

Performance of SKC Ultra Passive Samplers  
Containing Carboxen 1016, Carbopack Z, or Chromosorb 106  
When Challenged With a Mixture Containing Twenty of OSHA SLTC's Top Solvent Analytes

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## INTRODUCTION

The SKC Ultra sampler was previously tested at OSHA SLTC with a mixture of seven toxic industrial chemicals (TICs) as part of The Marines Project (Ref. 1). The Ultra sampler is based on SKC's 575 series of passive samplers. The Ultra passive sampler is constructed so that the contained sampling medium can be easily removed for analysis. This unique feature was specified by the Marine Corps to permit analysis by thermal desorption. OSHA's work showed that the Ultra sampler and the associated analytical techniques worked well, but that the Tenax TA sampling medium specified by the Marine Corps had low capacity for the TIC mixture. The Marines had specified Tenax TA because it gave satisfactory results for chemical warfare agents in work performed by a contract laboratory. The Marines recognized that exposure to TICs was much more likely than exposure to chemical warfare agents, but determination of the latter was the primary emphasis of their program. Determination of TICs has been termed by the Marines as the icing-on-the-cake.

This work was performed to test the sampling capabilities of Ultra samplers containing sampling media other than Tenax TA when challenged with a mixture containing twenty of SLTC's most requested solvent analytes. The other sampling media were Carboxen 1016, Carbopack Z, and Chromosorb 106. Carboxen 1016 was selected because it gave promising results when tested by Supelco to sample a 43-component gas mixture (Ref 2). Carbopack Z was tested because Supelco suggested its use as a possible alternative sampling medium, and Chromosorb 106 was tested because of personal recommendations.

## REAGENTS

The solvent analyte mixture was prepared using the volumes shown in Table 1 to create the mixture.

Table 1. Solvent Analyte Mixture.

solvent analyte	synonym	volume (mL)	source	lot number
toluene		23	Acros	B0502818
m-xylene		23	Acros	A012361601
limonene		23	Aldrich	11310PS
2-butanone	MEK	24	Acros	A015904701
methylene chloride		15	Fisher	964274
n-butyl acetate		22	Acros	B0052692
butyl cellosolve	butoxy ethanol	22	Aldrich	MS10054LS
1,3,5-trimethylbenzene	mesitylene, TMB	23	Aldrich	00608TU
heptane		29	Aldrich	CU03650CU
n-butanol		24	Acros	B0069040
ethyl acetate		22	Fisher	982737
trichloroethylene		13	Aldrich	PI1654LS
tetrachloroethylene		12	Aldrich	TR06115EN
styrene		22	Aldrich	14106TI
4-methyl-2-pentanone	MIBK	25	Aldrich	CU10369BU
benzene		22	Aldrich	BU03051PS
undecane		27	Aldrich	12514AI
2-heptanone	methyl-n-amyl ketone	24	Aldrich	15606DU
2-propanol	IPA	25	Fisher	002047
1-methoxy-2-propanol	propylene glycol methyl ether, PGME	21	Aldrich	0426BO

Carbon disulfide (99.9+%, low benzene, Lot No. TO 03038TO) was obtained from Aldrich chemical.

*N,N*-Dimethylformamide (DMF) (certified ACS grade, Lot No. 902902) was obtained from Fisher Chemical.

Dodecane (99+%, Lot EI 03040LV) was purchased from Aldrich Chemical. This material was used as an internal standard for solvent-desorbed samples.

A solution composed of 60% DMF, 40% carbon disulfide, and 0.5  $\mu\text{L}$  dodecane per milliliter of solution was prepared to analyze solvent-desorbed samples.

### **SAMPLING MEDIA**

The source of empty SKC Ultra Passive Sampler cases were those used in the Marines Project. These sampler cases were each refilled with cleaned sampling media and used in this work. Recycling Ultra samplers is possible because the section through which the air sample diffuses is not disturbed by either analysis or by refilling the device. A photograph of an Ultra sampler is shown in Figure 1. The sampling medium in the vial is Tenax TA.



Figure 1. SKC Ultra Passive Sampler.

Carboxen 1016 was obtained from Supelco in bulk form. The lot number was 6024355-10 and the mesh size was 60/80. This material was thermally conditioned at 415°C for 25 min before each use with the tube conditioning feature of the TurboMatrix ATD. The medium was reused three to five times before it was discarded and replaced with fresh medium.

Carbopack Z was also obtained from Supelco in bulk form. The lot number was 0540 and the mesh size was 60/80. This material was thermally conditioned at 415°C for 25 min before each use with the tube conditioning feature of the TurboMatrix ATD. The medium was reused three to five times before it was discarded and replaced with fresh medium.

Carbopack Z was also obtained from Supelco in bulk form. The lot number was 0540 and the mesh size was 60/80. This material was thermally conditioned at 415°C for 25 min before each use with the tube conditioning feature of the TurboMatrix ATD. The medium was reused three to five times before it was discarded and replaced with fresh medium.

The source of Chromosorb 106 was SKC Catalog No. 226-110, 20/40 mesh size, Lot No. 1066, sampling tubes. This medium was thermally conditioned at 250°C for 25 min before each use with the tube conditioning feature of the TurboMatrix ATD. The medium was reused three to five times before it was discarded and replaced with fresh medium.

Anasorb CMS active sampling tubes (Catalog No. 226-121, 75/150 mg sections, Lot No. 1961) were obtained from SKC. Sampling results from these tubes were used as independent means to confirm concentration of test atmospheres.

## APPARATUS

SKC Ultra samples were thermally desorbed using a Perkin Elmer TurboMatrix ATD (equipped with internal standard addition option) connected to the electronic-pressure controlled volatiles interface inlet of an Agilent 6890 Series GC system and an Agilent 5973 Network Mass Selective Detector (MSD). The ATD and GC carrier gas was helium. Each sample was desorbed two times to confirm that desorption was complete. ATD conditions: Thermal desorption tubes containing Chromosorb 106 were desorbed at 240°C for 9 min following a 1 min purge. Tubes containing Carboxen 1016 and Carboxen Z were desorbed at 415°C for the same times. The focusing trap was flash heated from -30°C to 300°C and maintained at the upper temperature for 2 min. The two-section trap contained 14-mm Tenax TA and 6-mm Carboxen B positioned so that the desorption flow first passes through the Tenax TA section. The GC transfer line temperature was 225°C and the valve temperature was 225°C. The inlet split flow was 28 mL/min, the desorb flow was 58 mL/min, the internal standard tube load flow was 23 mL/min, and the internal standard loop flow was 1.3 mL/min. GC conditions: A HP-5MS capillary GC column (30-m × 0.25-m i.d. × 1.0 µm dr) was used for this work. The GC column was temperature programmed from 40°C (following a 1 min hold) at 10°C/min to 200°C. The GC column was operated in the constant flow mode at 0.8 mL/min. The GC inlet temperature was 230°C, and the inlet split ratio was 67 to 1. MSD conditions: thermal auxiliary 2 was 280°C, MS source was 230°C, MS quad was 150°C. The MSD was operated in the full scan mode from 24 to 350 AMU. EM voltage was automatically set by the MSD software via an "autotune" performed every week of operation. Typically, a solvent delay of 2 min was employed.

SKC CMS samples were analyzed after desorption with one milliliter of 60/40 DMF/carbon disulfide mixture (containing 0.5 µL/mL dodecane internal standard) for one hour using a HP 5890 GC equipped with a Restek Stabilwax capillary column (60-m × 0.32-m i.d. × 1.0 µm dr), an automatic liquid injector, and an FID. The GC column was temperature programmed from 40°C (following a 1 min hold) at 6°C/min to 190°C. The FID was maintained at 250°C and the injector at 220°C. The GC column flow was 4.0 mL/min hydrogen. The inlet split ratio was 50 to 1. The FID gases were 35 mL/min hydrogen, 415 mL/min air, and 30 mL/min nitrogen (auxiliary).

Humid air (for use with controlled test atmospheres) was generated using a Miller-Nelson Model HCS 501 Flow-Temperature-Humidity Control System. This system was equipped with a 500 L/min mass flow controller.

Relative humidity and temperature of the test atmospheres were monitored with a Omega Digital Thermo-Hygrometer meter and probe. The probe was calibrated by the manufacturer. Pressure within the exposure chambers was monitored with an Omega meter and pressure transducer that was calibrated to read ambient barometric pressure for a fully vented exposure chamber before each run.

Dilution air flow rates (50-360 L/min) were measured with a Equimeter No. 750 gas meter. The meter readings for several different flow rates were compared to those of a Singer DTM 115 gas meter (which had been tested by the local natural gas distributor and found to be accurate) that was connected in series before the Equimeter. Both meters gave very similar readings.

The solvent mixture was metered into the system with an Isco 100 DM syringe pump equipped with a cooling/heating jacket and an insulation cover package. The pump was operated in the constant flow mode. The temperature of water in the cooling/heating jacket was maintained at 23°C with a Forma Scientific Model 2006 CH/P Bath and Circulator.

Solvent vapors were generated by pumping the liquid into a vapor generator where it evaporated into the dilution air stream. The vapor generator consisted of a 10-cm length of ¼-inch o.d. glass tubing with a small hole in the side. The hole was just large enough for 1/16-inch o.d. tubing to be inserted. The glass tubing was placed inside a ½-inch stainless steel Swagelok tee wrapped with heating tape. The 1/16-inch tubing entered the third port of the tee through an adaptor and was inserted about 1/8 inch (approximately in the center) into the glass tubing through the small hole. Solvent was pumped through the tubing and into the

glass tubing. The liquid flow rate was slow enough (about 10  $\mu\text{L}/\text{min}$ ) so that liquid did not accumulate in the evaporation tube. The entire dilution air stream passed through the tee and swept generated vapors into the apparatus.

The following is a description of the arrangement of the apparatus that was placed in a walk-in hood (Figure 2). Liquid from which vapors were to be dynamically generated was pumped with a precision Isco syringe pump (an identical pump and a small solvent mixing tee was available when its use was desired) into a heated manifold where it evaporated. The generated vapors were swept from the manifold with dilution air. Stainless steel tubing ( $\frac{1}{2}$ -inch o.d.) connected with stainless steel Swagelok fittings was used to transfer the test atmosphere. The dilution air was humidified using a Miller-Nelson Flow-Temperature-Humidity controller. The vapor/dilution air mixture then passed into a 3 $\times$ 24-inch stainless steel mixing chamber. The test atmosphere next passed through  $\frac{1}{2}$ -inch ball valves where it could be either diverted to waste, or directed into the exposure chamber. An additional ball valve allowed the chamber to be purged with room air. The transfer tubing diameter was increased from  $\frac{1}{2}$  inch to 1 inch at this point using a Swagelok adaptor attached to the chamber inlet. Tube and fitting diameter was increased to 1 inch after this fitting to help reduce any increased pressure to ambient. The 1-inch o.d. chamber inlets have small stainless steel deflectors to help insure that the test atmosphere completely fills the sampling chamber. Stainless steel screens were placed inside the chamber for the same purpose.



Figure 2. Sample exposure apparatus with small exposure chamber.

