# Research Report

## Validation of Pentane using SKC Passive Sampler 575-001


## Abstract

A sampling method for Pentane in air has been validated for concentration levels from 60 to 1200 ppm and for exposure times from 7.5 minutes to 12 hours. The 575-001 passive sampler used has a sample medium of coconut charcoal. Desorption was with carbon disulfide and analysis by gas chromatography with flame ionization detection.

The analytical recovery over the range of 60 to 1200 ppm (1.3 to 28 mg) was 105.2% with a relative standard deviation of 1.3%. There was no effect of humidity on recovery

The sampling rate is 14.9 ml/min which was confirmed by the precision and accuracy calculations using 124 results (see Background; Sampling Rate Determination). Samples can be taken from 10°C to 40° C.

Minimum recommended sampling time is 15 minutes. Maximum recommended sampling time is 8 hours.

Samples were stable for up to 14 days at room temperature, or in a refrigerator (≤ 39.2° F [4° C]).

A full validation of Pentane was done according to NIOSH Protocol.[1]



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# Importance of Validation of Passive Samplers

There are distinct differences between a passive sampler and a sample tube.

The most important difference is that a passive sampler does not have a foolproof back up section that guarantees that all the chemical hazard has been collected and there is a true and total measure of the worker exposure.

Secondly, the sorbent media is exposed to the external environment and this poses problems not associated with a sample tube where the air sample passes into the sample tube directly contacting the sorbent media. That is why it is critical to use a strong sorbent medium in passive samplers to assure complete capture and retention.

Therefore, for compliance purposes a passive sampler must be laboratory tested and validated under worst case field conditions for all factors that affect sampling accuracy as well as interaction between affects.

NIOSH has laid out a rigorous and complete validation protocol to assure that the sample collected is a complete and true measure of worker exposure. The following are the factors that the NIOSH protocol addresses:

## Factors That Affect Complete Sample Uptake & Retention

| | |
|---|---|
| Chemical Hazard Concentration | Temperature |
| Time of Exposure | Humidity |
| Sorbent Capacity | Interfering Chemicals |
| Sorbent Strength | Reverse Diffusion from Sorbent Surface |
| Wind Velocity | Sampler Orientation |

Interaction of Any of the Above Factors

Validation by NIOSH protocol assures that the sample results are a true and total measure of worker exposure.

**SKC Validation follows the NIOSH Validation Protocol.
Certain experiments may have been modified for practical
reasons, or to provide more rigorous tests.**

# User Responsibility

The sampler manager should be a professional trained in air sampling and aware of the limitations and advantages of the method being used. It is also very helpful if they have a working relationship with the analytical techniques being used and the requirements of record keeping.

In accordance with ASTM D6346-98 and ANSI 104-1998 standards, use of samplers outside the range of conditions used in these validation tests does not assure accurate results and is not recommended. It is the user's responsibility to determine whether the conditions of the sampling site fall within the range tested. For bi-level validations it can be assumed that the applicable range is that used for testing the lower member of the homologous series.

Workers should be trained in the use of the equipment. In collecting the sample, care should be taken in the location of the sampler on the worker. It is to be openly exposed near the breathing zone. Exact times of exposure must be recorded. No moisture condensation should occur on the sampler. Workers should not be allowed to touch the sampler as they may transfer contamination. Particular attention must be paid to environments where liquid aerosols may be present, since droplets of liquid solvent on the sampler face will invalidate the sample. Any other field conditions outside of the limits used in the NIOSH protocol, such as extreme temperatures or stagnant air conditions which might affect the sampler operation should be recorded.

Good laboratory practice must be followed. Follow the operating instructions for the desorption time needed for complete desorption. Use only the correct desorption instrument. If gas chromatography is used as the analysis method, base line separation should occur with the chemical hazard of interest and proper instrument calibration procedures used.

NIOSH or OSHA analytical methods should be used.

# Summary of NIOSH Validation Protocol[1]

| Characteristic | Experimental Design | Interpretation of Results |
|---|---|---|
| **1. Analytical Recovery** | Spike 16 samplers, 4 at each of 4 concentration levels (0.1, 0.5, 1.0 & 2.0 x STD) Equilibrate about 12 h and analyze. | For the higher 3 levels require ≥ 75% recoveries with $S_r \leq 0.1$. |
| **2. Sampling Rate and Capacity** | Expose samplers (4 per time period) for 1/8, 1/4, 1/2, 1, 2, 4, 6, 8, 10 & 12 h to 2 x STD, 80% RH and 20 cm/s face velocity. Plot concentration vs. time exposed. Determine MRST and SRST. | Verify sampling rate.<br>State useful range at 80% RH & 2 x STD.<br>Capacity - sample loading corresponding to the downward break in conc. vs time curve from constant concentration.<br>SRST - time linear uptake rate achieved.<br>MRST-0.67 x capacity (1 analyte)<br>MRST-0.33 x capacity (Multi-analyte) |
| **3. Reverse Diffusion** | Expose 20 samplers to 2 x STD. 80% RH for 0.5 x MRST. Remove and analyze 10 samplers. Expose others to 80% RH and no analyte for remainder of MRST. | Require ≤ 10% difference between means of the two sampler sets at the 95% CL. |
| **4. Storage Stability** | Expose 3 sets of samplers (10 per set) at 80% RH, 1 x STD, and 0.5 x MRST. Analyze first set within 1 day, second set after 2 weeks storage at about 25° C, third set after 2 weeks storage at about 4° C. | Require ≤ 10% difference at the 95% CL between means of stored sampler sets and set analyzed within 1 day. |
| **5. Factor Effects** | Test the following factors at the levels shown. Use a 16 -run fractional factorial design (4 samplers per exposure) to determine significant factors.<br>Factor — Test Levels<br>analyte concentration — 0.1 & 2 x STD<br>exposure time — SRST & MRST<br>face velocity — 10 & 150 cm/s<br>relative humidity — 10 & 80% RH<br>interferant — 0 & 1 x STD<br>sampler orientation — parallel & perpendicular (to air flow) | Indicate any factor that causes a statistically significant difference in recovery at the 95% CL. Investigate further to characterize its effect. |
| **6. Temperature Effects** | Expose samplers (10 per temp) to 0.5 x STD at 10, 25, & 40° C for 0.5 x MRST | Define temperature effect and verify correction factor, if provided. |
| **7. Accuracy and Precision** | Calculate precision and bias for samplers (10 per conc. level) exposed to 0.1, 0.5, 1 & 2 x STD at 80% RH for ≥ MRST. Use data from previous experiments. | Require bias within ± 25% of true value at 95% CL with precision $S_r \leq 10.5\%$ for 0.5, 1, & 2 x STD levels. |

