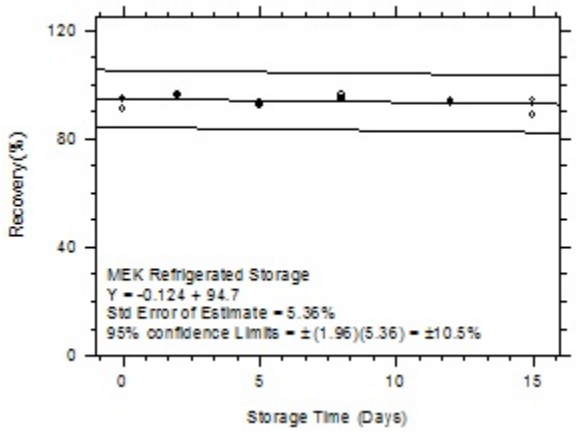


Figure 4.5.1.2. Refrigerated storage for MEK collected on SKC CMS sampling tubes.

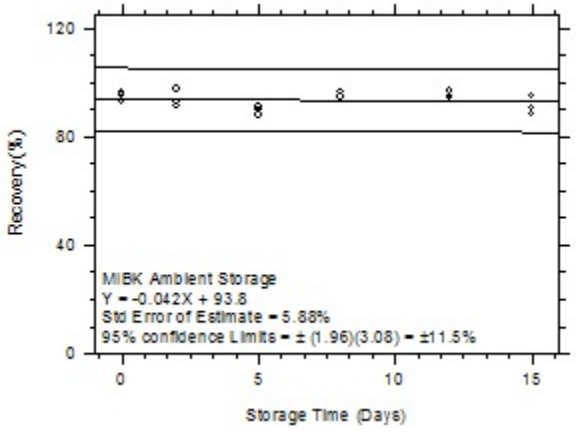


Figure 4.5.1.3. Ambient storage for MIBK collected on SKC CMS sampling tubes.

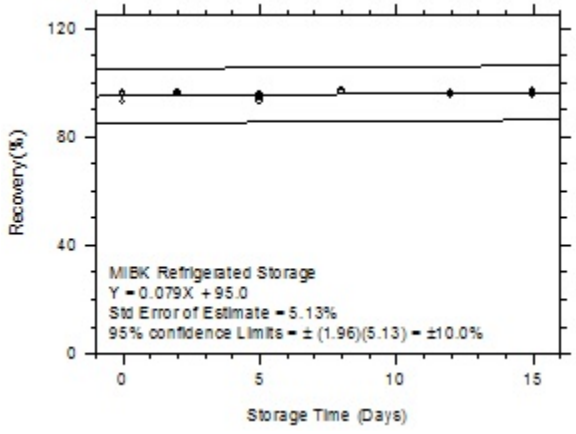


Figure 4.5.1.4. Refrigerated storage for MIBK collected on SKC CMS sampling tubes.

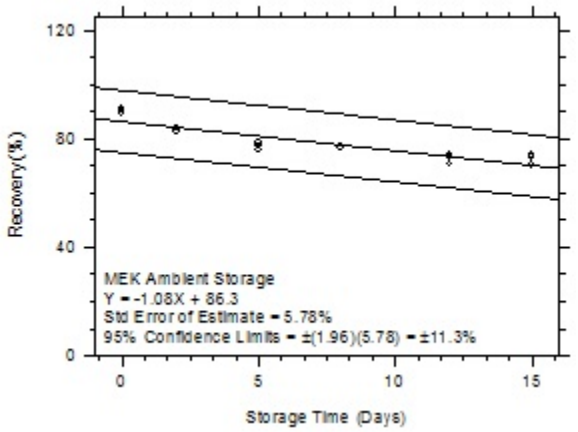


Figure 4.5.1.5. Ambient storage for MEK collected on SKC Anasorb 747 sampling tubes.

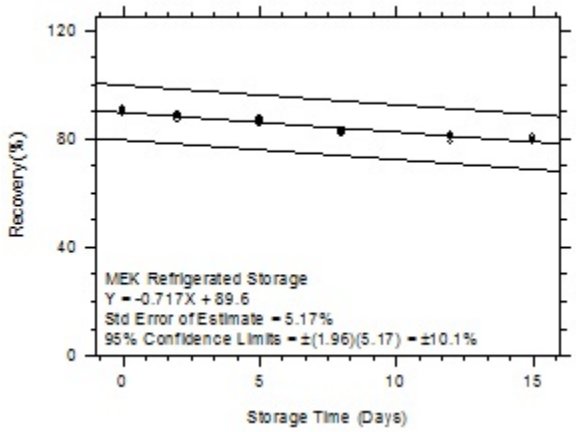


Figure 4.5.1.6. Refrigerated storage for MEK collected on SKC Anasorb 747 sampling tubes.

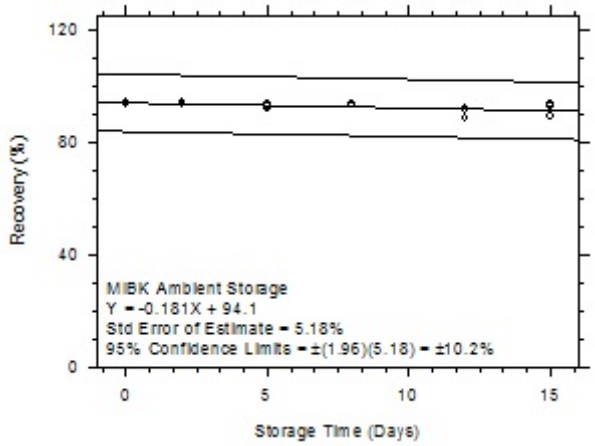


Figure 4.5.1.7. Ambient storage for MIBK collected on SKC Anasorb 747 sampling tubes.

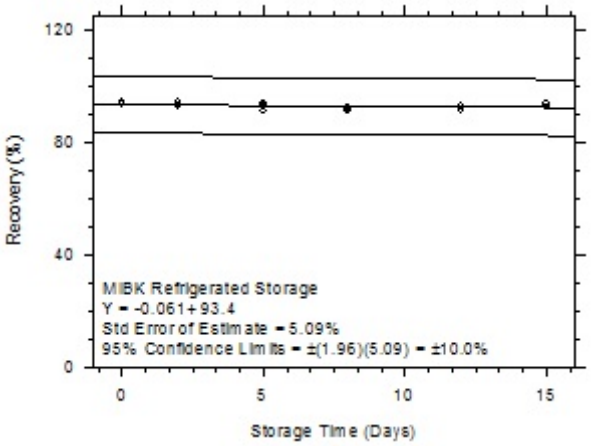


Figure 4.5.1.8. Refrigerated storage for MIBK collected on SKC Anasorb 747 sampling tubes.