This design should cause air flow through the chamber to be somewhat turbulent. Face velocities of the test atmospheres were calculated by dividing the volumetric flow of each atmosphere by the cross-sectional area available for air flow in the chamber. The cross-sectional area available for air flow was the cross-sectional area of the chamber reduced by the cross-sectional area of the sampler. The exposure chamber is used with a removable door (that is not shown in the photograph) to completely seal it when used with test atmospheres. Test atmospheres exit through a stainless-steel manifold connected in-line to permit collection of active samples.

## EXPERIMENTAL

### Preparation of Samples

Ultra Passive Samplers were prepared for analysis by prying open the back of the sampler with a screwdriver to reveal the end of the built-in aluminum funnel containing the sorbent. The sampling medium was then carefully transferred into the back of a clean, empty Perkin-Elmer thermal desorption tube using the funnel. The front of a thermal desorption tube is the end with the groove and the back is the opposite end. A gauze screen was then carefully placed on top of the sampling medium with the aid of a  $\frac{3}{16}$ -inch glass rod and a small screwdriver. The gauze screen can be inserted easier if its concave side is placed so that it faces towards the back of the tube. The tube was not completely filled with the sorbent and an empty

space of approximately ½ inch remained in the end of the tube. A retaining spring was then placed into this space at the end of the tube, and then seated on top of the gauze screen slightly below the end of the tube using the funnel.

CMS active sampling tubes were prepared for analysis by placing each section of sorbent into separate 2-mL automatic sampler vials and then adding 1 mL of 60/40 DMF/carbon disulfide desorbing solution. These vials were allowed to stand one hour, and were shaken by hand several times during this time.

#### Analytical Standards

Analytical standards for thermally-desorbed samples were prepared by spiking 5-µL aliquots of a series of diluted solvent analyte mixtures onto the front of thermal desorption tubes containing the appropriate sampling medium. Room air was drawn through these tubes at 50 mL/min for about 10 seconds immediately after they were spiked. The source of the thermal desorption tubes was Ultra samplers that had been previously analyzed, and then reconditioned for 25 min at the appropriate temperature using the thermal desorber tube conditioning feature. These thermal desorption tubes were reused no more than three to five times before recycling. Recycling thermal desorption tubes was accomplished by removing the retaining spring, the gauze screen, and the sorbent from previously analyzed samples. The empty tubes were washed twice with methyl alcohol and then air-dried overnight before reuse.

Analytical standards for solvent-desorbed samples were prepared by injecting microliter volumes of diluted solvent analyte mixtures into the same volume of 60/40 DMF/carbon disulfide desorption solution used to desorb the samples

#### Analytical Instrument Calibration

GC/MSD calibration curves were prepared for each analyte with a series of standards using the MSD software. The calibration range, in most cases, was one-half to two times the expected sample concentration. All calibration curves were linear. The MSD is saturated at approximately 50 ng per analyte. A combination of GC injector split and/or TD split should be employed to reduce mass reaching the MSD when samples exceed this level. Alternatively, MSD EM voltage can be reduced to decrease response. All MSD results were calculated without internal standard correction.

Similar calibration curves were prepared for samples analyzed by GC/FID using a Waters Associates Millennium Chromatography Manager data system to measure FID response. An internal standard was employed in these analyses.

#### Desorption Efficiency

Solvent-desorbed samplers were used in this work to monitor concentrations of test atmospheres. Desorption efficiency studies were performed using both wet and dry CMS sampling medium. Wet samplers were prepared by drawing clean, 80% humid air through the samplers at 0.05 L/min for 4 hours. Dry medium was as contained in sampling tubes.

#### Sampling Rate and Capacity

Sampling rates for the CMS active sampling tubes were 0.05 L/min, and these samples were collected simultaneously with diffusive samples. Methylene chloride was the only mixture component found on the sampling tube backup section. Five-percent breakthrough occurred after sampling for about 18 hours.

Sampling rates were determined at ambient temperature and pressure, but all sampling rates presented in this work are expressed at 760 mmHg and 25°C. Three samplers for each sampling medium were exposed to controlled-test atmospheres for increasing time periods for these experiments. Samples were removed at the end of each time period and analyzed. The exposure times ranged from two to thirty-one hours for Carboxen 1016 and for Chromosorb 106. Sampling times for Carbopack Z were eight to twenty-two hours. The relative humidity of the test atmospheres was approximately 80% at ambient temperature and

pressure. The face velocity of test atmospheres through the small exposure chamber was approximately 0.4 m/sec. The theoretical concentration of each solvent analyte in the test atmospheres was approximately 4.5 mg/m<sup>3</sup>. Sampler orientation was parallel to the flow direction of the test atmosphere. Four active samples were taken simultaneously with diffusive samples for each time period. Theoretical concentrations were used to calculate sampling rates because active-sampling results were near 100%.

## RESULTS and DISCUSSION

### Desorption Efficiency

The medium contained in active sampling tubes is often desorbed with 99/1 carbon disulfide/DMF solution at SLTC. It has been observed that desorption efficiencies are low for water-soluble analytes from wet sampling medium using this technique (Ref. 3). The reason for low recovery is that water-soluble analytes can partition into the water phase of the two-phase solutions that frequently occur when atmospheric water is collected (and desorbed) along with the analytes. A 60/40 mixture of DMF/carbon disulfide was used in previous work (Ref. 3) to prevent two-phase solutions and its use was again tested here.

Table 2. Desorption Efficiency of Solvent Analytes from CMS with DMF/Carbon Disulfide Solution.

solvent analyte	1/99 dry medium	1/99 wet medium	60/40 wet medium
2-propanol	94.2	37.0	107
methylene chloride	111	96.5	105.6
2-butanone	103	86.5	99.9
ethyl acetate	102	94.5	109
1-butanol	96.4	64.8	102
benzene	97.2	94.3	102
propylene glycol methyl ether	95.7	36.1	108
heptane	102	99.0	105
trichloroethylene	102	96.0	105
4-methyl-2-pentanone	101	91.3	107
toluene	96.0	93.8	101
butyl acetate	101	95.4	108
tetrachloroethylene	104	94.9	98.3
m-xylene	95.9	94.3	99.6
2-heptanone	101	93.9	106
styrene	78.3	71.4	70.2
butyl cellosolve	96.8	94.9	105
1,2,3-trimethylbenzene	96.3	94.1	99.3
limonene	97.0	95.0	90.6
undecane	99.5	98.3	100

The desorption efficiency for styrene was not constant over the studied concentration range. The same inconsistency has been observed in other work by other researchers (Ref. 5).

Thermal-desorption efficiency experiments were not performed because TurboMatrix ATD conditions were selected so that the desorption process was essentially complete after one run. Two runs were always conducted to confirm that desorption was complete.

### Sampling Rate and Capacity

Results in the following tables are the average of three individual samplers, and the experimental sampling rates at ambient conditions were converted to their equivalent at 760 mmHg and 25°C. Sampling rates of zero mL/min mean that no analyte was detected in the sample.

Table 3. Sampling Rates (mL/min) for the Solvent Analyte Mixture Using SKC Ultra Samplers Containing Carboxen 1016.

analyte	2 h	4 h	6 h	7 h	8 h	10 h	12 h	14 h	16 h	19 h	20 h	22 h	24 h	27 h	31 h
IPA	10.22	4.27	1.36	2.89	0.41	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methylene chloride	4.98	1.57	0.24	0.00	0.31	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MEK	14.93	11.72	9.53	10.82	7.94	6.10	6.14	1.02	2.59	0.00	0.14	0.00	0.00	0.00	0.00
ethyl acetate	14.29	11.91	10.34	11.17	9.36	7.62	8.27	4.60	5.48	0.00	1.47	0.49	0.00	0.00	0.00
1-butanol	14.37	12.15	10.98	12.36	10.51	8.87	11.90	8.64	9.94	5.69	6.57	5.59	0.74	0.00	0.07
benzene	16.71	14.11	13.31	13.50	13.09	10.60	13.74	11.80	11.89	7.36	8.41	6.88	5.01	2.55	1.64
PGME	13.41	11.86	11.92	12.77	11.58	10.20	13.44	10.34	11.92	8.19	9.31	8.04	5.00	3.76	3.46
heptane	14.09	12.19	12.66	12.26	12.86	11.01	14.00	13.66	13.60	12.72	13.10	12.28	12.87	12.43	11.92
trichloroethylene	14.50	12.96	12.32	12.72	12.01	9.95	11.63	9.96	10.25	6.58	7.00	5.87	3.35	1.55	1.10
MIBK	14.14	12.57	13.61	13.33	13.65	11.61	14.64	13.65	13.88	12.37	12.58	11.81	11.64	11.02	10.42
toluene	15.73	13.61	14.27	14.01	14.78	12.35	16.02	15.42	15.66	13.87	14.20	12.98	14.21	13.54	12.82
butyl acetate	13.10	12.03	13.30	12.95	13.33	11.21	14.20	13.33	13.54	12.33	12.60	12.15	11.95	11.60	11.25
tetrachlorethylene	13.85	12.06	13.43	13.23	13.54	11.47	14.09	14.01	14.12	12.36	12.63	11.40	13.47	12.86	12.05
<i>m</i> -xylene	14.31	12.86	14.01	13.50	14.28	12.11	15.07	14.75	14.95	13.77	13.79	12.97	14.22	13.88	13.27
2- heptanone	12.39	11.54	13.43	13.47	13.41	11.38	14.81	13.61	14.36	13.30	13.60	12.89	13.15	12.88	12.69
styrene	14.37	12.96	14.59	13.60	14.72	12.59	14.84	14.88	14.76	14.16	13.73	13.15	13.93	13.56	12.99
butyl cellosolve	8.99	10.37	13.10	13.23	13.12	11.78	14.13	12.93	13.16	11.87	12.70	12.07	11.75	11.58	11.18
TMB	12.84	11.86	12.90	12.80	13.18	11.18	13.99	13.62	13.96	13.14	12.94	12.25	12.97	12.71	12.34
limonene	10.27	10.51	13.86	12.48	14.07	13.04	13.44	13.79	13.16	14.06	12.77	13.17	12.59	12.40	12.09
undecane	11.51	9.94	10.95	11.24	12.01	11.32	11.47	10.32	10.91	11.29	10.90	10.56	10.52	10.65	10.70

Sampling times less than eight hours were not performed with Carbopack Z because it did not arrive at SLTC until this work was well underway. Its use was discontinued when it was found that its sampling capacity was inadequate for the more volatile components of the solvent analyte mixture.