## Summary of NIOSH Validation Protocol (cont.)

| Characteristic | Experimental Design | Interpretation of Results |
|---|---|---|
| **8. Shelf Life** | Observe samplers throughout evaluation for changes in blank values, physical appearance, etc. Test samplers from more than one lot, if possible. | Note shelf storage time at which changes begin to occur. Indicate whether correctable or not. |
| **9. Behavior in the Field** | Consider problems not predictable from laboratory experiments. | Record temperature, humidity, air velocity, other contaminants, etc. |
| *Area Sampling:* | Expose passive samplers and independent method samplers (13 each) to the same environment. | Calculate precision and bias. Compare with laboratory results. |
| *Personal Sampling:* | Conduct personal sampling with ≥ 25 sampler pairs. Place pairs of passive samplers and independent samplers on the same lapel of each worker. | Calculate bias. Compare with area sampling and laboratory results |

# Bi-Level Validation (previously designated by SKC as 5B)

Validation of passive samplers is essential to ensure accurate determination of airborne chemical levels. To assist manufacturers and users, the National Institute for Occupational Safety and Health (NIOSH), the Health and Safety Executive (HSE)[2], and the Comité Européen de Normalisation (CEN)[3,4] have developed comprehensive protocols for the validation of passive samplers.

Bi-level validation can also be used to assure a sample that gives the total and complete exposure to a chemical hazard.

Bi-level validation is only for a series of chemically related compounds, i.e., members of a homologous series. Bi-level validation includes a full protocol validation on key compounds followed by a partial validation on other members of the series.

The concept of a bi-level validation of chemically related compounds for a given sorbent and sampler design is based on the following premises and has been studied by Guild et al.[5]

1. Full validation by NIOSH, HSE, or CEN Protocol of a lower member of the series is essential to assure accurate, routine sampling under all field conditions without the need for error-corrective measures.

2. Capacity and retentivity are directly related to the affinity of a sorbent for a specific chemical. For a series of chemically related compounds, the affinity of a sorbent for a particular member compound will increase with the molecular weight and boiling point of the member. If a sorbent is suitable for collecting a low molecular weight member of the series, it will be suitable for the higher molecular weight members of the series as well.

3. For chemically stable compounds, sample loss by reverse diffusion and loss during storage are inversely related to the affinity of the sorbent for the adsorbate. Therefore, compounds with higher molecular weights and boiling points will exhibit less loss by reverse diffusion and storage. Again, if a sorbent is suitable for a member with a lower molecular weight and boiling point, it will be suitable for the higher members.

4. The linearity of uptake with time is also a function of sorbent affinity and capacity. Uptake becomes increasingly linear as the molecular weight and boiling point increases and the sample load decreases. (Protocol validation requires study of concentrations ranging from 0.1 to 2.0 x the permissible exposure limit.)

## Bi-Level Validation (cont.)

5. Temperature affects the accuracy of passive samplers in two different ways; the relation of temperature to adsorption affinity and the relation of the molecular diffusion of the sample to the sampler.

    a. It is well known that the affinity of a sorbent for a chemical decreases with increasing temperature. If the sorbent has adequate affinity for a low molecular weight member of the series at 40° C (the maximum temperature tested under protocol), it will also be adequate at lower temperatures, and for higher molecular weight members of the series.

    b. The effects of temperature on sample uptake follow established mathematical relationships and are not significant compared to other random sampling errors.

6. The effects of humidity because of competition or modification of sorbent affinity will be most pronounced for lower members of the series.

7. Adsorption affinity decreases with the mass adsorbed. Therefore, the "key" member chosen for full validation should have a high PEL relative to the other members of the series.

8. Air velocity and sampler-orientation effects are functions of sampler design and will be similar for all compounds.

9. If all the factors affecting sampling accuracy improve with increasing molecular weight and boiling point and there are no interacting effects of these parameters with a lower member of the series, then there will be no interacting effects with higher members.

10. The accuracy of a sampler is determined by its bias and precision. For most passive samplers, the bias is the result of the deviation of the calculated sample rate from the actual rate. By determining the sample rate under known conditions at 1 PEL, the bias is reduced to zero. Therefore, measured sample rates should be determined for all compounds.

11. The precision of a sampler is a function of the consistency of sampler manufacture and the analytical procedures in the laboratory.

12. Analytical recovery tends to decrease with increased sorbent affinity and is a function of the chemical compound, the concentration, and the sorbent. Therefore, analytical recovery should be determined for every compound over the concentration range of 0.1 to 2.0 PEL, as recommended by protocol.

**Conclusion:** The above premises have been verified, peer reviewed and published.[5] Therefore, Bi-Level validation (5B) is an excellent way to assure accurate performance of a passive sampler for higher members of a homologous series.

# Comments on the Relationship Between the NIOSH and CEN Diffusive Sampler Evaluation Protocols

The Comité Européen de Normalisation (CEN) is engaged in writing standards for air sampling equipment which include the limitations on precision and accuracy (EN 482) and the required performance tests. In the case of passive samplers the relevant performance test standard is yet to be published, but draft copies are available (prEN 838).

The precision and accuracy requirements in EN 482 are based on the use that will be made of the results, principally either for problem identification or compliance purposes. The standard for compliance purposes is a combined precision and accuracy of less than 30%, which is a looser standard than the 25% in the NIOSH protocol.

The performance tests are closely related to those in the NIOSH protocol, as might be expected, since they are trying to confirm the performance of the samplers over a similar range of environmental conditions. As in the NIOSH protocol there are tests for desorption efficiency, uptake rate at different concentrations and for different time-periods, reverse diffusion, storage stability, wind velocity and orientation, humidity, temperature, and the presence or absence of interferences. As in the NIOSH protocol these factors are normally tested using a "high" and a "low" measure, whether alone or in combination. Since there is little difference between workplace conditions in the U.S.A. and Europe, these "high" and "low" conditions are very similar in the two protocols. In general, the NIOSH test provides the more stringent conditions (e.g. 7.5 minutes up to 12 hours in the NIOSH uptake rate experiment versus 30 minutes and 8 hours in the CEN equivalent). In addition, for the majority of the experiments, the NIOSH protocol requires more samples to be taken for each data point (typically 10 rather than 6). The reverse diffusion test is one test that might be considered significantly different, and a paper showing that the results of the tests are actually comparable has been submitted for publication.[6]

In addition, the CEN protocol requires tests for shelf-life and packaging integrity that have been carried out for one analyte (n-Hexane) only. The 575 Series passive sampler successfully passed these tests.

