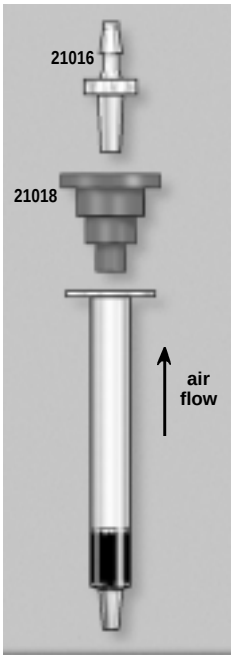
ASSET-32 Air Sampling Solid Extraction Tubes: Specifications – Performance – Validation Data – Round Robin Evaluation

Introduction

ASSET™-32 air sampling solid extraction tubes are an alternative to charcoal-containing glass sampling tubes, such as ORBO™-32 tubes. An ASSET tube is a single bed of coconut charcoal, equal to the front bed of a two-bed glass tube, packed in a polypropylene solid phase extraction tube. Polyethylene frits, rather than glass wool plugs, hold the adsorbent securely in place. This design enables the analyst to elute the adsorbed analyte(s) directly into a calibrated sample container, replacing the lengthy process of removing the adsorbent from the tube and desorbing the analyte(s) in solvent. Standard NIOSH and OSHA methods for sampling and analysis may be followed – the only difference is in the sample preparation. Reusable adapters for connecting an ASSET tube to a sampling pump are available separately. Advantages of this technology include:

- Time savings:
  – elution is faster than sample desorption
  – one adsorbent bed means one analysis per sample
- No glass – safe, convenient handling in field or laboratory
- Fewer adsorbent bed voids

Figure A. ASSET Tube and Adapter



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Specifications

Adsorbent:	80/100 mesh activated coconut charcoal
Bed Weight:	100mg
Tube Dimensions:	6.5cm x 5mm ID

Using ASSET Tubes

Sample Collection

1. Calibrate the sampling pump to the sampling rate recommended in the methodology to be followed.
2. Refer to Table 2 (page 3) for safe sampling volumes. When sampling in an unfamiliar environment, or in a high concentration environment, connect two ASSET tubes in series, using an adapter (Figures A and B).

   Using an adapter and fitting and appropriate sized tubing connect the ASSET tube(s) to the sampling pump in the flow direction indicated on the tube (Figure B).
3. Immediately after sampling seal both ends of the tube and place the tube in one of the white foil envelopes provided. Ship to the laboratory for analysis.

Figure B. ASSET Tubes Attached to Sampling Pump

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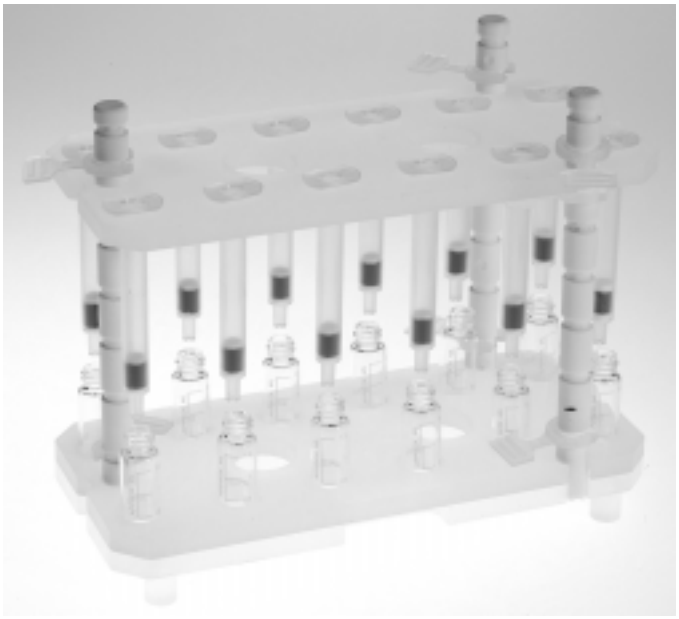
Sample Elution

1. Place the ASSET tubes in a universal elution rack (Catalog No. 21043-U, Figure C) or other suitable support. Align each tube with a graduated or volumetric sample receptacle, such as an autosampler vial or graduated test tube. To avoid sample loss when using autosampler vials, leave approximately 1/4 inch between the tip of the ASSET tube and the vial.
2. Add solvent to each ASSET tube and allow the solvent to elute through the tube by gravity, until 1.0mL of eluate is collected in the sample receptacle. If the solvent does not permeate the top frit, use a syringe with a luer tip and adapter to gently push the solvent into the adsorbent bed.