Table 4. Sampling Rates (mL/min) for the Solvent Analyte Mixture Using SKC Ultra Samplers Containing Carbopack Z.

analyte	8 h	10 h	14 h	19 h	22 h
IPA	0.78	0.62	0	0	0
methylene chloride	0.22	0.09	0	0	0
MEK	7.19	4.63	0	0	0
ethyl acetate	9.27	8.31	0	0	0
1-butanol	11.08	9.34	3.79	3.36	3.67
benzene	13.46	11.31	6.85	5.13	5.08
PGME	11.56	10.89	7.78	7.50	6.15
heptane	13.14	11.90	11.59	11.68	11.83
trichloroethylene	12.04	10.46	5.68	4.41	4.44
MIBK	13.67	12.27	10.74	11.42	11.15
toluene	14.42	12.98	11.94	12.23	12.54
but acetate	12.35	12.02	11.64	12.38	11.52
tetrachlorethylene	13.22	12.18	10.32	10.64	11.01
<i>m</i> -xylene	13.93	12.84	11.39	12.10	12.71
2-heptanone	13.20	12.26	11.20	12.51	12.57
styrene	14.56	13.23	12.00	12.67	13.07
butyl cellosolve	11.75	12.57	12.58	13.08	11.30
TMB	12.96	12.23	10.63	11.47	12.32
limonene	14.31	13.14	11.53	12.02	13.28
undecane	11.86	11.43	9.81	10.19	10.84



Sampling rate and capacity work with Chromosorb 106 was performed after it was found that Carboxen 1016 and Carboack Z did not have sufficient sampling capacity for many of the volatile solvent analytes of interest to OSHA.

Table 5. Sampling Rates (mL/min) for the Solvent Analyte Mixture Using SKC Ultra Samplers Containing Chromosorb 106.

analyte	2 h	4 h	7 h	12 h	16 h	20 h	24 h	27 h	31 h
IPA	13.70	11.55	8.57	6.46	6.17	4.54	4.19	2.63	3.01
methylene chloride	13.28	10.00	6.83	3.57	3.54	2.01	0.13	0.00	0.00
MEK	17.06	15.45	12.84	13.02	11.37	9.90	9.37	8.28	7.81
ethyl acetate	15.17	14.30	12.14	12.77	11.31	10.04	9.82	8.91	8.35
1-butanol	16.40	15.49	13.49	14.09	12.76	11.73	11.67	10.65	10.25
benzene	16.78	15.50	13.00	14.18	12.70	11.70	11.48	10.51	9.93
PGME	15.27	14.72	13.10	13.36	12.35	11.42	11.16	10.45	10.07
heptane	14.18	14.69	12.27	13.58	12.57	12.48	12.83	12.24	11.74
trichloroethylene	13.08	12.68	11.57	12.06	11.09	10.55	10.18	9.67	9.08
MIBK	14.80	14.97	12.71	14.38	13.08	12.60	13.11	12.52	12.06
toluene	16.14	15.64	13.26	14.94	13.60	13.15	13.67	12.79	11.99
butyl acetate	13.48	14.57	12.60	14.13	12.85	12.48	13.05	12.62	12.16
tetrachlorethylene	12.86	13.15	12.18	13.07	12.03	11.72	12.18	11.50	10.64
<i>m</i> -xylene	14.53	14.81	13.26	14.62	13.48	13.10	13.81	13.16	12.40
2-heptanone	14.60	14.99	13.43	14.81	13.59	13.24	13.70	13.37	12.86
styrene	8.04	9.95	10.36	11.82	10.99	11.12	11.01	11.13	10.42
butyl cellosolve	13.60	13.80	13.06	13.57	12.73	12.72	12.88	12.40	12.00
TMB	13.33	13.74	12.80	13.71	13.02	12.56	13.27	12.70	12.10
limonene	10.32	12.46	11.57	12.10	11.35	11.73	12.14	12.14	11.39
undecane	7.66	10.69	10.41	10.23	9.70	9.91	10.57	11.63	10.11

Graphed sampling rate and capacity data are shown in Figures 3 through 63. Sampling capacity for diffusive samplers is exceeded when the calculated sampling rate rapidly decreases. Two horizontal lines were constructed in some of the figures and used to estimate maximum sampling time when a sampling medium was judged to have sufficient capacity. The lines represent the average sampling rate  $\pm 10\%$ . The point that the plotted data intersected the lower line was used as an estimate exceeded sampling capacity. Obviously, sampling capacity was not exceeded if the plotted data did not intersect the lower line.

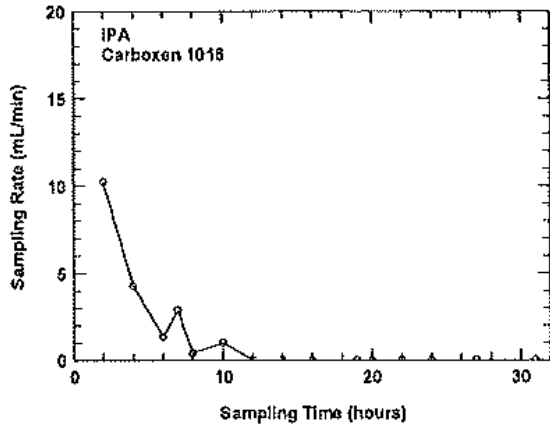


Figure 3. Sampling rate for IPA for SKC Ultra Samplers containing Carboxen 1016.

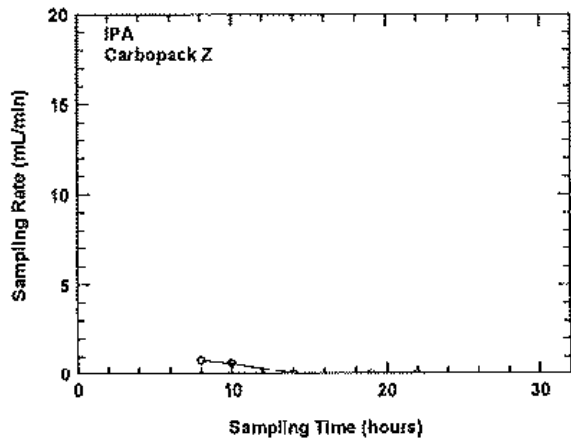


Figure 4. Sampling Rate for IPA SKC Ultra samplers containing Carbopack Z.

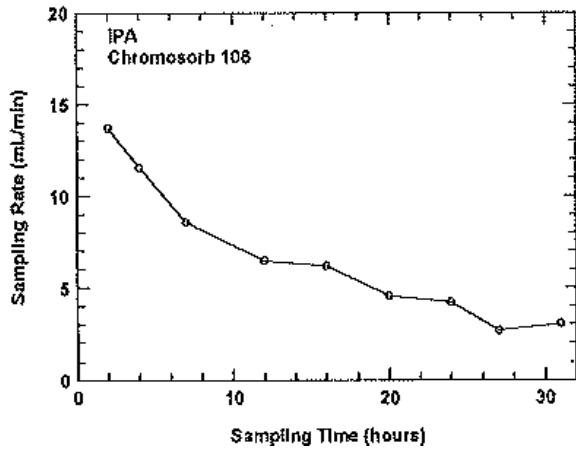


Figure 5. Sampling Rate for IPA for SKC Ultra samplers containing Chromosorb 106.

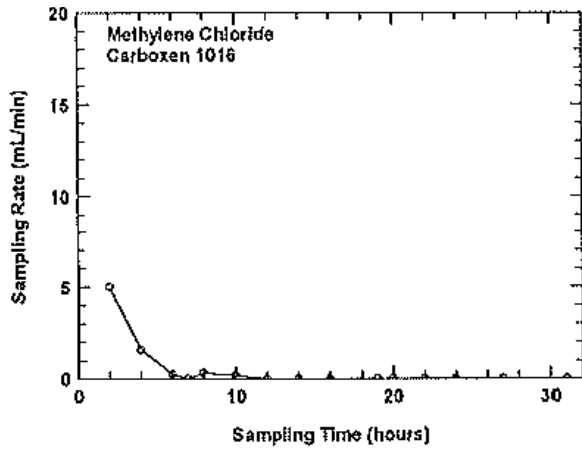


Figure 6. Sampling rate for methylene chloride for SKC Ultra samplers containing Carboxen 1016.

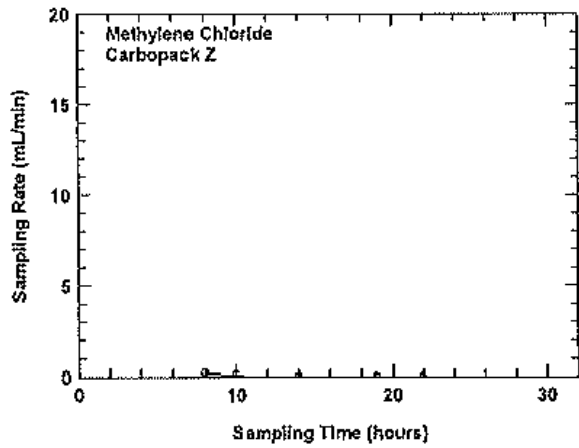


Figure 7. Sampling rate for methylene chloride for SKC Ultra samplers containing Carbopack Z.

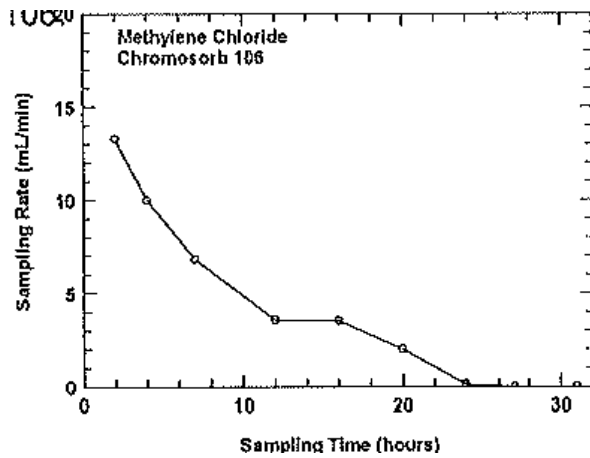


Figure 8. Sampling rate for methylene chloride for SKC Ultra samplers containing Chromosorb 106.

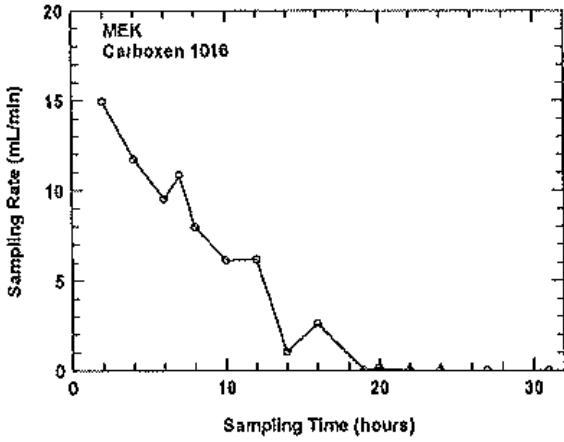


Figure 9. Sampling rate for MEK for SKC Ultra samplers containing Carboxen 1016.

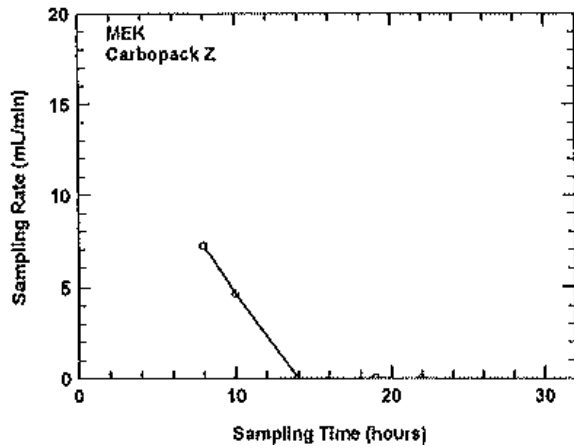


Figure 10. Sampling rate for MEK for SKC Ultra samplers containing Carbopack Z.