For the reasons given above, SKC considers the validations presented in these research reports to be at least sufficient to meet the requirements of the European Standards prEN 838 and EN 482 for compliance monitoring. This conclusion is supported by a detailed comparison which has been submitted for publication.[7]

The CEN protocol supports the BI-level theory of validation.

## SHELF-LIFE STUDY ON 575 SERIES PASSIVE SAMPLERS

**Protocol:** 4 expired and 2 unexpired 575-001 samplers were exposed to an atmosphere 100 ppm n-Hexane (2 X PEL) at 80% relative humidity (25° C) for 30 minutes, and then analyzed. Study was conducted August 1995.

**Results:**

| | |
|---|---|
| Calculated atmosphere concentration: | 106 ppm |
| Gas sample analysis concentration: | 102 ppm (RSD = 7.0%) |
| Sorbent tube analysis concentration: | 115 ppm (RSD = 3.2%) |
| Sampler analysis concentration:◊ | |
| Sampler expired 12/92: | 106 ppm |
| Sampler expired 4/94: | 106 ppm |
| Sampler expired 10/94: | 108 ppm |
| Sampler expired 10/94: | 110 ppm |
| Sampler unexpired (7/96): | 100 ppm |
| Sampler unexpired (7/96): | 100 ppm |

◊ Based on 111.6% desorption efficiency

**Conclusion**: Samplers will perform as expected up to their expiration date.

## PACKAGING INTEGRITY STUDY ON 575 SERIES SAMPLERS

**Protocol:** 6 575-001 samplers in unopened Tedlar® pouches were exposed to an atmosphere of 100 ppm n-Hexane (2 X PEL) at 80% relative humidity (25° C) for four hours, and then opened and analyzed.

**Results:**

| | |
|---|---|
| Calculated atmosphere concentration: | 103 ppm |
| Gas sample analysis concentration: | 104 ppm (RSD = 8.7%) |
| Sorbent tube analysis concentration: | 103 ppm (RSD = 2.7%) |

Sampler analysis: No detectable n-Hexane in any sampler.

(estimated LOD = 1.5 micrograms, equivalent to 0.125 ppm)

**Conclusion:** Packaging will prevent contamination of stored samplers.

# Scope of the Method

**Analyte:** Pentane

**Matrix:** Air

**Procedure:** Adsorption on a 575-001 SKC passive sampler, desorption with 2 ml of $CS_2$, and analysis by GC-FID.

**Exposure Guidelines:**

| | |
|---|---|
| ACGIH-TLV (1994/95) | 600 ppm TWA, 750 ppm STEL |
| OSHA (1995) | 600 ppm TWA, 750 ppm STEL |
| NIOSH (1995) | 120 ppm TWA, 610 STEL |

**Validation Range, Recovery:**

| Compound | Validation Range ppm in air | Mean % Recovery |
|---|---|---|
| Pentane | 60-1200 | 105.2 |

**Detection Limits:** 0.1 PEL concentration was easily determined. No studies were made to determine the absolute detection limit.

**Temperature Effects:** Samples could be taken from 10° C to 40° C.

**Factorial:** No significant effects were found due to the interaction of factors that affect sampling accuracy.

**Humidity Effects:** High humidity conditions (80% RH at 25° C) did not affect the recovery of Pentane on the 575-001 passive sampler, or the uptake rate.

**Storage Effects:** The passive sampler can store for at least 14 days at room temperature or in a refrigerator (≤ 39.2° F [4° C]).

**Interferences:** Any compound that has the same retention time as Pentane will interfere with the analysis. A study was also conducted where passive samplers were exposed to 200ppm hexane and 1600 ppm Pentane and no significant loss in recovery was observed.

**Validation Completion Date:** December 1989

**Physical Properties:**

| Mol. Weight (g/mole) | Boiling Pt. at 760 mm Hg | Density (g/ml) |
|---|---|---|
| 72.15 | 36.1° C | 0.6262 |

# Background

**History of Methodology**
Previous methodologies have used activated charcoal SKC Lot 120 in a sample tube.

**Research Purpose**
The present work was to evaluate and validate the SKC 575 Series passive sampler containing charcoal as a method for sampling Pentane. The passive sampler was validated over a concentration range of 0.1 to 2 x PEL. Critical parameters such as analytical recovery, concentration, relative humidity, reverse diffusion, storage stability, temperature, sampling time, wind speed and orientation, and the presence of interfering compounds were addressed.

**Experimental**
Optima-grade Pentane (Fisher Scientific) was used. The HPLC-grade carbon disulfide (99.9%) was obtained from Aldrich Chemical Company. The 575 passive sampler containing coconut charcoal (SKC Cat. No. 575-001) and the Anasorb 747 tubes used for atmosphere calibrations (SKC Cat. No. 226-81) are available from SKC, Inc.

A dynamic atmosphere generation apparatus was used to generate precise concentrations of Pentane in air for exposure of the passive samplers. The system is described in Appendix A and Figure 1. The atmosphere was fed into an exposure test chamber. The passive samplers were exposed on a rotating bracket inside the test chamber to simulate wind velocity and orientation.

**Analytical recoveries** for the passive samplers were conducted by injecting a known amount of Pentane (as a $CS_2$ solution) into the back of each sampler. The passive samplers were capped, allowed to equilibrate overnight, and analyzed the next day to determine analytical recovery or desorption efficiency. The tests were conducted at mass loadings equivalent to an 8-hour time weighted average sample (7.54 L at the expected sampling rate of 15.7 ml/min) at 0.1, 0.5, 1.0 and 2.0 PEL under dry conditions.

**The sampling rate, reverse diffusion and storage stability** experiments on the passive sampler were conducted under dynamic conditions in the test chamber described above.

The passive samplers were desorbed (in situ) with 2 ml of $CS_2$ and shaken on a flatbed shaker for 30 minutes. All extracts were transferred to autosampler vials and analyzed by flame ionization gas chromatography. A chromatogram with analytical conditions is shown in Figure 2.