   Do not leave the tube or extract receptacle open to the atmosphere for an extended period of time.
3. After 1.0mL of eluate has been collected in the sample receptacle, quickly cap the receptacle, mix, and analyze following the standard analytical method.

Figure C. Desorption of ASSET Tubes in a Universal Elution Rack



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In-House Validation

Recovery

NIOSH Criterion: recovery >75%

NIOSH *Guidelines for Air Sampling and Analytical Method Development and Evaluation* (1) was used as a reference. ASSET tubes were compared side-by-side with equivalent ORBO tubes containing charcoal from the same lot of raw material. Tubes were spiked, in triplicate, with solvent, alcohol, and ketone analytes at four concentration levels, 20µg, 200µg, 1000µg, or 2000µg per tube, using a dynamic impinger technique. Approximately 3L of air was passed through each tube, at a flow rate of 100mL/min. Compounds chosen for this validation study were selected from the NIOSH Proficiency Analytical Testing (PAT) Program and were intended to represent a range of common airborne solvents. This spiking technique allowed determination of both collection efficiency and desorption efficiency. Appropriate NIOSH methodology was followed for sample preparation.

In general, recoveries for the three solvents were equivalent on the ASSET tubes and ORBO tubes (Table 1). There were inconsistencies across the concentration ranges, however, particularly at the lowest level. Recoveries for both alcohols were equivalent for ASSET and ORBO tubes, although % RSDs were high for ASSET tubes. Because recoveries dropped off at the 1000µg concentration, the 2000µg level was not evaluated. MIBK recoveries also were comparable on the two types of tubes. Acetone was the only compound for which recoveries were significantly lower from ASSET tubes than from ORBO tubes. Charcoal generally is not the adsorbent of choice for monitoring either airborne alcohols or ketones, however, and the high % RSDs and low recoveries among these results might be good indications of why this is so.

Table 1. Analyte Recovery: ASSET vs. ORBO Tubes

	Concentration	ASSET-32		ORBO-32	
Analyte	(µg/tube)	% Recovery	% RSD[1]	% Recovery	% RSD[1]
Solvents					
Ethyl acetate	20	84	10.6	120	10.3
	200	99	5.2	88	2.0
	1000	94	7.0	103	5.0
	2000	72	6.3	79	5.1
Trichloroethylene	20	121	7.2	149	12.9
(TCE)	200	104	4.4	89	1.1
	1000	98	5.7	110	6.4
	2000	89	6.2	109	6.0
Toluene	20	120	10.4	156	14.8
	200	108	3.7	84	1.2
	1000	97	4.9	107	7.1
	2000	87	6.8	108	6.2
Alcohols					
Ethanol	20	73	9.3	73	2.9
	200	98	27.3	99	7.1
	1000	3	0.0	3	0.0
Isopropanol	20	79	8.3	86	4.2
	200	106	22.6	116	4.8
	1000	31	18.0	27	9.8
Ketones					
Acetone	20	55	25.7	111	2.8
	200	71	9.2	100	10.8
	1000	6	27.0	16	15.4
Methyl isobutyl	20	102	10.8	98	11.4
ketone (MIBK)	200	83	12.7	97	12.9
	1000	83	3.2	76	29.0

[1]n = 3.

Capacity/Breakthrough

Known atmospheres were generated with a syringe pump apparatus, using humidified air (70-85% relative humidity) as the dilution gas. Each compound was collected simultaneously on three tandem pairs of ASSET tubes and one ORBO tube. One tandem ASSET pair was sealed at each of 3 time intervals (sample volumes), to bracket the 5% breakthrough time. The entire test was performed a minimum of two times.