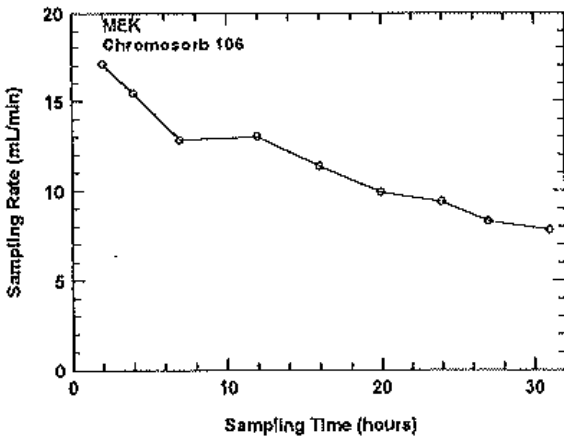


Figure 11. Sampling rate for MEK for SKC Ultra samplers containing Chromosorb 106.

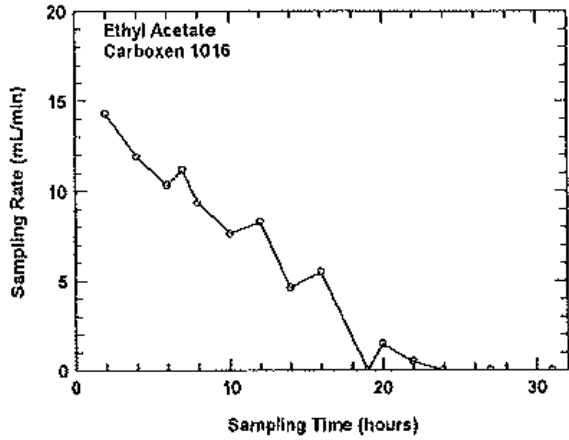


Figure 12. Sampling rate for ethyl acetate for SKC Ultra samplers containing Carboxen 1016.

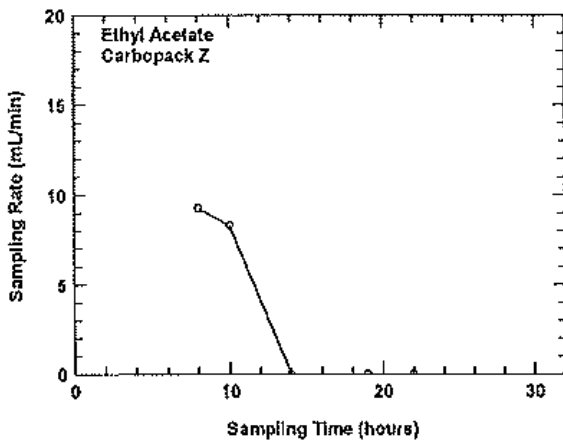


Figure 13. Sampling rate for ethyl acetate for SKC Ultra samplers containing Carbopack Z.

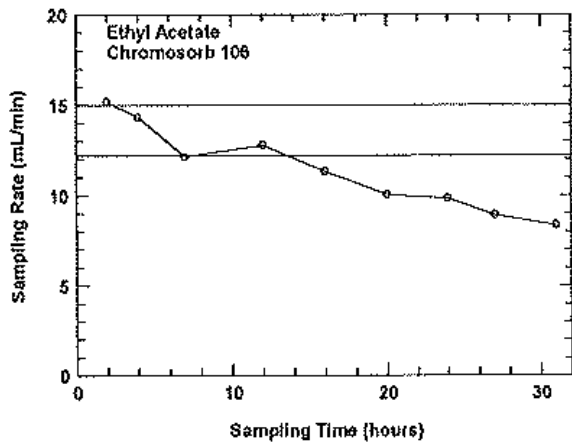


Figure 14. Sampling rate for ethyl acetate for SKC Ultra samplers containing Chromosorb 106.

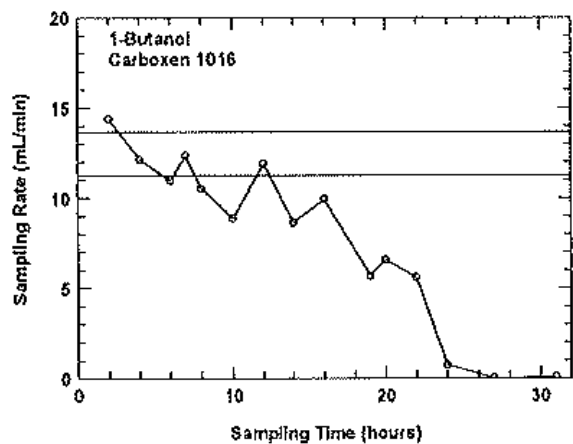


Figure 15. Sampling rate for 1-butanol for SKC Ultra samplers containing Carboxen 1016.

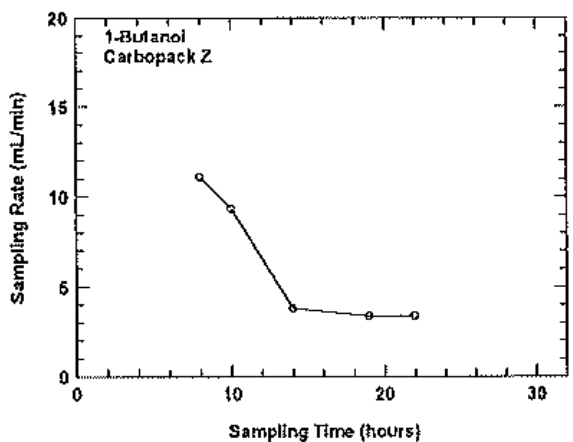


Figure 16. Sampling rate for 1-butanol for SKC Ultra samplers containing Carbopack Z.

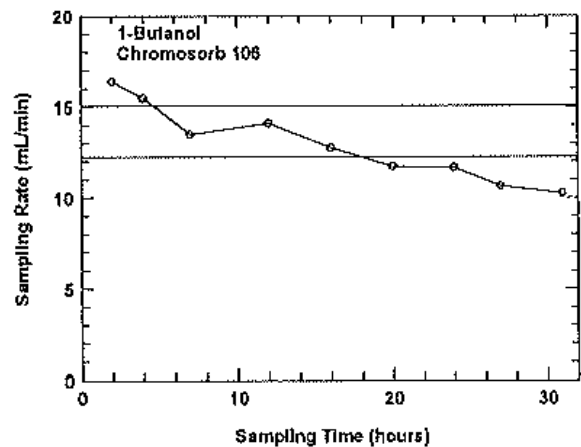


Figure 17. Sampling rate for 1-butanol for SKC Ultra samplers containing Chromosorb 106.

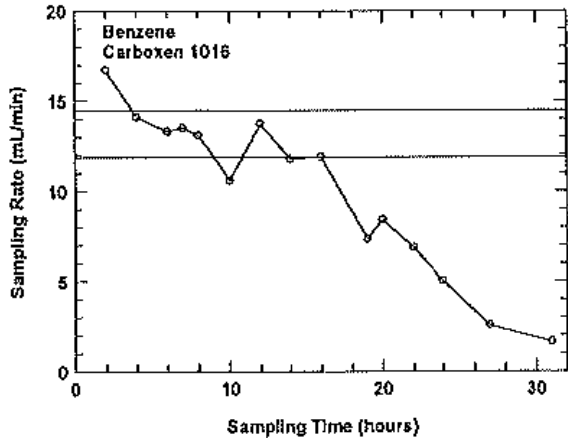


Figure 18. Sampling rate for benzene for SKC Ultra samplers containing Carboxen 1016.

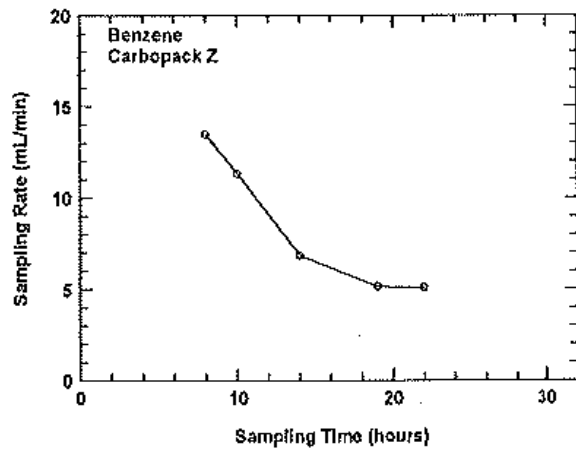


Figure 19. Sampling rate for benzene for SKC Ultra samplers containing Carbopack Z.

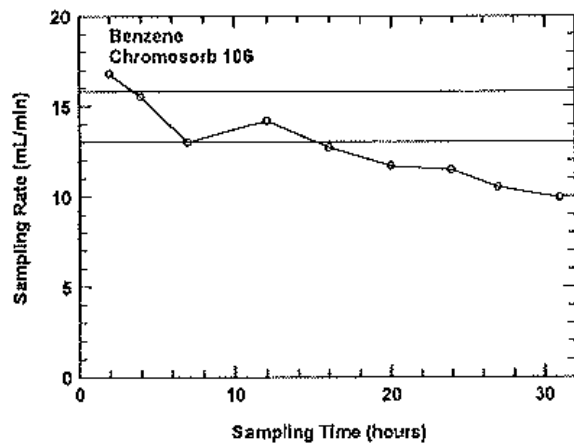


Figure 20. Sampling rate for benzene for SKC Ultra samplers containing Chromosorb 106.

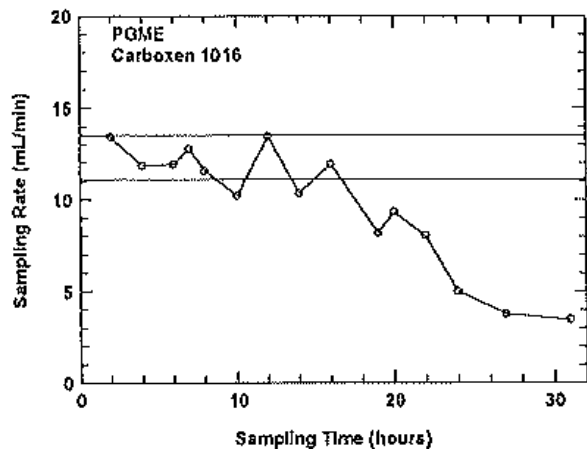


Figure 21. Sampling rate for PGME for SKC Ultra samplers containing Carboxen 1016.