**Sampling Rate Determination**
Sampling rates can be determined by one of several statistical methods from the experimental data and they differ by only a small amount. Any bias taken is toward the protection of the worker.

We use the time-weighted average from one to eight hours where results fall within NIOSH criteria.

We constantly review our data and conduct experimental work to provide the most precise sampling rate. This rate may differ slightly from previously published sampling rates. Use the rate listed in this report.

# Analytical Recovery

*NIOSH Requirements*

**Experimental Design**

Spike 16 samplers, 4 at each of 4 concentration levels (0.1, 0.5, 1.0 & 2.0 x STD) Equilibrate about 12 h and analyze.

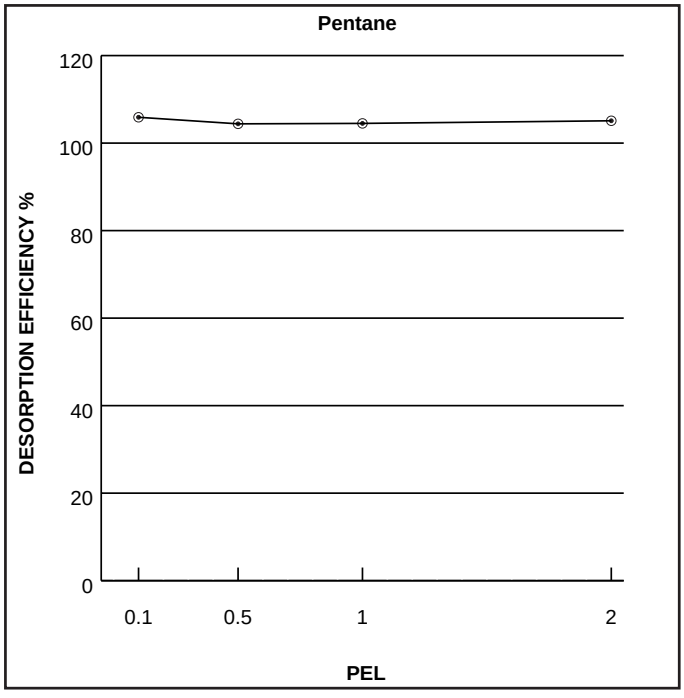
**Interpretation of Results**

For the 3 higher levels require ≥ 75% recoveries with $S_r \leq 0.1$.

## Results

| PEL Level | Spike (mg) | Recovery (mg) | Recovery % | Mean | RSD % |
|---|---|---|---|---|---|
| 0.1 | 1.335 | 1.397 | 104.6 | | |
| | | 1.446 | 108.3 | | |
| | | 1.400 | 104.9 | | |
| | | 1.411 | 105.7 | 105.9 | 1.6 |
| 0.5 | 6.262 | 6.646 | 106.1 | | |
| | | 6.543 | 104.5 | | |
| | | 6.513 | 104.0 | | |
| | | 6.457 | 103.1 | 104.4 | 1.2 |
| 1.0 | 12.524 | 13.272 | 105.8 | | |
| | | 13.084 | 104.5 | | |
| | | 12.942 | 103.3 | | |
| | | 13.078 | 104.4 | 104.5 | 1.0 |
| 2.0 | 28.179 | 29.959 | 106.3 | | |
| | | 30.209 | 107.2 | | |
| | | 29.820 | 105.8 | | |
| | | 29.609 | 105.1 | 105.1 | 0.8 |
| | | | Overall Mean | 105.2 | |

**Pooled mean (all levels) 105.2%**
**Pooled mean (highest 3 levels) 105.0%**



# Sampling Rate and Capacity

*NIOSH Requirements*

## Experimental Design

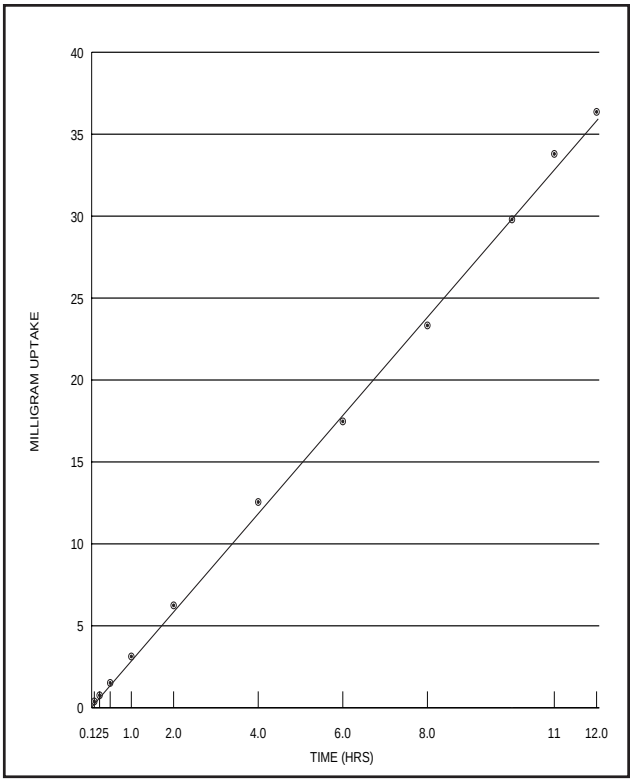
Expose samplers (4 per time period) for 1/8, 1/4, 1/2, 1, 2, 4, 6, 8, 10 and 12 h to 2 x STD, 80% RH and 20 cm/s face velocity. Plot concentration vs. time exposed. Determine MRST and SRST.