Relative to maximum recommended sampling volumes (MRSV) listed in applicable NIOSH methods, safe sampling volumes (SSVs) for all chlorinated compounds tested were lower for ASSET tubes (Table 2). This could be an effect of the challenging sampling conditions (2x TLV, high sampling flow rate, high humidity).

Stability on Storage

NIOSH Criterion: <10% loss after 7 days storage at ambient temperature

Triplicate ASSET tubes were spiked with liquid mixtures of solvents, alcohols, and ketones, to yield a concentration of 200µg each analyte per tube. A small volume of air was drawn through the tube to move the analytes into the adsorbent bed. After overnight equilibration, the tubes were analyzed according to the schedule in Table 3. All three solvents (ethyl acetate, trichloroethylene, and toluene) met the NIOSH 7-day criterion. TCE and toluene were stable for 30 days, but ethyl acetate showed higher loss at 21 days. Of the ketones, acetone did not meet the 7-day criterion, but MIBK was stable for 30 days. Neither of the alcohols met the 7-day specification.

Background/Shelf Life

NIOSH Criterion: minimum 6 months

Supelco Specification: <10µg total hydrocarbons/tube (as toluene)

Data have been collected for 6 months to date, and data collection will continue to two years. Tubes are sealed and stored in appropriate packaging bags at room temperature. Triplicate samples are analyzed at regular time intervals. Figure D shows that, after 6 months, less than 2µg hydrocarbon background is detected under the GC conditions shown.

Pressure Drop

NIOSH Criterion: >10 hours operation with personal sampling pump

Supelco Specification: <8 inches water at 200mL/min:

Measured Pressure Drop at 200mL/min:

ASSET (single tube): 5 inches water

ASSET (two tubes): 10 inches water

ORBO: 4 inches water

Table 2. Breakthrough Volumes[1] for Typical Analytes on ASSET-32 Tubes

Analyte	Test Concentration (ppm)	Capacity[2] (µg)	Safe Sampling Volume[3] (L)	Method MRSV (L)[4]
Benzene	20	2940	46	30
n-Butyl acetate	300	17,100	12	10
Chloroform	20	1560	16	50
1,2-Dichloroethane	20	2750	34	50
Ethyl acetate	800	5770	2	10
Isopropanol	800	5510	2.8	3
Methyl ethyl ketone	400	8120	7	—
Methyl isobutyl ketone	100	11,500	28	10
Trichloroethylene	100	23,300	34	40
Toluene	200	13,000	17	8
1,1,1-Trichloroethane	700	7640	2.0	8
Trichloroethylene	200	11,200	10	30
o-Xylene	200	16,000	18	23

[1]Conditions: sampling rate: 200mL/min; temperature: 22°-26°C, relative humidity: 70-85%

[2]Capacity at safe sampling volume.

[3]Safe sampling volume (SSV) = 2/3 breakthrough volume (determined at 2x TLV).

[4]Maximum recommended sampling volume in NIOSH method for glass tube.

Table 3. Stability of Analytes on Storage

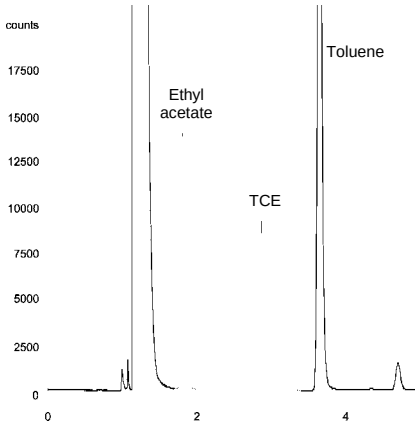
Storage Conditions	Analyte / % Recovery[1]						
	Acetone	Ethanol	Ethyl Acetate	Isopropanol	MIBK	TCE	Toluene
0 days	71	98	99	106	83	104	108
7 days / 22°C	30	48	99	55	98	104	101
10 days / 4°C	31	—	94	—	109	96	92
14 days / 4°C	28	54	103	61	98	107	109
21 days / 4°C	32	77	84	88	109	104	104
30 days / 4°C	39	—	80	—	96	98	108

[1]Mean values for 3 tubes; 200µg each analyte spiked onto tube.