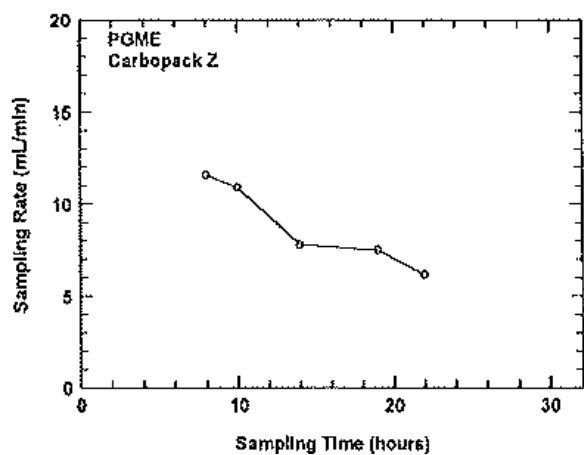


Figure 22. Sampling rate for PGME for SKC Ultra samplers containing Carbopack Z.

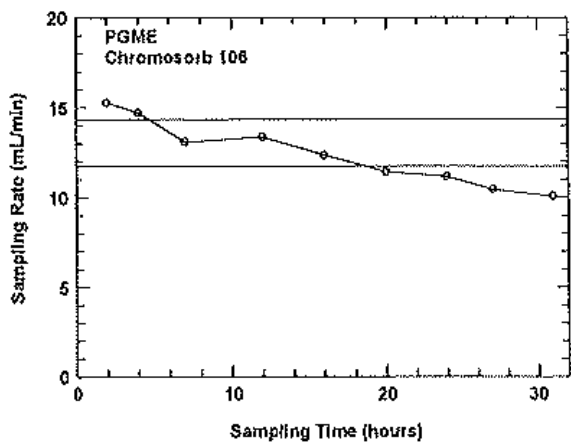


Figure 23. Sampling rate for PGME for SKC Ultra samplers containing Chromosorb 106.



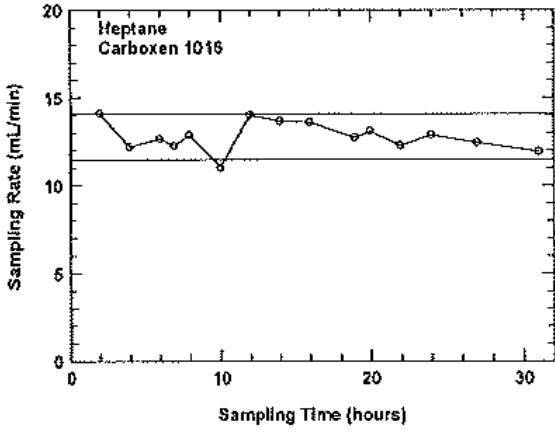


Figure 24. Sampling rate for heptane for SKC Ultra samplers containing Carboxen 1016.

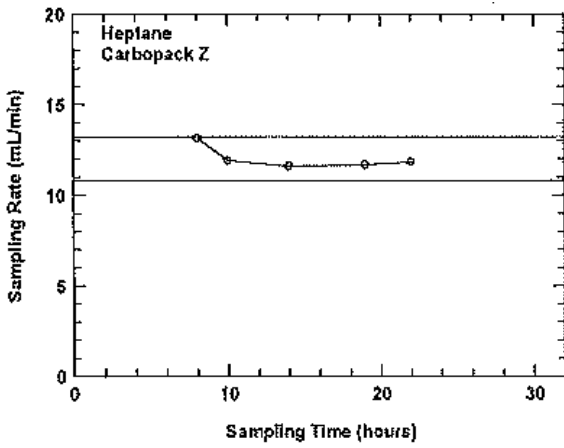


Figure 25. Sampling rate for heptane for SKC Ultra samplers containing Carbopack Z.

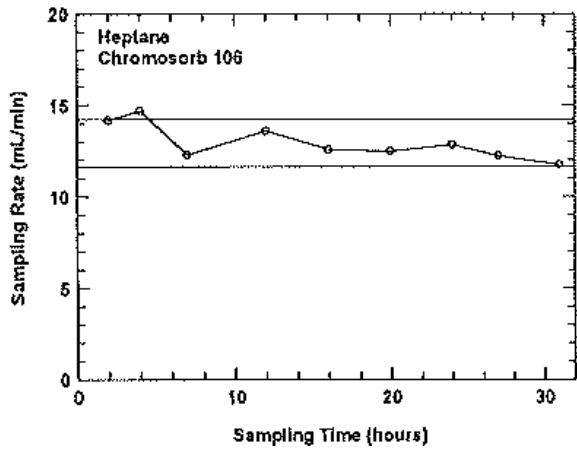


Figure 26. Sampling rate for heptane for SKC Ultra samplers containing Chromosorb 106.

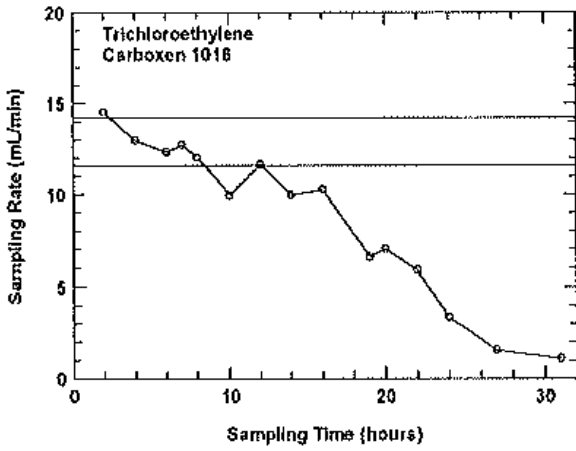


Figure 27. Sampling rate for trichloroethylene for SKC Ultra samplers containing Carboxen 1016.

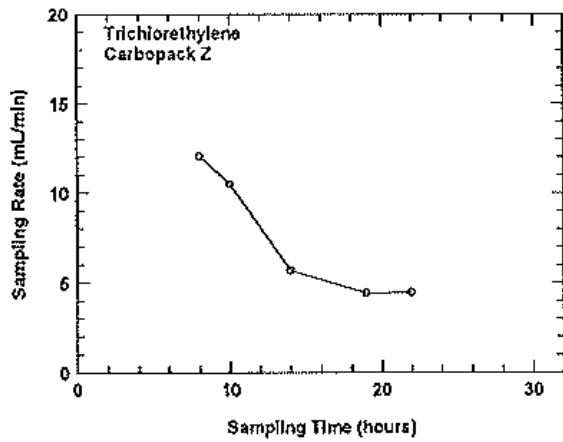


Figure 28. Sampling rate for trichloroethylene for SKC Ultra samplers containing Carbopack Z.

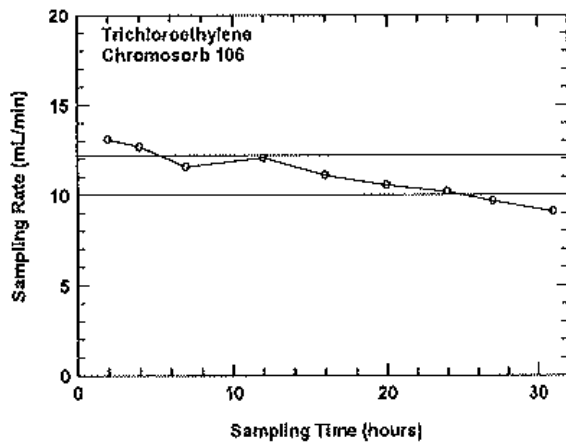


Figure 29. Sampling rate for trichloroethylene for SKC Ultra samplers containing Chromosorb 106.

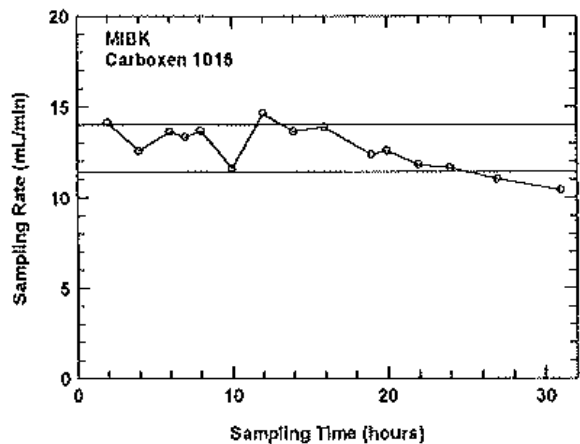


Figure 30. Sampling rate for MIBK for SKC Ultra samplers containing Carboxen 1016.

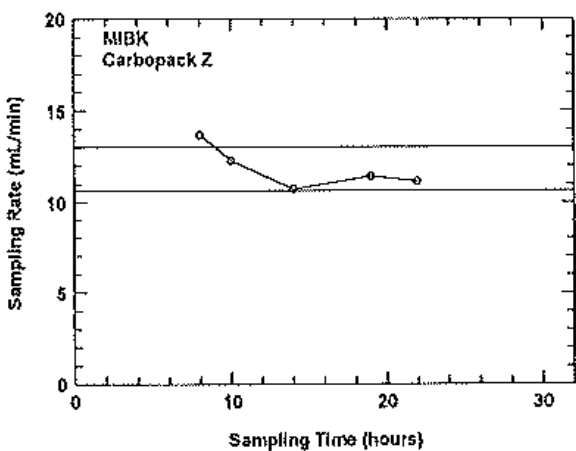


Figure 31. Sampling rate for MIBK for SKC Ultra samplers containing Carbopack Z.

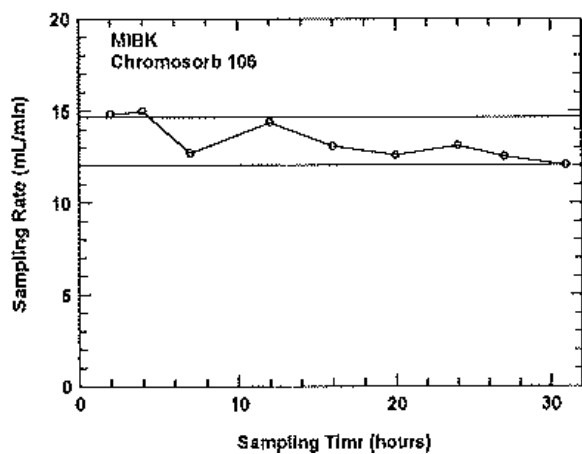


Figure 32. Sampling rate for MIBK for SKC Ultra samplers containing Chromosorb 106.

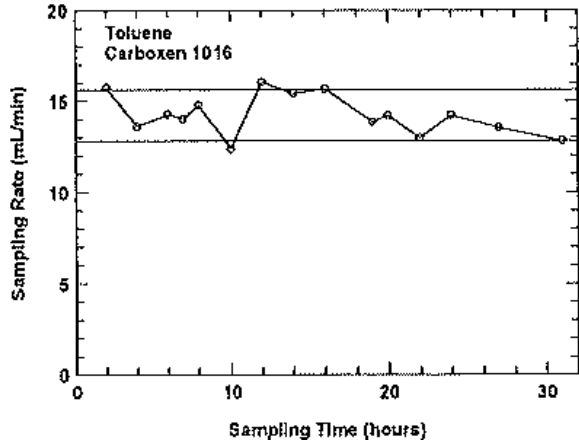


Figure 33. Sampling rate for toluene for SKC Ultra samplers containing Carboxen 1016.