4.5.2 Diffusive samplers

Storage samples for MEK and MIBK were generated by sampling controlled test atmospheres with SKC 575-002 Passive Samplers and with 3M 3520 OVMs for four hours. The analyte concentrations of the test atmospheres were the target concentrations with an absolute humidity of 14.3 milligrams of water per liter of air (77.2% at 21 °C). Thirty-three storage samples were collected with each sampler. Three of each sampler were analyzed on the day of generation. Fifteen of each sampler were stored at reduced temperature (about 4 °C) and the other fifteen were stored in a closed drawer at ambient temperature (about 22 °C). Three samples were selected from each of the storage sets and analyzed at 2-4 day intervals. Sample results were not corrected for extraction efficiency.

Table 4.5.2.1
Storage Tests for MEK on
SKC 575-002 Passive Samplers

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	96.6	98.9	89.2	96.6	98.9	89.2
2	95.5	95.7	98.5	94.6	97.7	99.5
5	90.2	90.5	87.2	95.9	96.8	95.8
8	83.6	86.0	89.9	90.5	92.0	93.8
12	84.1	84.3	83.0	91.2	91.2	93.2
15	79.3	79.5	78.8	91.3	90.3	93.7

Table 4.5.2.2
Storage Tests for MIBK on
SKC 575-002 Passive Samplers

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	96.9	99.2	89.8	96.9	99.2	89.8
2	96.6	95.9	97.0	94.3	96.7	98.4
5	92.1	93.2	88.1	95.2	95.0	93.9
8	89.9	93.0	92.5	86.7	91.4	93.0
12	89.3	89.7	89.3	89.9	89.6	90.5
15	84.8	85.1	85.7	87.5	87.6	89.4

Table 4.5.2.3
Storage Tests
for MEK on 3M 3520 OVMs

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	96.9	101.3	92.8	96.9	101.3	92.8
2	96.5	96.6	89.5	96.9	93.5	94.6
5	98.7	92.9	92.4	101.8	97.6	97.5
8	89.2	100.5	92.7	92.7	97.6	92.3
12	94.0	92.8	100.2	104.1	91.5	95.1
15	99.8	96.2	98.0	98.8	93.9	102.8

Table 4.5.2.4
Storage Tests
for MIBK on 3M 3520 OVMs

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	101.2	104.9	100.5	101.2	104.9	100.5
2	101.8	101.2	94.9	102.4	99.4	100.5
5	103.7	100.1	98.7	109.4	103.3	102.1
8	95.3	105.8	99.2	97.8	105.3	96.9
12	99.7	100.9	105.0	108.5	97.3	101.8
15	105.5	103.3	103.0	103.1	98.7	106.9

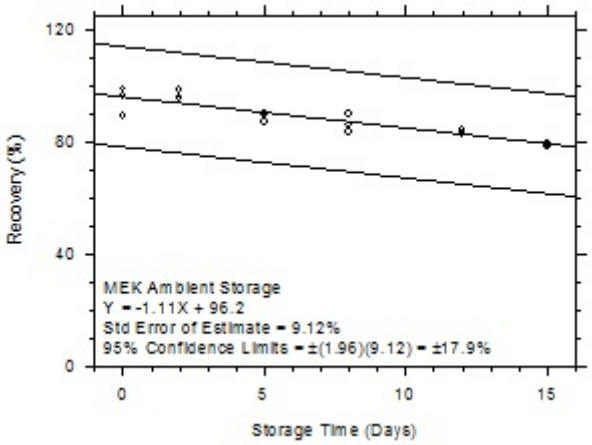


Figure 4.5.2.1. Ambient storage for MEK collected on SKC 575-002 Passive Samplers.

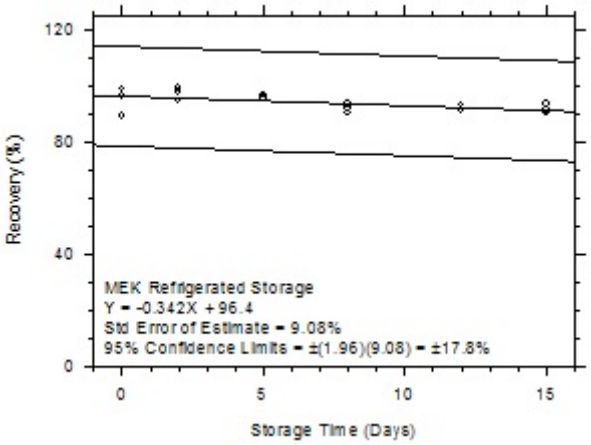


Figure 4.5.2.2. Refrigerated storage for MEK collected on SKC 575-002 Passive Samplers.

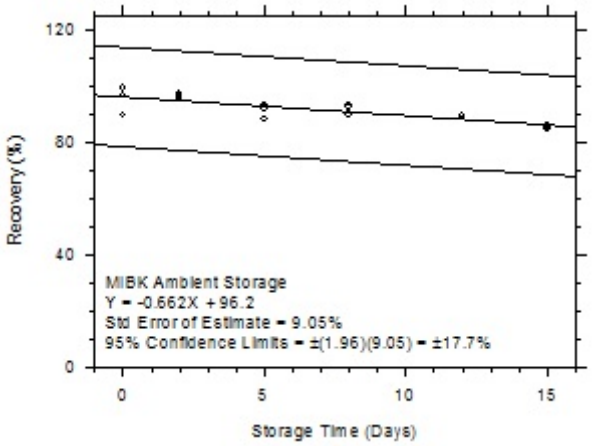


Figure 4.5.2.3. Ambient storage for MIBK collected on SKC 575-002 Passive Samplers.

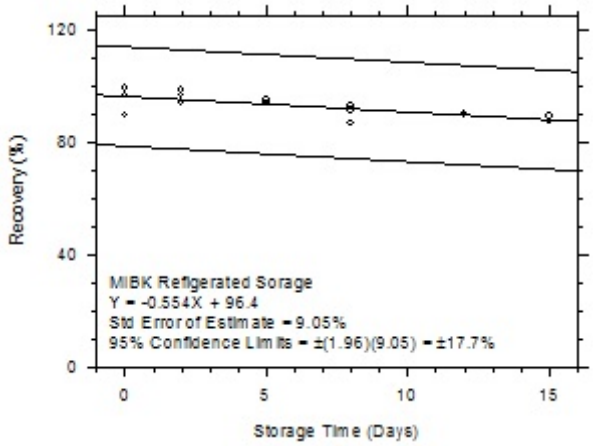


Figure 4.5.2.4. Refrigerated storage for MIBK collected on SKC 575-002 Passive Samplers.