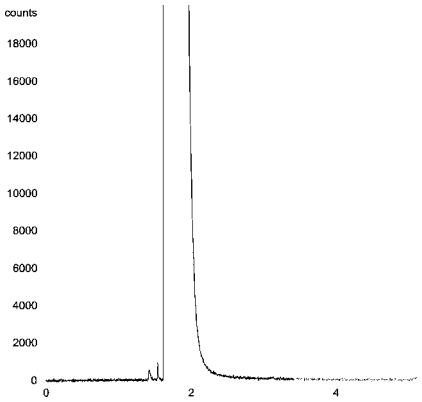
Figure D. ASSET Tubes Show Minimal Background after 6 Months Storage

Column: SUPELCOWAX™ 10, 30m x 0.53mm ID, 0.5µm film (**Cat. No. 25325**)
Carrier: helium, 8mL/min
Oven: 50°C (4 min) to 100°C at 8°C/min
Det.: FID, 300°C
Inj.: 1µL, direct (packed inlet liner), 220°C

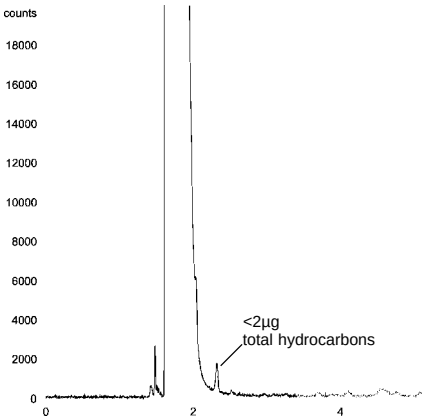
Calibration Standard (20µg/mL each analyte)



Carbon Disulfide Eluent



Blank ASSET-32 Tube After 6 months storage



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Round Robin

Participating Laboratories

DataChem Laboratories – Galson Laboratories – Kemper-NATLSCO Lab Corp Analytics – Lancaster Labs – NIOSH – Wisconsin Occupational Health Lab

Overview

The round robin consisted of 3 duplicate pairs of tubes spiked with a liquid mixture of 3 compounds (ethyl acetate, trichloroethylene, and toluene) in carbon disulfide at 40µg, 200µg, or 1000µg each, plus 1 blank tube. A small volume of air was drawn through each tube to move the analytes into the adsorbent bed. Participants were asked to analyze the tubes within 7 days of receipt, following the instructions provided. Figures E, F, and G show the spread of the data among laboratories and between tubes. The Y axis scale is set at control limits of 3 standard deviations.

Results

Overall mean recoveries were good, and % RSDs were reasonable for an interlaboratory study. Recoveries often were correlated with the analyte concentration on the tube. The lowest spiked concentration, 40µg, seemed to produce the greatest variability, and may have been below the typical range of PAT samples. In general, reproducibility was good between duplicate tubes. No conclusions were made regarding individual laboratory performance.

Ordering Information

Description	Qty.	Cat. No.
ASSET-32 Sampling Tubes*	50	**28301-U**
ASSET-32 Sample Pack**	5	**2042-U**
Adapters	10	**21018**
Male Luer Fittings for 1/8" tubing	20	**21016**
Male Luer Fittings for 3/16" tubing	20	**23364**
Male Luer Fittings for 1/4" tubing	10	**24856**
Universal Elution Rack	1	**21043-U**

*Storage pouches included; order adapters separately.

**Adapters included.

Reference

1. *Guidelines for Air Sampling and Analytical Method Development and Evaluation* NIOSH Technical Report, May 1995. (DHHS (NIOSH) Publication No. 95-117.)

   Reference not available from Supelco. Request from: NIOSH, Mail Stop R2, 4676 Columbia Parkway, Cincinnati, OH 45226 USA (Tel. 513-841-4354).

Trademarks

ASSET, ORBO, SUPELCOWAX – Sigma-Aldrich Co.

