



Characterization of Carbon SPE for the Extraction of Polar Analytes

Cory Szafranski, Lydia Nolan, and William R. Betz

Supelco, Supelco Park, Bellefonte, PA 16823 USA

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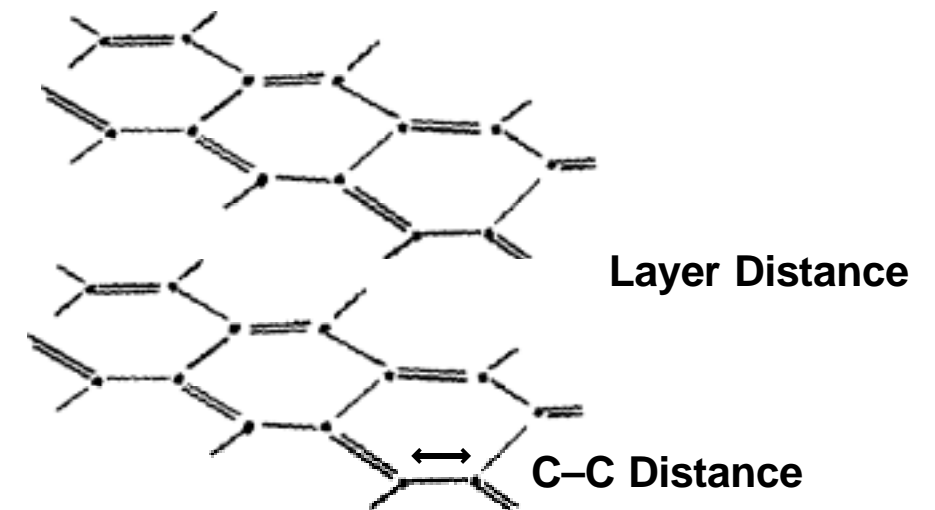
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Introduction

The purpose of these studies was to define the possible types of interactions for carbon-based solid phase extraction (SPE) adsorbents and to determine how the performance of carbon materials might differ from that of a silica-based, polymerically bonded octadecyl adsorbent. We compared the physical characteristics of the different sorbents and determined the dynamic breakthrough capacities of several new carbon-based adsorbents for SPE, using dilute aqueous sample systems. Several types of polar organic compounds were selected as model analytes to examine possible differences in the mode of interaction between analyte functional groups and the adsorbent. (These analytes – aliphatic and aromatic acids, amines, and alcohols – are difficult to retain under reversed phase conditions.) We also compared typical GC-FID backgrounds from the tubes to determine which sorbent provides cleaner extracts. In addition to these studies, methods are presented for the extraction of drugs of abuse from biological fluids and fractionation of acidic and base/neutral pesticides from drinking water or groundwater, using carbon-based SPE tubes.

Structural Classification of Carbons

Carbon Class	C–C Distance (nm)	Layer Distance (nm)
Amorphous (hexagonal)	0.139	—
Turbostratic	0.142	0.365
Graphitic	0.142	0.335
Diamond (cubic)	0.155	—

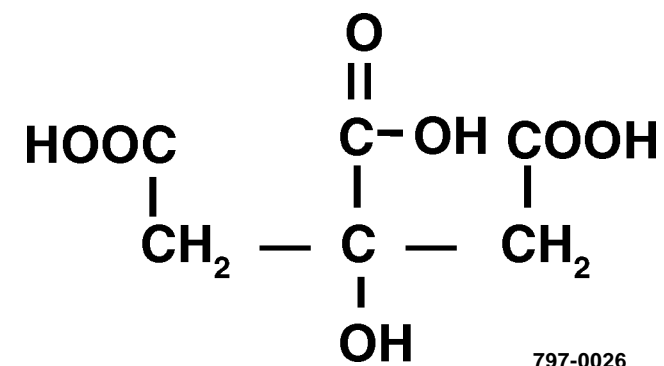


Adsorbents Used in the Study

Adsorbent	Description	Mesh Size	Surface Area (m ² /g)	Porosity (cc/g)	pH
ENVI™-Carb	graphitized carbon black	120/400	100	none	9.5
ENVI-Carb X	graphitized carbon black	120/400	240	0.15	9.7
Carboxen™ 1002	carbon molecular sieve	60/100	1100	0.94	10.7
ENVI-18	C18 polymerically bonded to silica	120/400	500	0.80	7.2