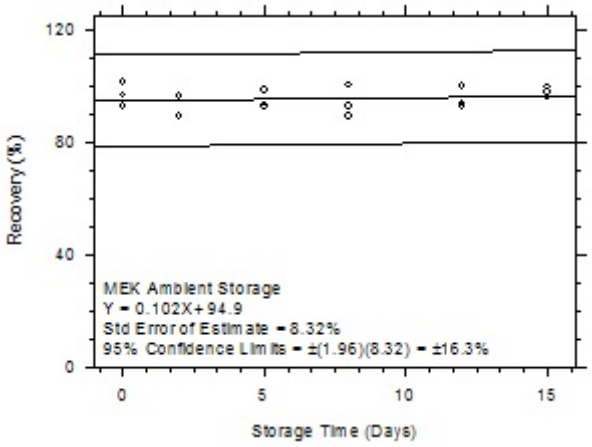


Figure 4.5.2.5. Ambient storage for MEK collected on 3M 3520 OVMs.

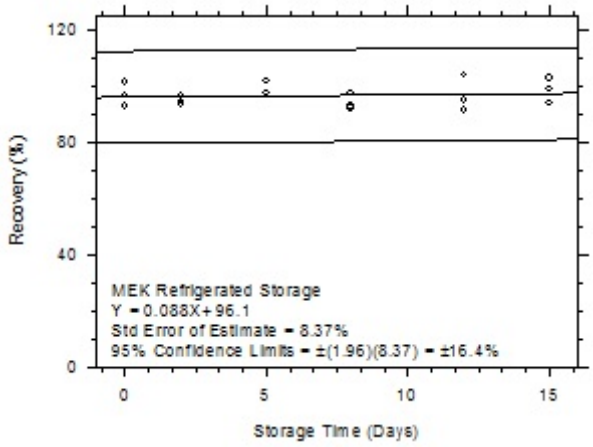


Figure 4.5.2.6. Refrigerated storage for MEK collected on 3M 3520 OVMs.

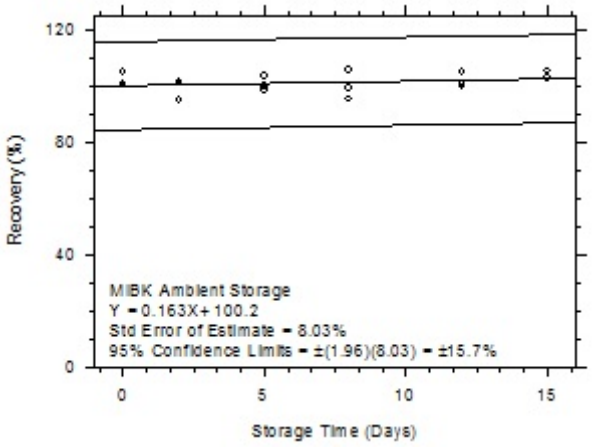


Figure 4.5.2.7. Ambient storage for MIBK collected on 3M 3520 OVMs.

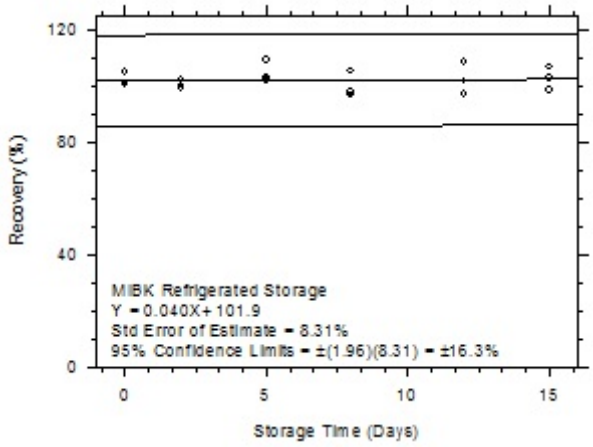


Figure 4.5.2.8. Refrigerated storage for MIBK collected on 3M 3520 OVMs.

4.6 Reproducibility

Six samples for each of the three samplers evaluated in this method were collected from a controlled test atmosphere and were submitted to OSHA SLTC for analysis. The concentration of the test atmosphere was 593.46 mg/ m^3 for MEK and 393.68 mg/m^3 for MIBK. The absolute humidity was 16.9 milligrams of water per liter of air (77.8% RH at 24 °C). The face velocity of the sampled air was 0.4 m/s. The samples were analyzed utilizing a draft copy of this procedure for analyst instruction. The samples were analyzed after being stored for 2 days at 4 °C. Sample results were corrected for extraction efficiency. No sample result for either analyte had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6.1
Reproducibility Data for MEK and MIBK Collected on SKC CMS Sampling Tubes

MEK				MIBK			
theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)	theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
7157.1	6715.1	93.8	-6.2	4747.8	4508.6	95.0	-5.0
6991.0	6514.4	93.2	-6.8	4367.6	4388.5	100.5	0.5
7151.2	6551.4	91.6	-8.4	4743.8	4331.7	91.3	-8.7
6688.3	6101.4	91.2	-8.8	4436.8	4137.9	93.3	-6.7
7353.0	6743.1	91.7	-8.3	4877.7	4379.1	89.8	-10.2
6991.0	6570.5	94.0	-6.0	4637.6	4399.1	94.9	-5.1

Table 4.6.2
Reproducibility Data for MEK and MIBK Collected on SKC 575-002 Passive Samplers

MEK				MIBK			
theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)	theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
2772.7	2719.3	98.1	-1.9	1484.1	1548.1	104.3	4.3
2772.7	3062.3	110.4	10.4	1484.1	1729.8	116.6	16.6
2772.7	2818.2	101.6	1.6	1484.1	1602.4	108.0	8.0
2772.7	2720.2	98.1	-1.9	1484.1	1558.0	105.0	5.0
2772.7	2738.9	98.8	-1.2	1484.1	1598.7	107.7	7.7
2772.7	2688.3	97.0	-3.0	1484.1	1559.5	105.1	5.1

Table 4.6.3
Reproducibility Data for MEK and MIBK Collected on 3M 3520 OVMs

MEK				MIBK			
theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)	theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
5353.1	5430.2	101.4	1.4	2942.0	3194.7	108.6	8.6
5353.1	5398.6	100.9	0.9	2942.0	3171.8	107.8	7.8
5353.1	5469.8	102.2	2.2	2942.0	3193.9	108.6	8.6
5353.1	5488.4	102.5	2.5	2942.0	3216.8	109.3	9.3
5353.1	5112.4	95.5	-4.5	2942.0	3102.2	105.4	5.4
5353.1	4725.2	88.3	-11.7	2942.0	2957.9	100.5	0.5