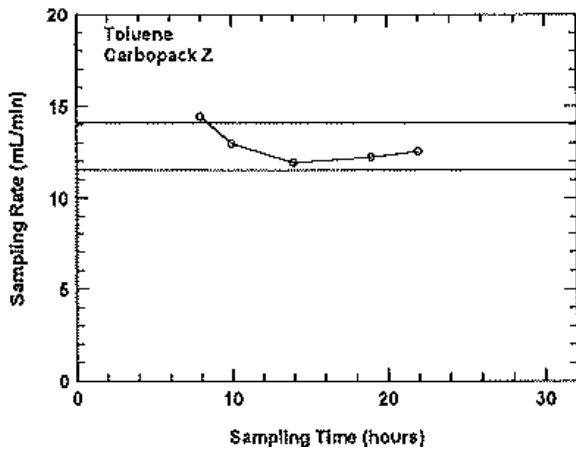


Figure 34. Sampling rate for toluene for SKC Ultra samplers containing Carboxen Z.

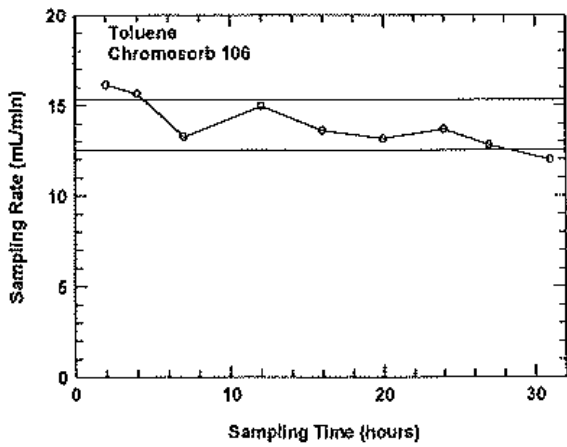


Figure 35. Sampling rate for toluene for SKC Ultra samplers containing Chromosorb 106.

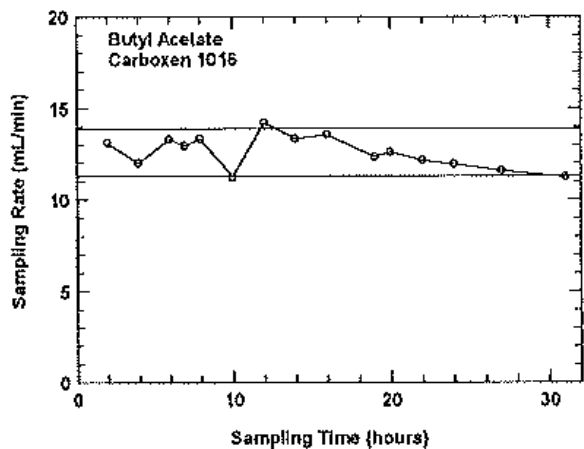


Figure 36. Sampling rate for butyl acetate for SKC Ultra samplers containing Carboxen 1016.

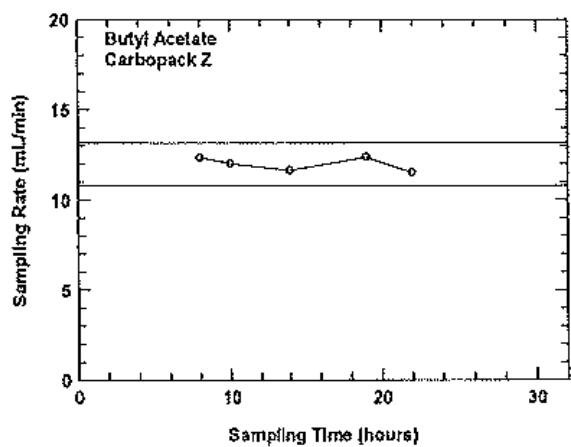


Figure 37. Sampling rate for butyl acetate for SKC Ultra samplers containing Carbopack Z.

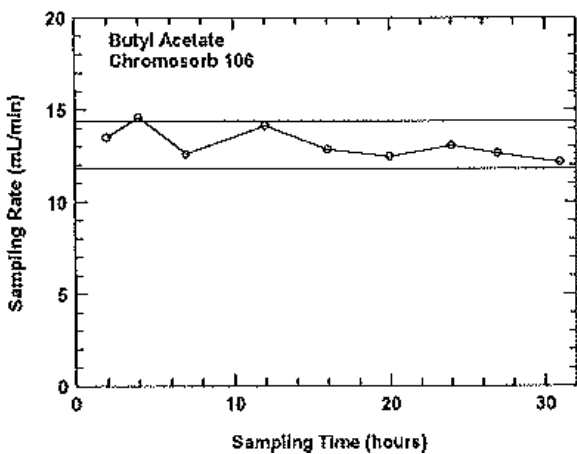


Figure 38. Sampling rate for butyl acetate for SKC Ultra samplers containing Chromosorb 106.

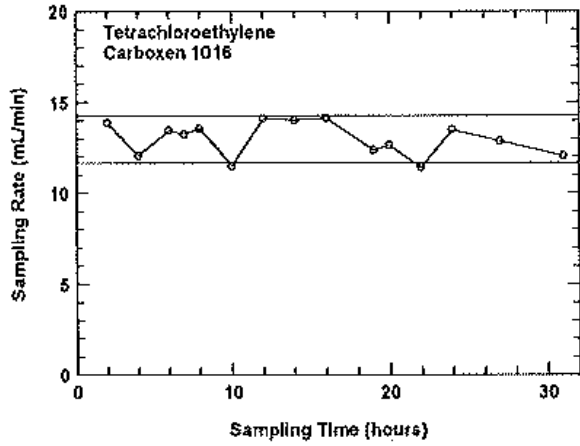


Figure 39. Sampling rate for tetrachloroethylene for SKC Ultra samplers containing Carboxen 1016.

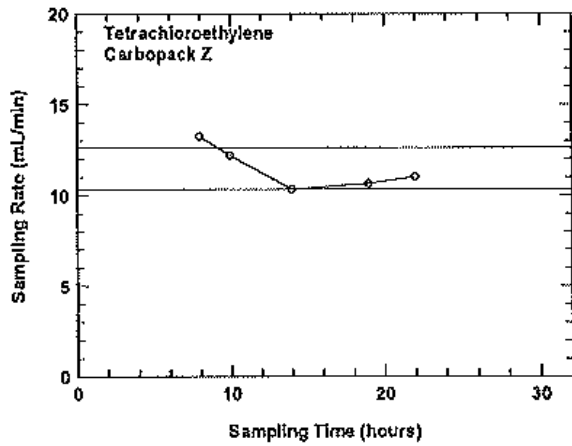


Figure 40. Sampling rate for tetrachloroethylene for SKC Ultra samplers containing Carbopack Z.

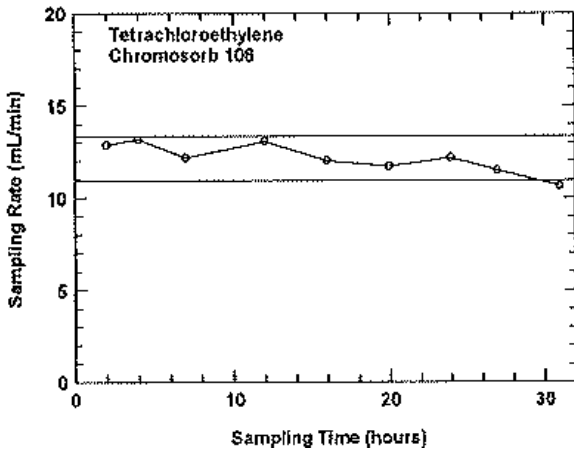


Figure 41. Sampling rate for tetrachloroethylene for SKC Ultra samplers containing Chromosorb 106.

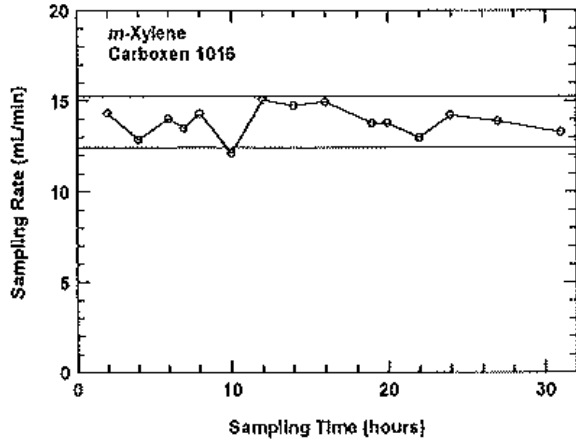


Figure 42. Sampling rate for m-xylene for SKC Ultra samplers containing Carboxen 1016.

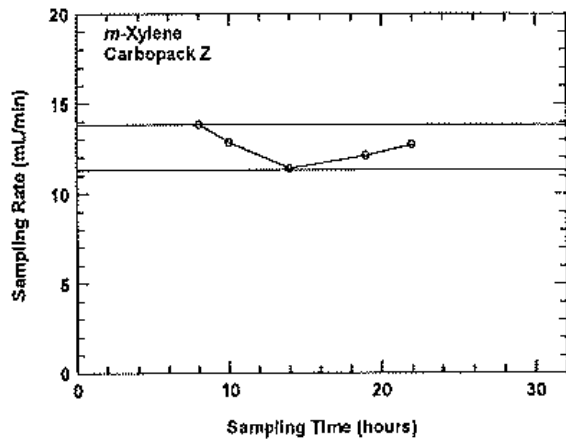


Figure 43. Sampling rate for m-xylene for SKC Ultra samplers containing Carbopack Z.

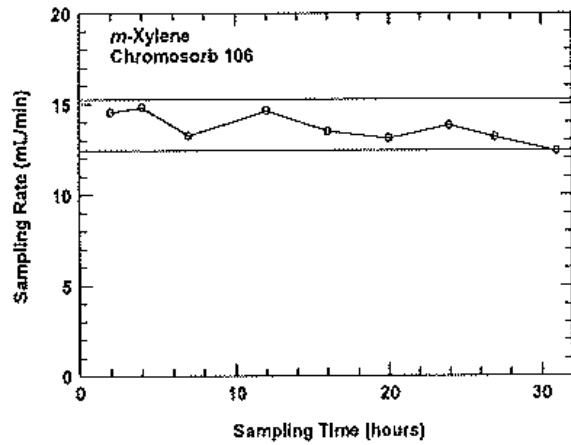


Figure 44. Sampling rate for m-xylene for SKC Ultra samplers containing Chromosorb 106.

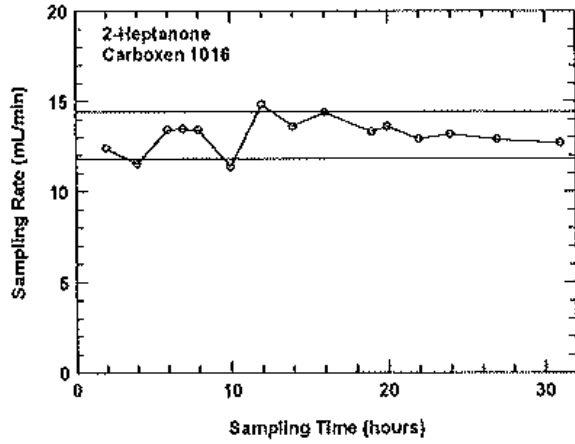


Figure 45. Sampling rate for 2-heptanone for SKC Ultra samplers containing Carboxen 1016.