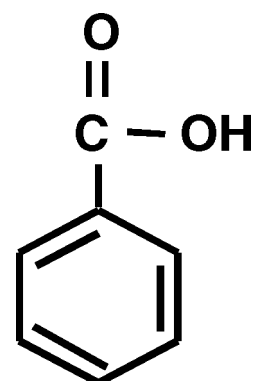
Analytes Studied

Citric Acid



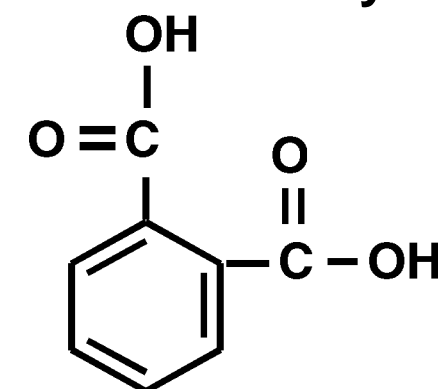
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Benzoic Acid



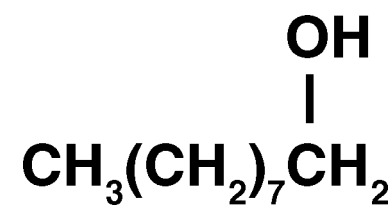
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Phthalic Acid
(1,2-Benzenedicarboxylic Acid)



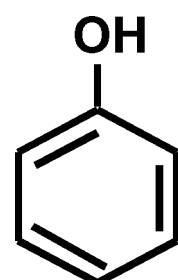
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1-Nonanol



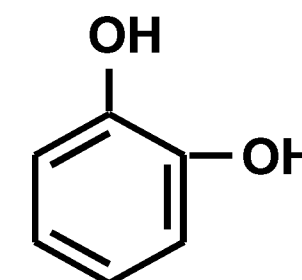
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Phenol



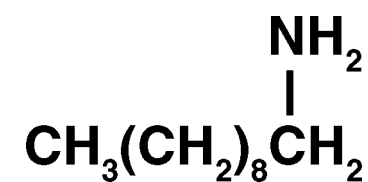
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Catechol



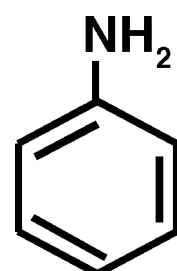
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Decylamine



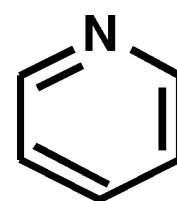
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Aniline



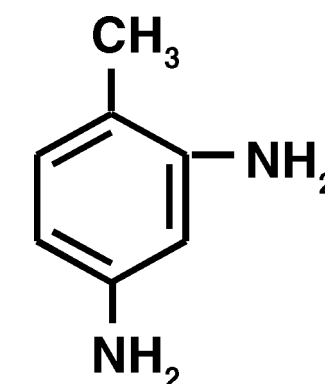
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Pyridine



797-0036

2,4-Diaminotoluene



797-0034

Materials and Methods

Materials

Adsorbents were packed, dry, into 5cm x 4.6mm ID HPLC hardware. The columns were conditioned with methanol and water, and were cleaned with acetonitrile, methanol, and water after each test.

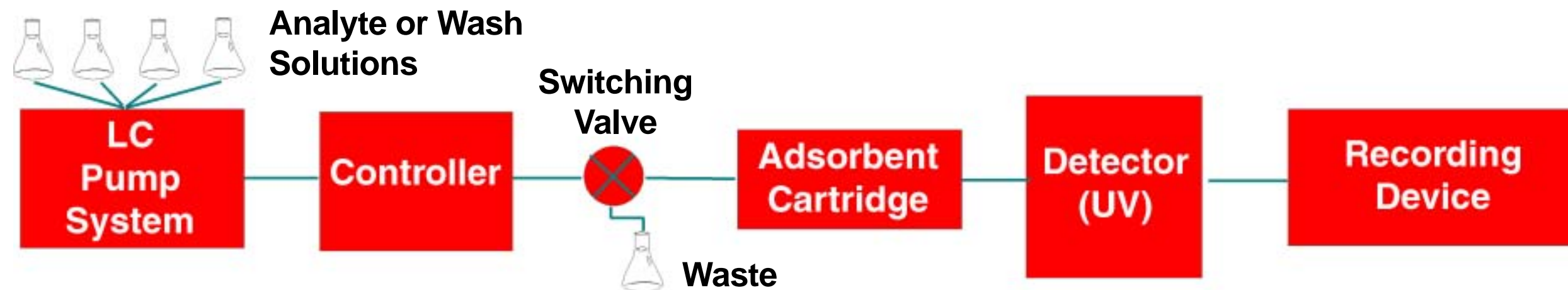
The dynamic testing system is shown in Figure A.