4.7 Sampler capacity

4.7.1 SKC Anasorb CMS sampling tubes

The sampling capacity of the front section of SKC Anasorb CMS sampling tubes was tested by sampling from a dynamically generated test atmosphere of 1131 mg/m^3 (384 ppm) MEK and 774 mg/m^3 (189 ppm) MIBK with an absolute humidity of 13.9 milligrams of water per liter of air (74% relative humidity at 22 °C). Four samples were collected at about 50 mL/min. CMS sampling tubes were placed in-line behind the front test sections and they were changed every 15 min after initial collection for four hours. Five-percent breakthrough for MEK occurred after 15 L of air had been sampled. This air volume is that which would be collected in a 5-h air sample. Breakthrough of MIBK was never observed in any of the sampler capacity tests in which samples were collected for as long as ten hours. The recommended sampling time for SKC Anasorb CMS sampling tubes is 4 hours. This sampling time provides a considerable capacity safety margin for MEK because of the presence of MIBK in the test atmosphere.

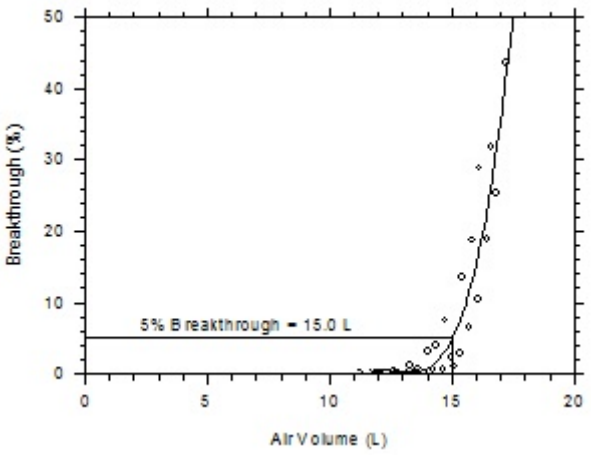


Figure 4.7.1. Five percent breakthrough air volume for MEK from SKC Anasorb CMS.

Table 4.7.1
Breakthrough of MEK from SKC Anasorb CMS

test no.	air vol (L)	sampling time (min)	downstream concn (mg/m^3)	break-through (%)	test no.	air vol (L)	sampling time (min)	downstream concn (mg/m^3)	break-through (%)
1	11.97	240	0.0	0.0	3	12.09	240	0.0	0.0
	12.72	15	0.0	0.0		12.84	15	0.0	0.0
	13.47	15	0.0	0.0		13.60	15	9.2	0.8
	14.22	15	6.7	0.6		14.35	15	44.3	3.9
	14.96	15	25.8	2.3		15.11	15	11.5	1.0
	15.71	15	73.4	6.5		15.86	15	211.5	18.7
	16.46	15	212.3	18.8		16.82	15	360.6	31.9
	17.21	15	493.1	43.6		17.37	15	613.2	54.2
	17.96	15	915.6	81.0		18.13	15	879.8	77.8
2	11.70	240	0.0	0.0	4	11.21	240	0.0	0.0
	12.43	15	0.0	0.0		11.91	15	0.0	0.0
	13.17	15	0.0	0.0		12.61	15	4.2	0.4
	13.90	15	0.0	0.0		13.31	15	12.0	1.1
	14.63	15	7.7	0.7		14.01	15	35.7	3.2
	15.36	15	33.3	2.9		14.71	15	84.9	7.5
	16.09	15	117.9	10.4		15.41	15	153.1	13.5
	16.82	15	286.4	25.3		16.11	15	326.8	28.9
	17.55	15	625.8	55.3		16.81	15	598.4	52.9

4.7.2 Diffusive samplers

Sampling rate and sampler capacity were determined using SKC and 3M samplers that were exposed to a controlled test atmosphere for increasing time intervals. Three of each sampler were exposed for each time interval. Sampler capacity is defined as exceeded when the sampling rate appears to decrease, as was the case for MEK collected on 3M 3520 OVMs. The concentration of the test atmospheres was about two times the target concentration with an absolute humidity of about 16.4 milligrams of water per liter of air (80% RH at 23 °C). Preliminary sampling rates were determined by averaging the values for the 0.5, 1 and 2 h samples. Horizontal lines were placed 10% above and 10% below the preliminary sampling rates. Sampling rates were calculated by averaging all the individual sampling rates that were between the two horizontal lines. Sampling rates, RSDs of individual runs, and RSDs of average sampling rates are shown in Table 4.7.2. Data shown in Table 4.7.2 are for the front section of the 3M samplers. A five-hour experiment was performed for the 3M sampler because its capacity for MEK was exceeded before six hours. The recommended sampling time is four hours.

Table 4.7.2.1
Determination of Sampling Rate and Recommended Sampling Time

	SKC 575-002 Passive Sampler				3M 3520 OVM			
	MEK		MIBK		MEK		MIBK	
time (h)	mL/min	RSD	mL/min	RSD (%)	mL/min	RSD (%)	mL/min	RSD (%)
0.083	16.12	6.4	14.32	3.2	33.28	0.3	27.29	3.9
0.167	16.87	3.2	13.58	1.7	33.80	3.9	27.39	3.6
0.50	16.55	0.5	13.84	2.8	33.52	1.6	26.64	0.7
1.00	17.38	1.8	13.47	1.3	33.64	3.3	26.95	1.4
2.00	17.53	0.6	13.59	0.7	31.21	1.5	25.74	0.9
3.00	17.21	0.9	13.60	0.8	32.22	4.4	26.88	4.3
4.00	16.87	3.8	13.52	3.8	31.36	0.8	26.49	3.8
5.00					31.71	3.8	27.50	3.8
6.00	16.88	0.5	13.29	0.5	27.24	5.0	26.64	3.4
8.00	16.94	1.8	13.62	3.4	22.47	3.5	28.04	1.6
10.00	16.49	1.5	13.40	1.5	17.83	2.2	27.41	2.2
mean	16.88		13.62		32.59		27.00	
RSD (%)	2.5		2.1		3.3		2.3	

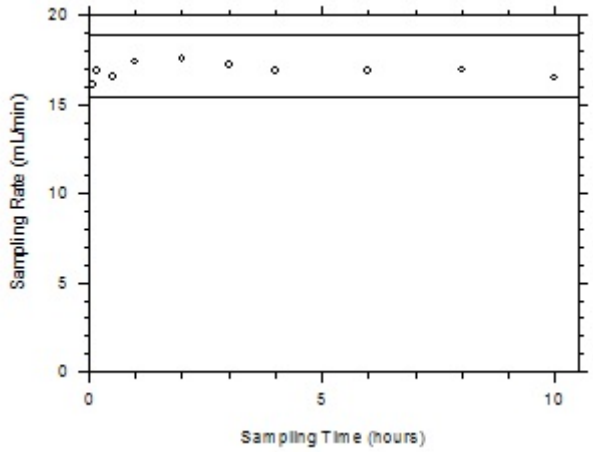


Figure 4.7.2.1. Sampler capacity data for MEK collected on SKC 575-002 Passive Sampler.