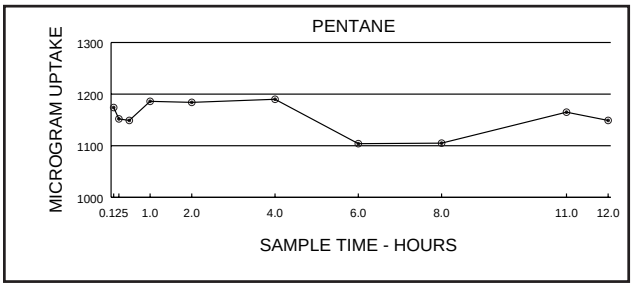
## Interpretation of Results

Verify sampling rate. State useful range at 80% RH and 2 x STD. Capacity - sample loading corresponding to the downward break in conc. vs time curve from constant concentration. SRST-time linear uptake rate achieved. MRST - 0.67 x capacity (1 analyte)
MRST-0.33 x capacity (Multi-analyte)

## Results

| Time (hrs) | Uptake (mg) | Mean (mg) | RSD% | DE Corr (mg) | Concn. (ppm) |
|---|---|---|---|---|---|
| 0.125 | 0.387 | | | | |
| | 0.412 | | | | |
| | 0.402 | | | | |
| | 0.427 | 0.407 | 4.1 | 0.387 | 1174 |
| 0.25 | 0.743 | | | | |
| | 0.793 | | | | |
| | 0.829 | | | | |
| | 0.835 | 0.800 | 5.3 | 0.760 | 1152 |
| 0.5 | 1.695 | | | | |
| | 1.552 | | | | |
| | 1.598 | | | | |
| | 1.536 | 1.595 | 4.5 | 1.516 | 1149 |
| 1 | 3.249 | | | | |
| | 3.237 | | | | |
| | 3.269 | | | | |
| | 3.414 | 3.292 | 2.5 | 3.129 | 1186 |
| 2 | 6.855 | | | | |
| | 6.381 | | | | |
| | 6.624 | | | | |
| | 6.438 | 6.574 | 3.3 | 6.249 | 1184 |
| 4 | 12.782 | | | | |
| | 13.359 | | | | |
| | 13.429 | | | | |
| | 13.266 | 13.209 | 2.2 | 12.556 | 1190 |
| 6 | 18.257 | | | | |
| | 18.595 | | | | |
| | 18.296 | | | | |
| | 18.385 | 18.383 | 0.8 | 17.474 | 1104 |
| 8 | 25.214 | | | | |
| | 25.527 | | | | |
| | 23.055 | | | | |
| | 24.402 | 24.544 | 4.5 | 23.331 | 1105 |
| 11 | 35.356 | | | | |
| | 35.087 | | | | |
| | 36.491 | | | | |
| | 35.286 | 35.555 | 1.8 | 33.798 | 1165 |
| 12 | 39.977 | | | | |
| | 36.162 | | | | |
| | 38.237 | | | | |
| | 38.635 | 38.253 | 4.1 | 36.362 | 1149 |




**Concentration values are calculated using a sampling rate of 14.9 ml/min based on a time-weighted average of the 1 through 8 hour results assuming the standard atmosphere concentration is 1131 ppm (theoretical, checked by independent method).**

# Reverse Diffusion

*NIOSH Requirements*

**Experimental Design**

Expose 20 samplers to 2 x STD 80% RH for 0.5 x MRST. Remove and analyze 10 samplers. Expose others to 80% RH and no analyte for remainder of MRST.

**Interpretation of Results**

Require ≤ 10% difference between means of the two sampler sets at the 95% CL.

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**Results** (in milligrams)

| Exposed 4 hours to analyte | | Exposed 4 hours to analyte plus 4 hours at zero analyte concentration | |
|---|---|---|---|
| **Milligrams** | **DE Corr** | **Milligrams** | **DE Corr.** |
| 11.913 | 11.324 | 12.678 | 12.051 |
| 12.136 | 11.536 | 12.165 | 11.564 |
| 12.364 | 11.753 | 12.198 | 11.595 |
| 12.230 | 11.625 | 12.386 | 11.774 |
| 11.374 | 10.812 | 12.191 | 11.588 |
| 12.689 | 12.062 | 12.290 | 11.683 |
| 11.630 | 11.055 | 11.895 | 11.307 |
| 11.956 | 11.365 | 11.917 | 11.328 |
| 10.722 | 10.192 | 11.307 | 11.318 |
| 11.969 | 11.377 | 12.093 | 11.495 |
| **Mean:** | **11.310** | | **11.570** |
| **SD:** | **0.525** | | **0.232** |
| **RSD:** | **4.6%** | | **2.0%** |

**The difference between the two sets of results is less than 10%.**

The calculated atmosphere for this experiment was 1138 ppm, not 1200 ppm as required for the accuracy/precision calculations, therefore the amounts used in the accuracy/precision calculation were adjusted upwards to account for this discrepancy.

# Storage Stability

*NIOSH Requirements*

**Experimental Design**

Expose 3 sets of samplers (10 per set) at 80% RH, 1 x STD, and 0.5 x MRST. Analyze first set within 1 day, second set after 2 weeks storage at about 25° C, third set after 2 weeks storage at about 4° C.

**Interpretation of Results**

Require ≤ 10% difference at the 95% CL between means of stored sampler sets and set analyzed within 1 day.

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**Results** (in milligrams)

| Day 1 (Room Temp) | | Day 14 (Room Temp) | | Day 14 (4°C) | |
|---|---|---|---|---|---|
| **Uptake** | **DE Corr.** | **Uptake** | **DE Corr** | **Uptake** | **DE Corr.** |
| 6.248 | 5.939 | 6.323 | 6.010 | 6.697 | 6.366 |
| 6.434 | 6.116 | 6.636 | 6.308 | 6.174 | 5.869 |
| 6.528 | 6.205 | 6.413 | 6.096 | 6.741 | 6.408 |
| 6.426 | 6.108 | 6.065 | 5.765 | 6.379 | 6.064 |
| 6.386 | 6.070 | 6.333 | 6.020 | 6.343 | 6.029 |
| 6.694 | 6.363 | 6.077 | 5.777 | 6.396 | 6.080 |
| 6.443 | 6.125 | 6.368 | 6.053 | 6.957 | 6.613 |
| 6.662 | 6.333 | 6.663 | 6.334 | 6.511 | 6.189 |
| 6.467 | 6.147 | 6.581 | 6.256 | 6.218 | 6.541 |
| 6.754 | 6.420 | 6.642 | 6.314 | 6.529 | 6.206 |
| **Mean:** | **6.183** | | **6.093** | | **6.204** |
| **SD:** | **0.15** | | **0.21** | | **0.21** |
| **RSD:** | **2.4%** | | **3.4%** | | **3.4%** |

**There is no significant loss of sample on storage.**

# Factorial Results

*NIOSH Requirements*

## Experimental Design

Test the following factors at the levels shown. Use a 16 run fractional factorial design (4 samplers per exposure) to determine significant factors.

| Factor | Test Levels |
|---|---|
| analyte concentration | 0.1 & 2 x STD |
| exposure time | SRST & MRST |
| face velocity | 10 & 150 cm/s |
| relative humidity | 10 & 80% RH |
| interferant | 0 & 1 x STD |
| sampler orientation | parallel & perpendicular (to air flow) |

## Interpretation of Results

Indicate any factor that causes a statistically significant difference in recovery at the 95% CL. Investigate further to characterize its effect.