XAD – Rohm and Haas Co.

Figure E. Round Robin Results: Ethyl Acetate

Overall Mean Recovery: 89%
Overall Std. Dev.: 17µg
Overall RSD: 19%
Tubes 1&4: 40µg, Tubes 2&6: 200µg, Tubes 3&5: 1000µg

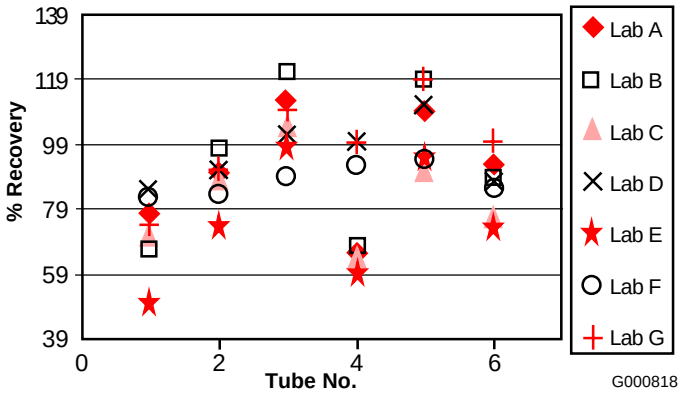


Figure F. Round Robin Results: Trichloroethylene

Overall Mean Recovery: 103%
Overall Std. Dev.: 15µg
Overall RSD: 14%
Tubes 1&4: 40µg, Tubes 2&6: 200µg, Tubes 3&5: 1000µg

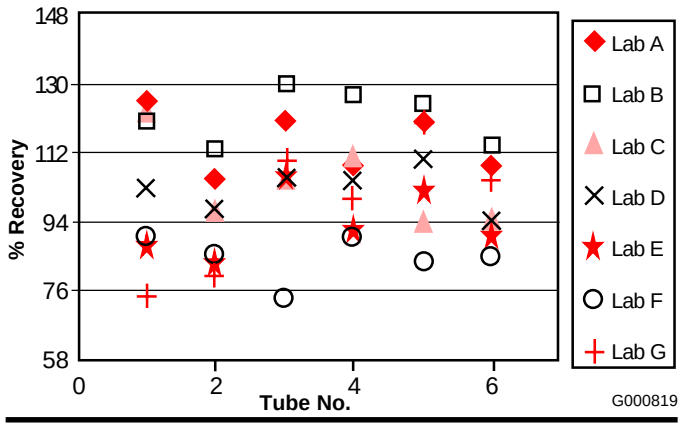
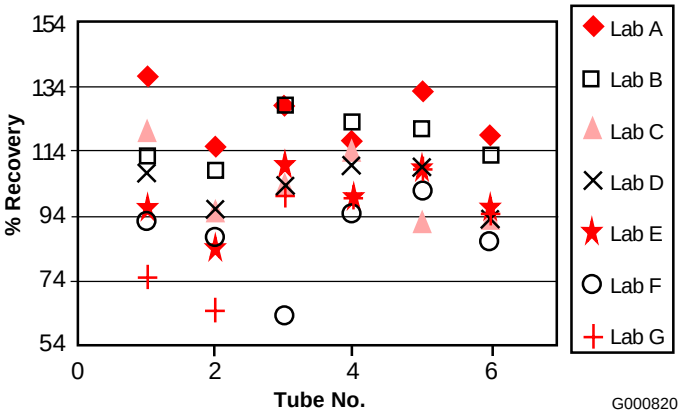


Figure G. Round Robin Results: Toluene

Overall Mean Recovery: 104%
Overall Std. Dev.: 16µg
Overall RSD: 16%
Tubes 1&4: 40µg, Tubes 2&6: 200µg, Tubes 3&5: 1000µg



Without a back-up bed how can I be assured that I don't have breakthrough?
Breakthrough studies have been completed on 13 common solvents, such as those included in the Proficiency Analytical Testing Program. The safe sampling volumes recommended in this report have a built-in measure of safety: they represent 2/3 of the breakthrough volume. In addition, the breakthrough study was conducted under worst-case conditions: 2x TLV, high humidity (70-85% relative humidity), and a fast sampling rate (200mL/min).