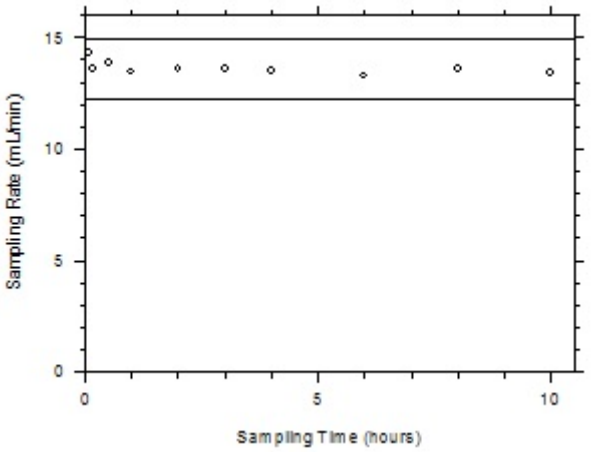


Figure 4.7.2.2. Sampler capacity data for MIBK collected on SKC 575-002 Passive Sampler.

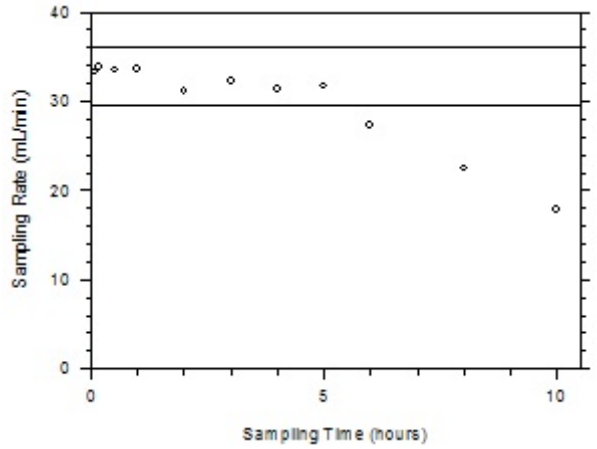


Figure 4.7.2.3. Sampler capacity data for MEK collected on 3M 3520 OVM.

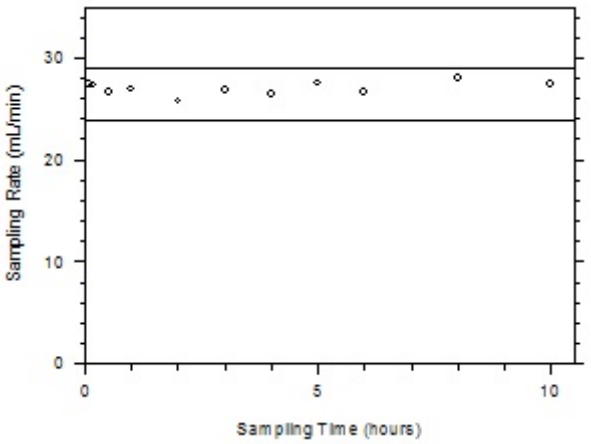


Figure 4.7.2.4. Sampler capacity data for MIBK collected on 3M 3520 OVM.

Sampling rate is normally calculated using only the front section of two-section samplers. The 3M 3520 OVM is a two-section sampler. When MEK collected on the back section was included in the total amount, the resultant MEK sampling rates were comparable with those obtained above. This data should not be used to justify sampling times longer than four hours, but it does show the value of a two-section sampler.

Table 4.7.2.2
MEK Sampling Rates for
3M 3520 OVM With Back Section Included

time (h)	mL/min	RSD (%)
6	31.54	4.0
8	32.84	0.7
10	32.29	1.5

4.8 Extraction efficiency and stability of extracted samples

A summary of extraction efficiencies (at concentrations near the RQL to 2 times the target concentration) for all the sampling media used in this work is shown in Table 4.8. The extraction efficiency is dependent on the extraction solvent as well as the internal standard. Other extraction solvents or internal standards may be used provided they are tested as described below.

Table 4.8
Extraction Efficiency Summary

medium	MEK (%)	MIBK (%)
Anasorb CMS	100.3	102.3
Anasorb 747	97.9	99.0
SKC 575-002	92.2	92.9
3M 3520 OVM	98.0	96.5

4.8.1 SKC Anasorb CMS sampling tubes

Extraction efficiency

The extraction efficiencies of MEK and MIBK were determined by liquid-spiking 150 mg portions of Anasorb CMS with the analytes at concentrations from the RQL to 2 times the target concentration. These samplers were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 100.3% for MEK and 102.3% for MIBK. The extraction efficiency for MEK from wet samplers was lower than for dry samplers. These results were expected because of the instability of MEK on wet carbon-based sorbents. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results. Wet sampling media used in extraction efficiency tests were all prepared by sampling contaminant-free, humid air (about 80% relative humidity at 22 °C) for four hours at the recommended sampling rate.

Table 4.8.1.1
Extraction Efficiency of MEK From Anasorb CMS (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.808	100.7	101.6	92.8	98.7	98.5
0.25	1781	98.4	98.1	98.4	98.7	98.4
0.5	3562	99.7	101.0	98.2	100.6	99.9
1.0	7125	104.0	96.9	104.7	104.4	102.5
1.5	10450	101.8	101.1	101.8	99.6	101.1
2.0	14250	101.3	100.6	99.5	103.5	101.2
1.0 (wet)	7125	89.9	86.3	87.1	91.5	88.7

Table 4.8.1.2
Extraction Efficiency of MIBK From Anasorb CMS (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.423	111.0	111.9	114.5	109.3	111.7
0.25	1219	98.6	98.7	98.7	98.4	98.6
0.5	2438	98.0	99.8	97.8	99.1	98.7
1.0	4876	103.7	98.0	104.1	103.6	102.4
1.5	7152	101.4	102.3	101.8	100.4	101.5
2.0	9753	100.8	100.4	99.6	102.7	100.9
1.0 (wet)	4876	98.6	95.4	96.2	99.5	97.4

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples a day after the initial analysis. After the original analysis was performed two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. Each septum was punctured 6 times for each injection.