---

**Results** (in micrograms per ppm per hour ($\mu g\ ppm^{-1}\ h^{-1}$), desorption efficiency corrected)

| Run # | Individual Monitor Results | | | | Average | %RSD |
|---|---|---|---|---|---|---|
| 1 | 2.5483 | 2.7284 | 2.5571 | 2.7075 | 2.6353 | 3.6 |
| 2 | 2.6744 | 2.6117 | 2.6531 | 2.4706 | 2.6025 | 3.5 |
| 3 | 2.2730 | 2.4082 | 2.5186 | 2.3496 | 2.3874 | 4.3 |
| 4 | 2.6188 | 2.6383 | 2.5988 | 2.5113 | 2.5918 | 2.2 |
| 5 | 2.5410 | 2.5907 | 2.5628 | 2.5917 | 2.5716 | 0.9 |
| 6 | 2.7777 | 2.4201 | 2.7558 | 2.6191 | 2.6432 | 6.2 |
| 7 | 2.7661 | 2.6874 | 2.5962 | 2.6526 | 2.6756 | 2.7 |
| 8 | 2.5831 | 2.7522 | 2.4167 | 2.5838 | 2.5840 | 5.3 |
| 9 | 2.7102 | 2.6615 | 2.7410 | 2.6101 | 2.6807 | 2.1 |
| 10 | 2.7447 | 2.5343 | 2.7335 | 2.6683 | 2.6702 | 3.6 |
| 11 | 2.4357 | 2.3704 | 2.5292 | 2.4805 | 2.4540 | 2.8 |
| 12 | 2.3294 | 2.3631 | 2.3911 | 2.1923 | 2.3190 | 3.8 |
| 13 | 2.6259 | 2.7126 | 2.5542 | 2.7609 | 2.6634 | 3.4 |
| 14 | 2.6815 | 2.7707 | 2.5794 | 2.6499 | 2.6704 | 3.0 |
| 15 | 2.6362 | 2.8168 | 2.7151 | 2.7860 | 2.7385 | 2.9 |
| 16 | 2.3213 | 2.3546 | 2.3831 | 2.2919 | 2.3377 | 1.7 |

Notes:
- Low face velocity = 20 cm/sec
- Low concentration = 0.1 PEL
- Minimum sample time = 0.5 hours

200 ppm hexane used in the interference experiments.

# Factorial Summary

| Run Number | | μg/ppm/hour |
|---|---|---|
| Run# | 1 = | 2.6353 |
| Run# | 2 = | 2.6025 |
| Run# | 3 = | 2.3874 |
| Run# | 4 = | 2.5918 |
| Run# | 5 = | 2.5716 |
| Run# | 6 = | 2.6432 |
| Run# | 7 = | 2.6756 |
| Run# | 8 = | 2.5840 |
| Run# | 9 = | 2.6807 |
| Run# | 10 = | 2.6702 |
| Run# | 11 = | 2.4540 |
| Run# | 12 = | 2.3190 |
| Run# | 13 = | 2.6634 |
| Run# | 14 = | 2.6704 |
| Run# | 15 = | 2.7385 |
| Run# | 16 = | 2.3377 |
| **Average** | **=** | **2.5766 = 14.6 mL/min** |

| | Factor | Effect | Percent | Significance |
|---|---|---|---|---|
| A - | Concentration | 0.09 | 3.4% | N.S. |
| B - | Relative Humidity | 0.08 | 3.0% | N.S. |
| C - | Interferants | 0.00 | 0.1% | N.S. |
| D - | Time | 0.08 | 2.9% | N.S. |
| E - | Face Velocity | 0.01 | 0.3% | N.S. |
| F - | Orientation | 0.00 | 0.1% | N.S. |
| E1 - | ABC | -0.01 | 0.6% | N.S. |
| E2 - | ABD | 0.02 | 0.8% | N.S. |
| E3 - | AB + EF | -0.06 | 2.2% | N.S. |
| E4 - | AC + DF | -0.05 | 2.1% | N.S. |
| E5 - | AD + CF | -0.13 | 5.1% | N.S. |
| E6 - | AE + BF | 0.07 | 2.6% | N.S. |
| E7 - | CD + BE | -0.09 | 3.3% | N.S. |
| E8 - | BC + DE | 0.08 | 3.0% | N.S. |
| E9 - | BD + CE | -0.05 | 1.9% | N.S. |

**Minimum Significant Effect (MSE) = ± 0.16**
**No significant effect of factors or their tested interactions**

N.S. = Not Significant

# Temperature Effects

*NIOSH Requirements*

**Experimental Design**

Expose samplers (10 per temp) to 0.5 x STD at 10, 25, & 40° C for 0.5 x MRST.

**Interpretation of Results**

Define temperature effect and verify correction factor, if provided.

---

**Results** (in milligrams)

| 10° C | | 25° C | | 40° C | |
|---|---|---|---|---|---|
| **Sample (mg)** | **DE Corr. (mg)** | **Sample (mg)** | **DE Corr (mg)** | **Sample (mg)** | **DE Corr. (mg)** |
| 3.438 | 3.268 | 3.067 | 2.915 | 3.194 | 3.036 |
| 3.301 | 3.138 | 3.107 | 2.953 | 3.328 | 3.163 |
| 3.438 | 3.268 | 3.363 | 3.197 | 3.325 | 3.161 |
| 3.230 | 3.070 | 3.342 | 3.177 | 3.390 | 3.222 |
| 3.177 | 3.020 | 3.391 | 3.223 | 3.468 | 3.297 |
| 3.473 | 3.301 | 3.382 | 3.215 | 3.377 | 3.210 |
| 3.551 | 3.375 | 3.425 | 3.256 | 3.586 | 3.409 |
| 3.536 | 3.361 | 3.319 | 3.155 | 3.469 | 3.298 |
| 3.279 | 3.117 | 3.456 | 3.285 | 3.494 | 3.321 |
| 3.391 | 3.223 | 3.646 | 3.466 | 3.512 | 3.338 |
| **Mean:** | **3.214** | | **3.185** | | **3.246** |
| **RSD:** | **3.8%** | | **5.3%** | | **3.3%** |
| **Concentration[1]:** | **290** | | **299** | | **325** |
| **Uptake[2]:** | **2.771** | | **2.662** | | **2.497** |
| **Theoretical[3]:** | **2.595** | | | | **2.729** |

**Uptake is within 10% of theoretical (based on 25° C result) at both 10° C and 40° C.**

[1] Concentration (in ppm at the sampling temperature) determined by calculation and confirmed by and independent method.