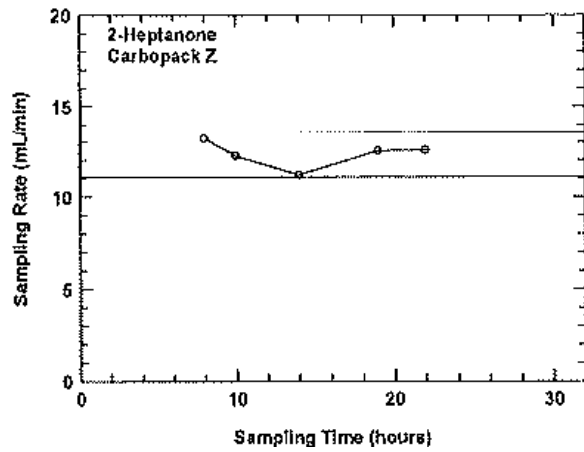


Figure 46. Sampling rate for 2-heptanone for SKC Ultra samplers containing Carbo-pack Z.

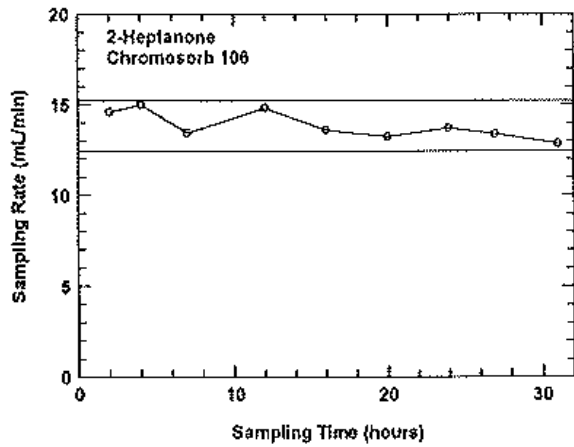


Figure 47. Sampling rate for 2-heptanone for SKC Ultra samplers containing Chromosorb 106.



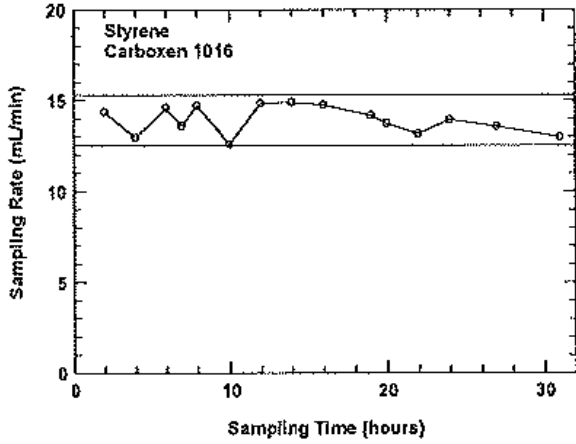


Figure 48. Sampling rate for styrene for SKC Ultra samplers containing Carboxen 1016.

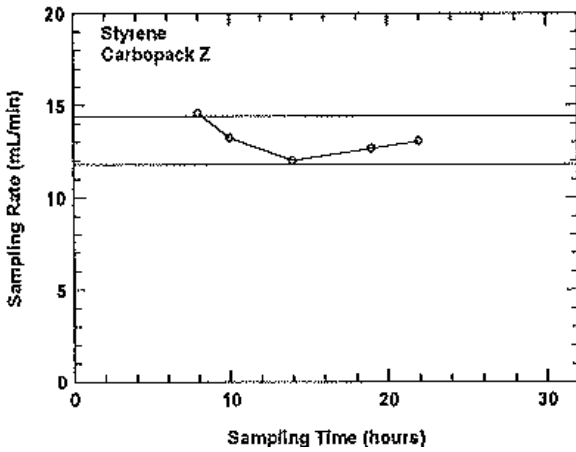


Figure 49. Sampling rate for styrene for SKC Ultra samplers containing Carbopack Z.

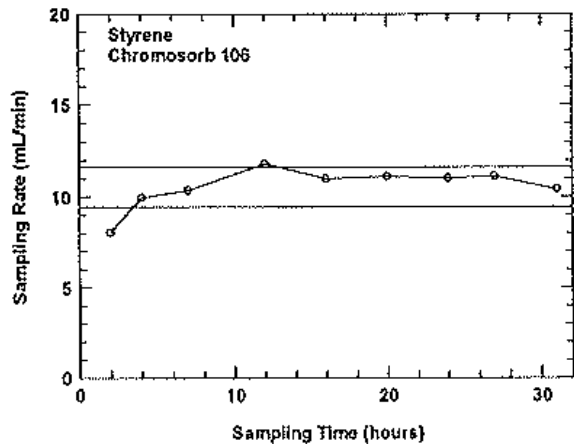


Figure 50. Sampling rate for styrene for SKC Ultra samplers containing Chromosorb 106.

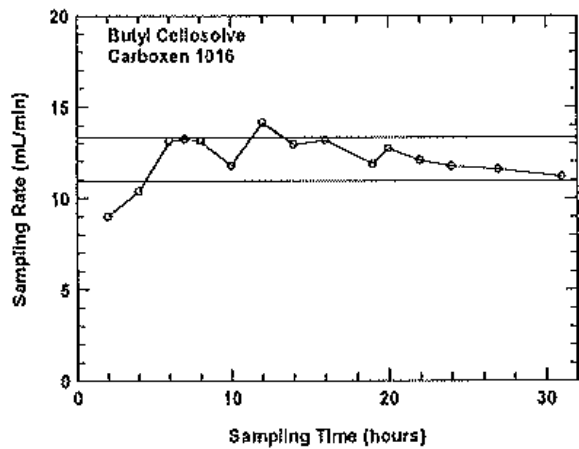


Figure 51. Sampling rate for butyl cellosolve for SKC Ultra samplers containing Carboxen 1016.

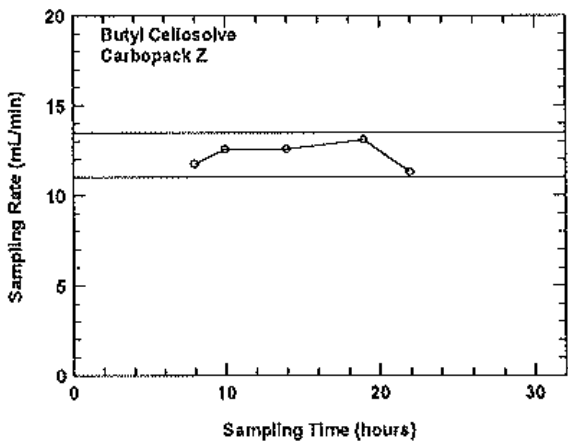


Figure 52. Sampling rate for butyl cellosolve for SKC Ultra samplers containing Carbo-pack Z.

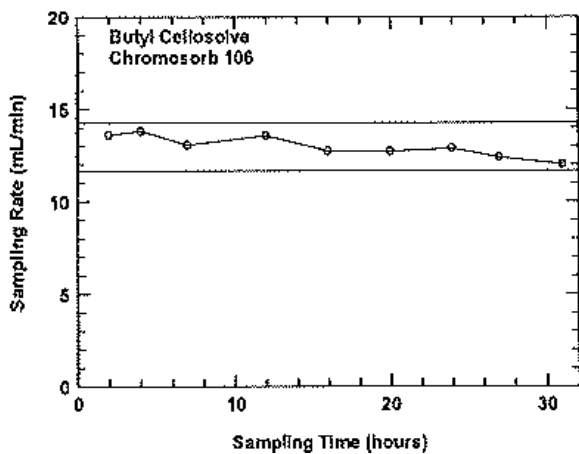


Figure 53. Sampling rate for butyl cellosolve for SKC Ultra samplers containing Chromosorb 106.

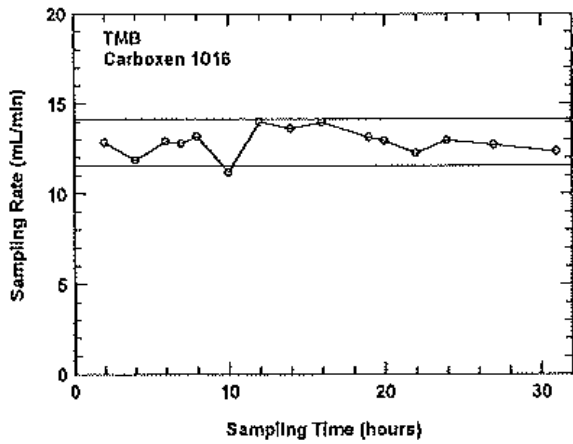


Figure 54. Sampling rate for TMB for SKC Ultra samplers containing Carboxen 1016.

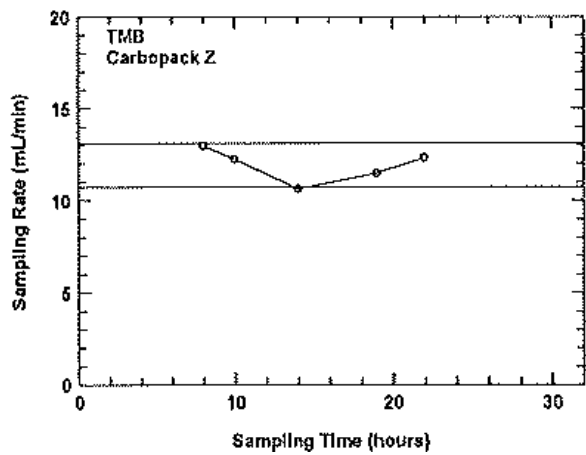


Figure 55. Sampling rate for TMB for SKC Ultra samplers containing Carbopack Z.

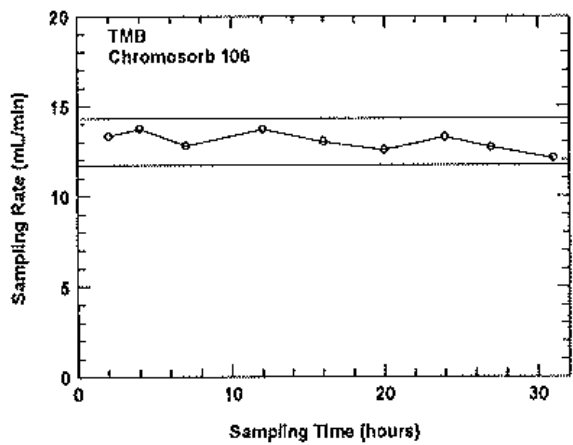


Figure 56. Sampling rate for TMB for SKC Ultra samplers containing Chromosorb 106.