An option is to collect *distributed volume tube pairs*. This technique, described in US EPA Method TO-17 for volatile organic compounds, involves using two tubes in parallel for the same period of time at two different sampling rates. Sampling for four hours with one tube at 50mL/min and one tube at 200mL/min, for example, would give you a 12L sample and a 48L sample, respectively. If the difference for the analyte concentration between the two tubes is <25%, breakthrough has not occurred.

Alternatively, when sampling in an uncharacterized atmosphere, or in a high concentration atmosphere for which a secondary tube is recommended, simply connect two ASSET tubes in tandem, using an adapter.

How do I connect an ASSET tube to my sampling pump? *Will it provide a good seal*?
Reusable adapters and connectors to fit 1/8", 3/16" or 1/4" tubing can be ordered separately. These adapters safely and conveniently connect the tube to tubing and sampling pump, while providing leak-tight connections.

Sample preparation is very different from what I'm used to. It's not convenient to bring extracts to known volume. How can I make it easier? Won't I lose sample when I try to elute directly into an autosampler vial?
An elution rack, as shown in Figure C, provides a convenient and fast way to elute up to 12 samples simultaneously. Using the appropriate rack set-up, no adjustments are required when aligning the tube and the collection vial. Graduated autosampler vials enable you to bring the extract to a known volume without sample transfer. Simply fill the ASSET reservoir completely with solvent and allow it to drain completely into the vial. This will yield approximately 0.9mL. Then add solvent directly to the vial to bring the volume to 1.0mL. To prevent sample loss during elution, be sure to have the tip of the ASSET tube positioned slightly above the vial.

Won't there be contamination from the polypropylene tube?
For routine sample elution, the tube should not introduce any contamination. Carbon disulfide will leach components from the polypropylene if left in the tube for a long period of time (30 minutes or more). Long residence time of other solvents, such as methanol, in the tube did not increase background levels.

Will there be loss of analyte during elution, due to volatility and heat generation?
Based on our recovery data and comparison with glass tubes, analyte losses are insignificant. To determine loss through heat generation, we performed a side-by-side comparison of "frozen" tubes and tubes at room temperature. There was no difference in recovery.

Will I need to perform my own method validation?
That will depend, to a large extent, on your laboratory QA requirements and on what compounds you're collecting and analyzing. As a minimum, we recommend desorption efficiency determinations. All Supelco validation data presented here, and the interlaboratory round robin information, are intended to provide reasonable confirmation of ASSET tubes' equivalent performance to glass; they are not performance specifications. Bear in mind that the adsorbent and analytical procedure are not changed from methodology, the only change is in the manner in which the tubes are prepared for analysis.

Does this mean that all solvent desorption tubes can be made into ASSET tubes?
Not necessarily. We are working to validate and introduce other adsorbents, such as silica gel and XAD®-2, in ASSET tubes. Methods that require several steps or reactions in the sample preparation process may not be applicable to ASSET technology.

Will ASSET tubes be approved by NIOSH and OSHA?
NIOSH participated in the ASSET round robin and OSHA has been asked to perform their own independent evaluation. While response has been favorable, it is unlikely that either agency will expend the time and effort to perform an extensive validation on a coconut charcoal sampling device. On the other hand, a high level of user interest could re-direct their thinking.

How much time am I really saving by using ASSET tubes?
The time saving is easily half the time required to extract a glass tube. There is no sample preparation with an ASSET tube – the adsorbent does not have to be removed from the tube and transferred to a vial. The desorption step for a glass tube equates to the elution step for an ASSET tube, but gravity elution through an ASSET tube takes 2-3 minutes, then the sample is ready for injection, as opposed to a 30-minute desorption of the contents of a glass tube.

The real time savings come in preparing multiple samples. Although there is initial set-up time to using an elution rack, it subsequently takes the same amount of time to elute 12 ASSET tubes as it does to elute 1, which certainly is not the case with glass tubes.