[2] Uptake measured as micrograms/ppm (sampling temperature)/hour.

[3] Based on 25° C result.

# Accuracy and Precision

*NIOSH Requirements*

## Experimental Design

Calculate precision and bias for samplers (10 per conc. level) exposed to 0.1, 0.5, 1 & 2 x STD at 80% RH for ≥ MRST. Use data from previous experiments.

## Interpretation of Results

Requires bias within ± 25% of true value at 95% CL with precision $S_r \leq 10.5\%$ for 0.5, 1 & 2 x STD levels.

---

**All Values in μg/ppm/hr**

**Monitors run at 2.0 X PEL**

Values for individual monitors for the Rate/Capacity Experiment

| | | | | |
|---|---|---|---|---|
| 4 Hour - | 2.6629 | 2.7831 | 2.7977 | 2.7637 |
| 6 Hour - | 2.5357 | 2.5826 | 2.5411 | 2.5535 |
| 8 Hour - | 2.6265 | 2.6591 | 2.4016 | 2.5419 |

Values for individual monitors for the Reverse Diffusion Experiment

| | | | | | |
|---|---|---|---|---|---|
| 4 Hour - | 2.4877 | 2.5344 | 2.5821 | 2.5540 | 2.3752 |
| | 2.6498 | 2.4285 | 2.4967 | 2.2390 | 2.4994 |
| 8 Hour - | 2.6475 | 2.5404 | 2.5473 | 2.5867 | 2.5458 |
| | 2.5650 | 2.4840 | 2.4885 | 2.4865 | 2.5252 |

Values for individual monitors for the Factorial Experiment

| | | | | |
|---|---|---|---|---|
| Run #2 - | 2.6744 | 2.6117 | 2.6531 | 2.4706 |
| Run #4 - | 2.6188 | 2.6383 | 2.5988 | 2.5113 |
| Run #13 | 2.6259 | 2.7126 | 2.5542 | 2.7609 |
| Run #15 - | 2.6362 | 2.8168 | 2.7151 | 2.7860 |

**Monitors run at 1.0 x PEL**

Values for individual monitors for the Storage Stability Experiment

| | | | | | |
|---|---|---|---|---|---|
| Day 1 - | 2.4746 | 2.5483 | 2.5854 | 2.5450 | 2.5292 |
| | 2.6513 | 2.5521 | 2.6387 | 2.5612 | 2.6750 |
| R.T. - | 2.5042 | 2.6283 | 2.5400 | 2.4021 | 2.5083 |
| | 2.4071 | 2.5221 | 2.6392 | 2.6067 | 2.6308 |
| 5 deg - | 2.6525 | 2.4454 | 2.6700 | 2.5267 | 2.5121 |
| | 2.5333 | 2.7554 | 2.5787 | 2.7254 | 2.5858 |

**Monitors run at 0.5 x PEL**

Values for individual monitors for the Temperature Effects Experiment

| | | | | | |
|---|---|---|---|---|---|
| 10 deg - | 2.8170 | 2.7050 | 2.8170 | 2.6470 | 2.6030 |
| | 2.8460 | 2.9090 | 2.8970 | 2.6870 | 2.7780 |
| 25 deg - | 2.4370 | 2.4690 | 2.6730 | 2.6560 | 2.6950 |
| | 2.6880 | 2.7220 | 2.6380 | 2.7470 | 2.8980 |
| 40 deg - | 2.3350 | 2.4330 | 2.4320 | 2.4780 | 2.5360 |
| | 2.4690 | 2.6220 | 2.5370 | 2.5550 | 2.5680 |

**Monitors run at 0.1 x PEL**

Values for individual monitors for the Factorial Experiment

| | | | | |
|---|---|---|---|---|
| Run #1 - | 2.5483 | 2.7284 | 2.5571 | 2.7075 |
| Run #3 - | 2.2730 | 2.4082 | 2.5186 | 2.3496 |
| Run #14 - | 2.6815 | 2.7707 | 2.5794 | 2.6499 |
| Run #16 - | 2.3213 | 2.3546 | 2.3831 | 2.2919 |

---

## Summary

| PEL | Relative Standard Deviation | Degrees of Freedom |
|---|---|---|
| 0.1 | 3.3% | 12 |
| 0.5 | 4.1% | 27 |
| 1.0 | 3.3% | 27 |
| 2.0 | 3.3% | 39 |

**Average Values in μg/ppm/hr**

| Experiment | Average | RSD |
|---|---|---|
| Rate/Capacity | 2.6208 | 2.9% |
| Reverse Diffusion | 2.5132 | 3.5% |
| Factorial, 2 PEL | 2.6490 | 3.1% |
| Storage Stability | 2.5712 | 3.3% |
| Temperature | 2.6431 | 4.1% |
| Factorial 0.1 PEL | 2.5077 | 3.3% |
| **Overall average** | **2.5856** | **3.5%** |

**Overall sampling rate = 14.6 mL/min ± 1.0 mL/min**

## Appendix A

# Atmosphere Generation Apparatus

The instrument is designed to expose a known concentration of a chemical hazard to a passive sampler under controlled conditions of: 1. Concentration, 2. Temperature, 3. Humidity, 4. Wind Velocity Effect, 5. Time, and 6. Up to four multicomponent hazards.

**Description**

The instrument consists of:

1. an exposure chamber in which the wind velocity effects are controlled by internal rotating holders,

2. an air supply and purification train such that dry air is blended with saturated air under desired temperature conditions so as to provide air at a known flow and selectable humidity,

3. an injection system composed of precision motor driven syringes in which 1 to 4 chemical hazards can be injected into the flow system and in which the temperature of the injectors is closely controlled,

4. an electrical control system that controls the entire instrument operation,

5. the chamber concentration can be verified by either solid sorbent sampling tubes actively sampled or by gas analysis of the gas phase. The particular verification method used will depend on the analyte of interest.