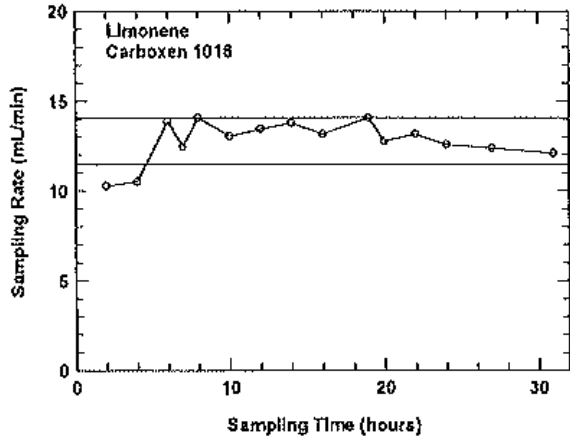


Figure 57. Sampling rate for limonene for SKC Ultra samplers containing Carboxen 1016.

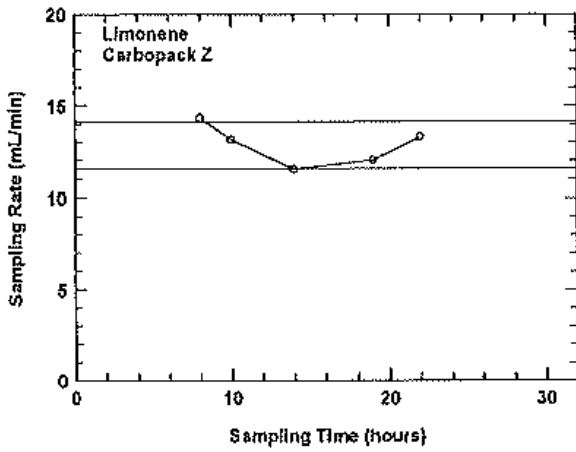


Figure 58. Sampling rate for limonene for SKC Ultra samplers containing Carbopack Z.

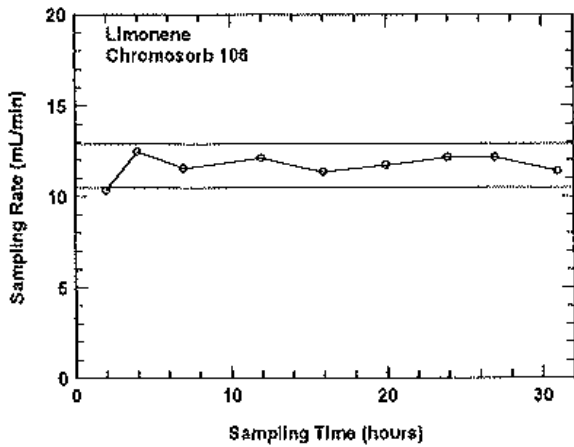


Figure 59. Sampling rate for limonene for SKC Ultra samplers containing Chromosorb 106.

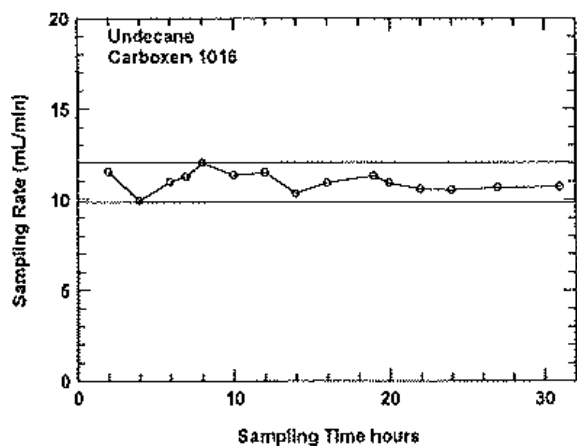


Figure 60. Sampling rate for undecane for SKC Ultra samplers containing Carboxen 1016.

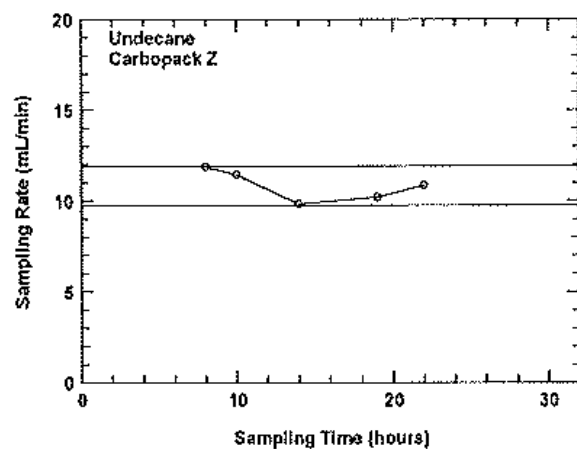


Figure 61. Sampling rate for undecane for SKC Ultra samplers containing Carbo-pack Z.

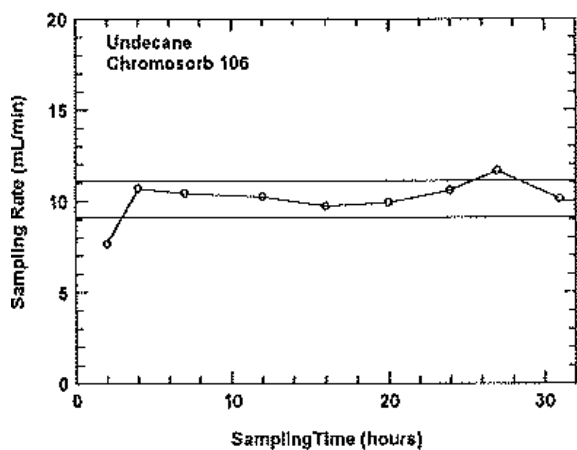


Figure 62. Sampling rate for undecane for SKC Ultra samplers containing Chromosorb 106.

Sampling rates are shown in Tables 6-8. and average sampling rates are shown in Table 9. The average was calculated using the last tested time (samp time) before sampling capacity was exceeded as shown in Figures 3-62. The two-hour sampling time was not included in the undecane average for Chromosorb 106. An average sampling rate and a RSD for the individual sampling rates was calculated for each medium. A

pooled RSD was also calculated for the RSDs for each medium. The individual RSDs for each medium were homogeneous by the Cochran Test at the 95% confidence level. NA means not applicable.

Table 6. Sampling Rates for Carboxen 1016.

analyte	sampling time (hours)	sampling rate (mL/min)	RSD
IPA	NA		
methylene chloride	NA		
MEK	NA		
ethyl acetate	NA		
1-butanol	7	12.47	11.32
benzene	8	14.14	10.48
PGME	8	12.31	6.17
heptane	31	12.78	6.93
trichloroethylene	8	12.90	7.47
MIBK	24	13.04	7.68
toluene	31	14.23	7.82
butyl acetate	31	12.59	7.08
tetrachlorethylene	31	12.97	7.18
m-xylene	31	13.85	5.90
2-heptanone	31	13.13	6.93
styrene	31	13.92	5.51
butyl cellosolve	31	12.13	10.72
TMB	31	12.85	5.80
limonene	31	12.78	8.98
undecane	31	10.95	4.84

Table 7. Sampling Rates for Carbopack Z.

analyte	sampling time (hours)	sampling rate (mL/min)	RSD
IPA	NA		
methylene chloride	NA		
MEK	NA		
ethyl acetate	NA		
1-butanol	NA		
benzene	NA		
PGME	NA		
heptane	22	11.83	7.65
trichloroethylene	10	11.25	9.98
MIBK	22	11.85	9.80
toluene	22	12.82	7.61
butyl acetate	22	11.98	3.31
tetrachlorethylene	22	11.47	10.46
m-xylene	22	12.59	7.48
2-heptanone	22	12.35	5.90
styrene	22	13.11	7.19
butyl cellosolve	22	12.26	5.86
TMB	22	11.92	7.51
limonene	22	12.85	8.55
undecane	22	10.83	7.83

Table 8. Sampling Rates for Chromosorb 106.

analyte	sampling time (hours)	sampling rate (mL/min)	RSD
IPA	NA		
methylene chloride	NA		
MEK	12	14.59	13.93
ethyl acetate	12	13.59	10.22
1-butanol	16	14.44	10.26
benzene	12	14.87	11.01
PGME	16	13.76	8.72
heptane	31	12.95	7.60
trichloroethylene	24	11.60	9.27
MIBK	31	13.36	8.06
toluene	27	14.15	8.83
butyl acetate	31	13.10	6.13
tetrachlorethylene	27	12.34	6.58
m-xylene	31	13.68	5.99
2-heptanone	31	13.84	5.50
styrene	31	10.54	10.27
butyl cellosolve	31	12.97	4.61
TMB	31	13.03	4.18
limonene	31	11.69	5.47
undecane	31	10.41	5.71

Table 9. Average Sampling Rates

medium	average sampling rate (mL/min)	sampling rate RSD (mL/min)	pooled RSD
Carboxen 1016	12.94	6.42	7.78
Carbopack Z	12.09	5.52	7.84
Chromosorb 106	13.05	9.92	8.30

## CONCLUSIONS

Results of this work shows some of the limitations of diffusive sampling and of thermal desorption. Thermal desorption permits use of mass spectrometry to identify and to quantitate sample components. This technique is extremely sensitive because the entire sample can enter the mass spectrometer. Obviously, the sample cannot be reanalyzed because it is entirely consumed. Sampling media must be relatively weak to permit thermal desorption because heat cannot effectively desorb many chemicals from strong media such as charcoal. Sampling media used with thermal desorption generally has unsatisfactory sampling capacity for comparatively volatile chemicals. One reason for poor capacity in diffusive sampling is reverse diffusion. A chemical reaching the surface of the sampling medium can migrate further into the medium and be retained, or can diffuse off the sampler and be lost. The usual cause of reverse diffusion is use of an inappropriate sampling medium. Inspection of the sampling rate and capacity figures shows that none of the tested media gave entirely satisfactory sampling performance. Chromosorb 106 had slightly more sampling capacity than Carboxen 1016. Carbopack Z was difficult to work with, and its capacity was inferior to Carboxen 1016 for the more volatile components of the solvent analyte mixture. Precision of sampling rates was similar for all three media within their respective effective sampling capacities. All three media presented substantial artifact backgrounds for blank samplers. This background could cause very low level analyses to be difficult. Chromosorb 106 was judged to provide the best overall sampling results of the

three tested media. SKC Ultra samplers containing Chromosorb 106 were shown to be an effective means to sample the solvent analyte mixture with exceptions of IPA, methylene chloride, and perhaps MEK. It is anticipated that this sampler could be used to develop a new fully-validated OSHA method that would find its best application in low-level, long-term workplace sampling.

#### REFERENCES

1. Warren Hendricks. U.S. Department of Labor, Occupational Safety and Health Administration Website. (accessed January 2003). The Marines Project: A Laboratory Study of Diffusive Sampling/Thermal Desorption/Mass Spectrometry Techniques for Monitoring Personal Exposure to Toxic Industrial Chemicals.
2. Jamie Brown and Bob Shirey. Supelco.(accessed January 2003). A Tool for Selecting an Adsorbent for Thermal Desorption Applications.
3. Warren Hendricks. U.S. Department of Labor, Occupational Safety and Health Administration Website. (accessed January 2003), OSHA Method 100 Ethyl Alcohol.