Table 4.8.1.3
Stability of Samples
for MEK Extracted From Anasorb CMS

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
104.0	100.3	-3.7	104.7	89.3	-15.4
96.9	100.2	3.3	104.4	84.9	-19.5
	mean			mean	
100.5	100.3	-0.2	104.6	87.1	-17.5

Table 4.8.1.4
Stability of Samples
for MIBK Extracted From Anasorb CMS

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
103.7	100.8	-2.9	104.1	96.8	-7.3
98.0	100.2	2.2	103.6	96.8	-6.8
	mean			mean	
100.9	100.5	-0.4	103.9	96.8	-7.1

The stability test for MEK was repeated with the reanalysis performed 12 hours after the initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. Each septum was punctured 6 times for each injection.

Table 4.8.1.5
Stability of Samples
for MEK Extracted From Anasorb CMS

punctured septa replaced			punctured septa retained		
initial (%)	after 12 h (%)	difference (%)	initial (%)	after 12 h (%)	difference (%)
98.3	96.6	-1.7	99.1	92.6	-6.5
97.5	96.1	-1.4	99.0	94.0	-5.0
	mean			mean	
97.9	96.4	-1.6	99.1	93.3	-5.8

4.8.2 SKC Anasorb 747 sampling tubes

Extraction efficiency

The extraction efficiencies of MEK and MIBK were determined by liquid-spiking 400 mg portions of Anasorb 747 with the analytes at concentrations from the RQL to 2 times the target concentration. These samplers were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 97.9% for MEK and 99.0% for MIBK. The extraction efficiency for MEK from wet samplers was lower than for dry samplers. These results were expected because of the instability of MEK on wet sorbents. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results.

Table 4.8.2.1
Extraction Efficiency of MEK From Anasorb 747 (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.950	86.5	114.5	104.1	100.7	101.5
0.25	1781	94.4	94.9	94.5	94.8	94.7
0.5	3562	94.8	97.1	94.7	95.4	95.5
1.0	7125	98.8	98.8	99.4	96.7	98.4
1.5	10450	101.9	99.7	99.1	99.5	100.1
2.0	14250	92.7	98.7	99.0	98.2	97.2
1.0 (wet)	7125	87.3	86.4	86.0	91.7	87.9

Table 4.8.2.2
Extraction Efficiency of MIBK From Anasorb 747 (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.683	103.6	91.1	100.2	97.8	98.2
0.25	1219	97.3	96.6	96.6	96.6	96.8
0.5	2438	96.9	99.6	96.8	97.4	97.7
1.0	4876	100.2	101.1	101.7	99.5	100.6
1.5	7152	102.9	101.3	101.0	101.3	101.6
2.0	9753	96.0	100.7	100.7	100.2	99.4
1.0 (wet)	4876	96.3	95.0	94.9	99.6	96.5

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples a day after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. Each septum was punctured 6 times for each injection.

Table 4.8.2.3
Stability of Samples
for MEK Extracted From Anasorb 747

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
98.8	97.8	-1.0	99.4	88.6	-10.8
98.8	100.2	1.4	96.7	84.4	-12.3
	mean			mean	
98.8	99.0	0.2	98.1	86.5	-11.6

Table 4.8.2.4
Stability of Samples
for MIBK Extracted From Anasorb 747

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
100.2	100.5	0.3	101.7	98.0	-3.7
101.1	102.1	1.0	99.5	96.0	-3.5
	mean			mean	
100.7	101.3	0.7	100.6	97.0	-3.6

The stability test for MEK was repeated with the reanalysis performed 12 hours after the initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. Each septum was punctured 6 times for each injection.

Table 4.8.2.5
Stability of Samples
for MEK Extracted From Anasorb 747

punctured septa replaced			punctured septa retained		
initial (%)	after 12 h (%)	difference (%)	initial (%)	after 12 h (%)	difference (%)
98.5	99.0	0.5	98.9	96.0	-2.9
97.4	97.4	0.0	98.1	93.3	-4.8
	mean			mean	
98.0	98.2	0.3	98.5	94.7	-3.9

4.8.3 SKC 575-002 Passive Samplers

Extraction efficiency

The extraction efficiencies of MEK and MIBK were determined by liquid spiking SKC 575-002 Passive Samplers with the analytes at concentrations from the RQL to 2 times the target concentration. These samplers were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 92.2% for MEK and 92.9% for MIBK. The extraction efficiency for MEK from wet samplers was lower than for dry samplers. These results were expected because of the instability of MEK on wet sorbents. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results.

Table 4.8.3.1
Extraction Efficiency of MEK From
SKC 575-002 Passive Samplers (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	1.282	80.8	101.8	85.5	93.3	90.4
0.25	594	92.7	97.2	91.8	95.1	94.2
0.5	1188	87.4	87.6	90.9	89.3	88.8
1.0	2375	94.4	92.4	99.4	94.7	95.2
1.5	3800	89.9	94.1	90.2	95.2	92.4
2.0	4750	95.1	93.4	91.5	88.5	92.1
1.0 (wet)	2375	89.8	85.7	83.7	87.9	86.8

Table 4.8.3.2
Extraction Efficiency of MIBK From
SKC 575-002 Passive Samplers (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	1.268	71.6	74.7	94.3	83.3	81.0
0.25	325	91.0	92.9	90.0	90.9	91.2
0.5	650	94.8	96.6	92.8	94.9	94.8
1.0	1300	98.2	97.2	99.4	96.0	97.7
1.5	1950	98.1	97.6	97.0	95.5	97.1
2.0	2601	98.2	92.1	95.3	97.5	95.8
1.0 (wet)	1300	97.0	96.6	97.7	99.5	97.7

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples a day after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. Each septum was punctured 6 times for each injection.

Table 4.8.3.3
Stability of Samples for MEK Extracted From SKC 575-002 Passive Samplers

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
94.4	93.0	-1.4	99.4	77.2	-22.2
92.4	92.7	0.3	94.7	83.6	-11.1
	mean			mean	
93.4	92.9	-0.6	97.1	80.4	-16.7

Table 4.8.3.4
Stability of Samples for MIBK Extracted From SKC 575-002 Passive Samplers

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
98.2	95.3	-2.9	99.4	92.8	-6.6
97.2	97.0	-0.2	96.0	87.8	-8.2
	mean			mean	
97.7	96.2	-1.6	97.7	90.3	-7.4

The stability test for MEK was repeated with the reanalysis performed 12 hours after the initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. Each septum was punctured 6 times for each injection.