Means are also included to check the relative humidity.

**Figure 1**
**Atmosphere Generation Apparatus**

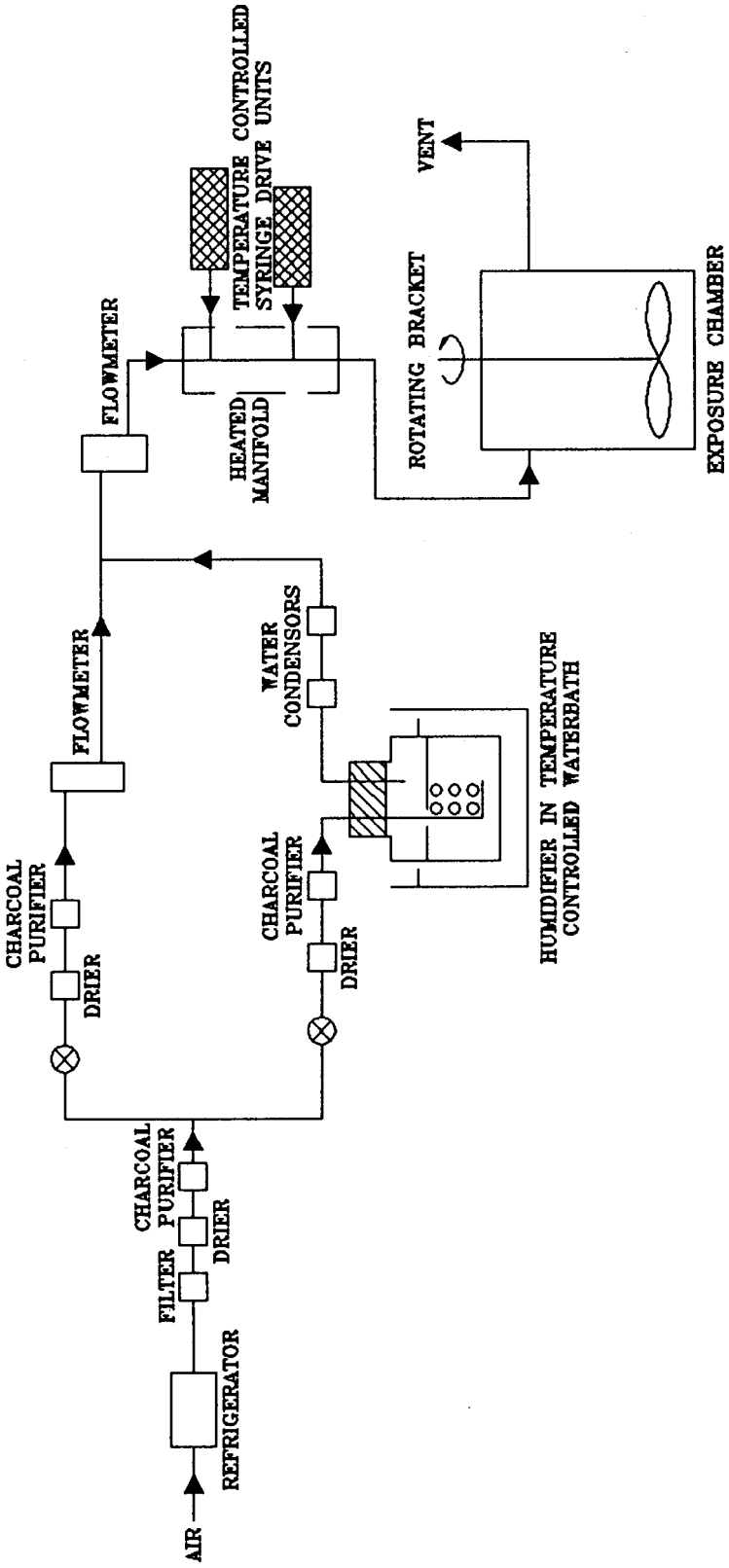
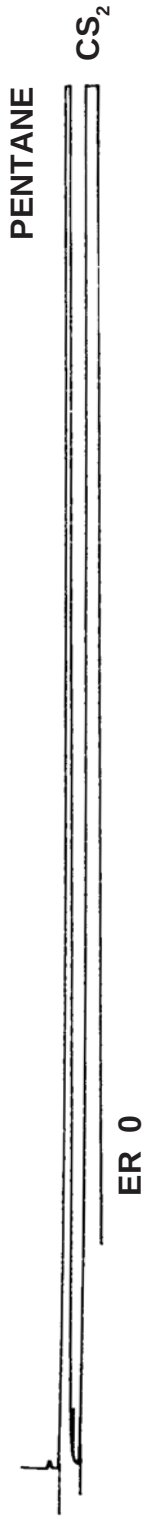


**Figure 2**
**Analytical Instrument**

**Sample Chromatogram**
**Pentane in $CS_2$**




**GC Conditions**

| | |
|---|---|
| **Column:** | 10 ft x 1/8 " 10% SP-2100 on 80/10 mesh Supelcoport |
| **Temperatures:** | Column 40° C<br>FID 60° C |
| **Carrier Gas:** | $N_2$ |
| **Injection:** | 1µL |

# Abbreviations

| | |
|---|---|
| C | Celsius |
| CL | confidence level |
| cm | centimeter |
| ml | milliliter |
| min | minute |
| g | gram |
| GC-FID | gas chromotography - flame ionization detector |
| h | hour |
| L | liter |
| LOD | limit of detection |
| MRST | maximum recommended sampling time |
| N.S. | not significant |
| PEL | permissible exposure limit |
| RH | relative humidity |
| TLV | threshold limit value |
| TWA | time-weighted average |
| RSD | relative standard deviation |
| SD | standard deviation |
| SRST | shortest recommended sampling time |
| STD | the appropriate exposure standard (OSHA PEL, ACGIH TVA , or NIOSH recommended standard) |
| S | second |
| $S_r$ | Pooled relative standard deviation |
| V | volume |

# Trademarks

Anasorb is a registered trademark of SKC Inc.
Tedlar is a registered trademarik of DuPont Corporation.
Porapak is a registered trademark of Waters Associates, Inc.

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# Validation of Pentane using SKC Passive Sampler 575-001

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# Contents