Table 4.8.3.5
Stability of Samples for MEK Extracted From SKC 575-002 Passive Samplers

punctured septa replaced			punctured septa retained		
initial (%)	after 12 h (%)	difference (%)	initial (%)	after 12 h (%)	difference (%)
89.7	94.6	4.9	89.7	89.6	-0.1
90.3	93.2	2.9	94.5	86.4	-8.1
	mean			mean	
90.0	93.9	3.9	92.1	88.0	-4.1

4.8.4 3M 3520 OVM

Extraction efficiency

The extraction efficiencies of MEK and MIBK were determined by liquid-spiking 3M 3520 OVM charcoal wafers with the analytes at concentrations from the RQL to 2 times the target concentration. These samples were stored overnight at ambient temperature and then analyzed. The mean extraction efficiency over the working range of the RQL to 2 times the target concentration is 98.0% for MEK and 96.5% for MIBK. The extraction efficiency for MEK from wet samplers was lower than for dry samplers. These results were expected because of the instability of MEK on wet sorbents. The extraction efficiency for the wet samplers was not included in the overall mean because it would bias the results.

Table 4.8.4.1
Extraction Efficiency of MEK From 3M 3520 OVM Charcoal Wafers (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.760	108.6	91.7	107.2	113.7	105.3
0.25	1188	100.1	93.2	92.4	94.7	95.1
0.5	2375	97.9	102.1	103.8	98.3	100.5
1.0	4750	96.4	96.8	94.0	95.0	95.6
1.5	7125	97.1	95.6	100.9	93.9	96.9
2.0	9500	89.4	98.8	95.7	94.3	94.6
1.0 (wet)	4750	88.2	89.3	90.1	91.4	89.8

Table 4.8.4.2
Extraction Efficiency of MIBK From 3M 3520 OVM Charcoal Wafers (%)

level		sample number				
× target concn	µg per sample	1	2	3	4	mean
RQL	0.943	92.0	87.3	84.8	81.5	86.4
0.25	650	98.2	96.1	93.2	97.1	96.2
0.5	1300	97.2	98.7	98.4	98.9	98.3
1.0	2601	99.7	98.2	96.8	96.2	97.7
1.5	3901	98.5	101.3	98.3	100.2	99.6
2.0	5201	100.7	97.2	103.0	101.3	100.6
1.0 (wet)	2601	98.7	97.5	93.8	98.1	97.0

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples a day after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. Each septum was punctured 6 times for each injection.

Table 4.8.4.3
Stability of Samples for MEK
Extracted From 3M 3520 OVM Charcoal Wafers

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
96.4	97.2	0.8	94.0	84.2	-9.8
96.8	94.3	-2.5	95.0	77.9	-17.1
	mean			mean	
96.6	95.8	-0.9	94.5	81.1	-13.5

Table 4.8.4.4
Stability of Samples for MIBK
Extracted From 3M 3520 OVM Charcoal Wafers

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
99.7	99.4	-0.3	96.8	93.8	-3.0
98.2	100.1	1.9	96.2	96.1	-0.1
	mean			mean	
99.0	99.8	0.8	96.5	95.0	-1.6

The stability test for MEK was repeated with the reanalysis performed 12 hours after the initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. Each septum was punctured 6 times for each injection.

Table 4.8.4.5
Stability of Samples for MEK
Extracted From 3M 3520 OVM Charcoal Wafers

punctured septa replaced			punctured septa retained		
initial (%)	after 12 h (%)	difference (%)	initial (%)	after 12 h (%)	difference (%)
100.0	95.3	-4.7	102.7	94.1	-8.6
103.5	94.9	-8.6	103.6	94.4	-9.2
	mean			mean	
101.8	95.1	-6.7	103.2	94.3	-8.9

4.9 Interferences (sampling)

4.9.1 SKC Anasorb CMS sampling tubes

Retention

The ability of SKC Anasorb CMS sampling tubes to retain MEK and MIBK after collection was tested by sampling an atmosphere containing 1178 mg/m^3 MEK and 806 mg/m^3 MIBK at an absolute humidity of 14.6 milligrams of water per liter of air (77.8% relative humidity at 21.4 °C). Six samplers had contaminated air drawn through them at about 50 mL/min for 60 min. Sampling was discontinued and three samples set aside. The generation system was flushed with contaminant-free air. Sampling was resumed with the other three samples with contaminant-free humid air drawn through them at 50 mL/min for 3 h and then all six samplers were analyzed. Recoveries for the two sets are expressed as percent of theoretical.

Table 4.9.1
Retention (%) of MEK and MIBK on Anasorb CMS

	1		2		3		mean	
set	MEK	MIBK	MEK	MIBK	MEK	MIBK	MEK	MIBK
first	96.7	96.1	96.2	94.7	97.2	96.5	96.7	95.8
second	92.2	93.4	93.1	93.4	91.9	92.5	92.4	93.1
second/first							95.6	97.2

Low humidity

The ability of SKC Anasorb CMS sampling tubes to collect MEK and MIBK from a relatively dry atmosphere was tested by sampling an atmosphere containing 1203 mg/m^3 of MEK and 823 mg/m^3 of MIBK at an absolute humidity of 2.7 milligrams of water per liter of air (13.2% relative humidity at 22.6 °C). Three samplers had contaminated air drawn through them at 50 mL/min for 240 min. All three samples were immediately analyzed. The sample results were 96.3%, 97.2% and 95.1% of theoretical for MEK; and 98.6%, 99.3%, 98.2% of theoretical for MIBK.

Low concentration

The ability of SKC Anasorb CMS sampling tubes to collect MEK and MIBK at low concentrations was tested by sampling an atmosphere containing 60.4 mg/m^3 of MEK and 41.3 mg/m^3 of MIBK at an absolute humidity of 15.5 milligrams of water per liter of air (79.7% relative humidity at 22.3 °C). Three samplers had contaminated air drawn through them at 50 mL/min for 240 min. All three samples were immediately analyzed. The sample results were 94.9%, 98.2% and 97.2% of theoretical for MEK and 101.1%, 104.7% and 104.4% of theoretical for MIBK.

Sampling interferences

The ability of SKC Anasorb CMS sampling tubes to collect MEK and MIBK was tested in the presence of potential interferences by sampling an atmosphere containing 578 mg/m^3 of MEK and 395 mg/m^3 of MIBK at an absolute humidity of 15.6 milligrams of water per liter of air (79.0% relative humidity at 22.23 °C) and 553.3 mg/m^3 acetone, 253.7 mg/m^3 isopropyl alcohol, 190.1 mg/m^3 toluene, 92.5 mg/m^3 xylene isomers, and 16.3 mg/m^3 ethyl benzene. Three samplers had contaminated air drawn through them at 50 mL/min for 240 min. All three samples were immediately analyzed. The sample results were 99.1%, 99.3% and 99.0% of theoretical for MEK; and 102.2%, 103.0% and 102.4% of theoretical for MIBK.

4.9.2 SKC 575-002 Passive Samplers and 3M 3520 OVMs

Reverse diffusion

The ability of SKC 575-002 Passive Samplers and of 3M 3520 OVMs to retain MEK and MIBK after collection was tested by sampling an atmosphere containing 1178 mg/m^3 MEK and 806 mg/m^3 MIBK at an absolute humidity of 14.6 milligrams of water per liter of air (77.8% relative humidity at 21.4 °C). Six of each sampler were exposed to contaminated air for one hour. Sampling was discontinued and three of each sampler were set aside (1st set). The generation system was flushed with contaminant-free air. Sampling was resumed with the remaining six samplers exposed to contaminant-free humid air for an additional three hours (2nd set). Results are presented in terms of micrograms of analyte found on the sampler. The means of the second set were 99.3% for MEK and 100.0% for MIBK of the means of the first set for SKC 575-002 Passive Samplers. The means of the second set were 96.0% for MEK and 98.6% for MIBK of the means of the first set for 3M 3520 OVMs.

Table 4.9.2.1
Reverse Diffusion For
SKC 575-002 Passive Sampler (µg)

set	1		2		3	
	MEK	MIBK	MEK	MIBK	MEK	MIBK
1st	1357.45	741.52	1368.54	732.50	1405.26	753.41
2nd	1355.55	739.86	1360.50	737.37	1387.31	750.30
means						
1st	1377.08	742.48				
2nd	1367.79	742.51				

Table 4.9.2.2
Reverse Diffusion For
3M OVM (µg)

set	1		2		3	
	MEK	MIBK	MEK	MIBK	MEK	MIBK
1st	2700.73	1520.43	2627.96	1464.63	2811.44	1535.59
2nd	2580.20	1471.29	2607.50	1510.12	2628.50	1477.16
means						
1st	2713.38	1506.88				
2nd	2605.40	1486.19				

Low humidity

Three SKC and three 3M diffusive samplers were used to sample a test atmosphere containing 1203 mg/m^3 MEK and 823 mg/m^3 MIBK. The absolute humidity of the test atmosphere was 2.7 milligrams of water per liter of air (13.2% relative humidity at 22.6 °C). The recoveries (% theoretical) are shown in Table 4.9.2.3.

Table 4.9.2.3
Low Humidity
(Recovery, % of Theoretical)

sampler	1		2		3	
	MEK	MIBK	MEK	MIBK	MEK	MIBK
SKC 575-002	92.2	102.5	94.9	104.9	92.8	103.1
3M 3520	95.5	109.2	93.9	102.6	92.9	101.0

Low concentration

Three SKC and three 3M diffusive samplers were used to sample a test atmosphere containing 60.3 mg/m^3 MEK and 41.3 mg/m^3 MIBK. The absolute humidity of the test atmosphere was 15.5 milligrams of water per liter of air (79.7% relative humidity at 22.3 °C). The recoveries (% theoretical) are shown in Table 4.9.2.4.

Table 4.9.2.4
Low Concentration
(Recovery, % of Theoretical)

sampler	1		2		3	
	MEK	MIBK	MEK	MIBK	MEK	MIBK
SKC 575-002	92.0	101.6	95.6	105.2	90.3	96.8
3M 3520	89.8	95.0	93.4	97.9	92.2	98.5

Sampling interferences

Three SKC and three 3M diffusive samplers were used to sample a test atmosphere containing 578 mg/m^3 of MEK and 395 mg/m^3 of MIBK; and 553.3 mg/m^3 of acetone, 253.7 mg/m^3 of isopropyl alcohol, 190.1 mg/m^3 of toluene, 92.5 mg/m^3 of xylene isomers, and 16.3 mg/m^3 of ethyl benzene. The absolute humidity was 15.6 milligrams of water per liter of air (79.0% relative humidity at 22.3 °C). The recoveries (% theoretical) are shown in Table 4.9.2.5.

Table 4.9.2.5
Sampling Interference
(Recovery, % of Theoretical)

sampler	1		2		3	
	MEK	MIBK	MEK	MIBK	MEK	MIBK
SKC 575-002	103.2	108.5	97.6	102.2	101.6	107.3
3M 3520	95.0	103.1	93.6	101.8	93.5	102.8

4.10 Qualitative analysis

The identity of suspected MEK or MIBK GC peaks can be confirmed by GC/Mass Spectrometry. Mass spectra for the analytes are shown below.

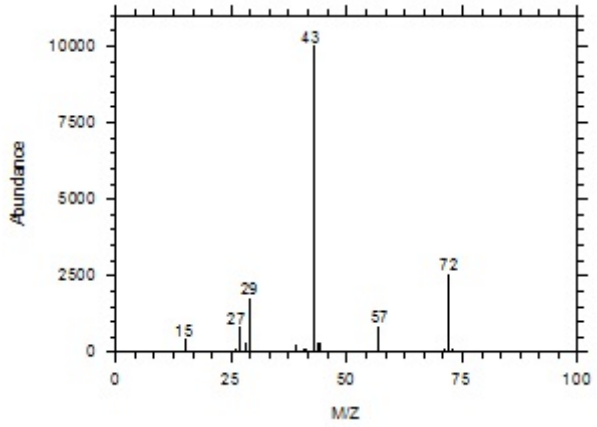


Figure 4.10.1. Mass spectrum of MEK.

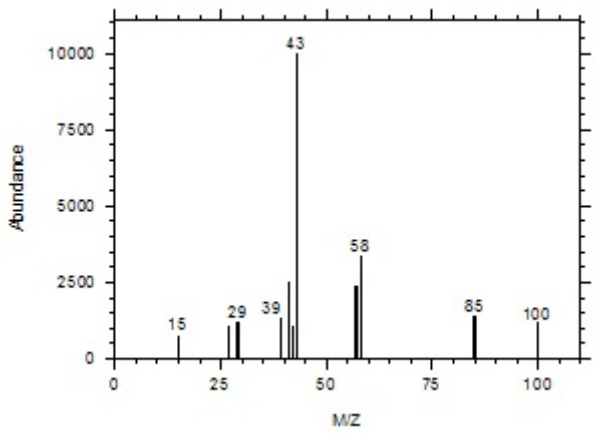


Figure 4.10.2. Mass spectrum of MIBK.