All analyte solutions were in water alone, with no organic component, buffer, or pH adjustment, unless 1% methanol was required to dissolve the analyte. Isotherms were plotted for selected analytes to ensure that the concentrations used were within the equilibrium range of ENVI-Carb.

Analysis

Flow through the cartridges was constant at 2mL/min. Calculations of breakthrough capacity were based on the time until a response was obtained at the UV detector. Breakthrough was measured at 50% of the maximum of the response curve, with corrections for dead volume in the cartridge and test system. *Maximum capacity values reported here are a relative measure of retention, not absolute values which apply to routine SPE extractions. In future studies we will investigate the correlation of these systems to each other.*

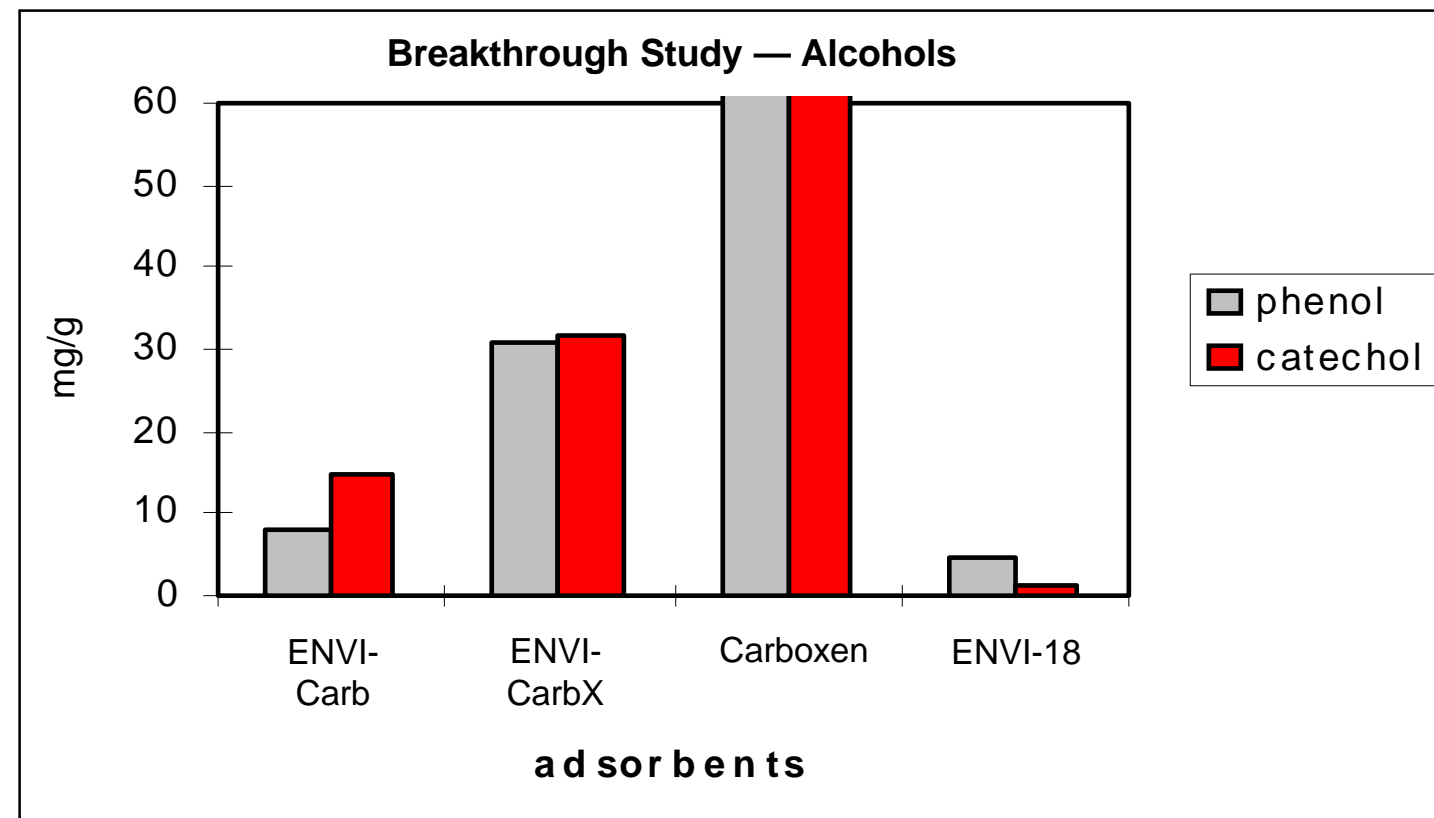
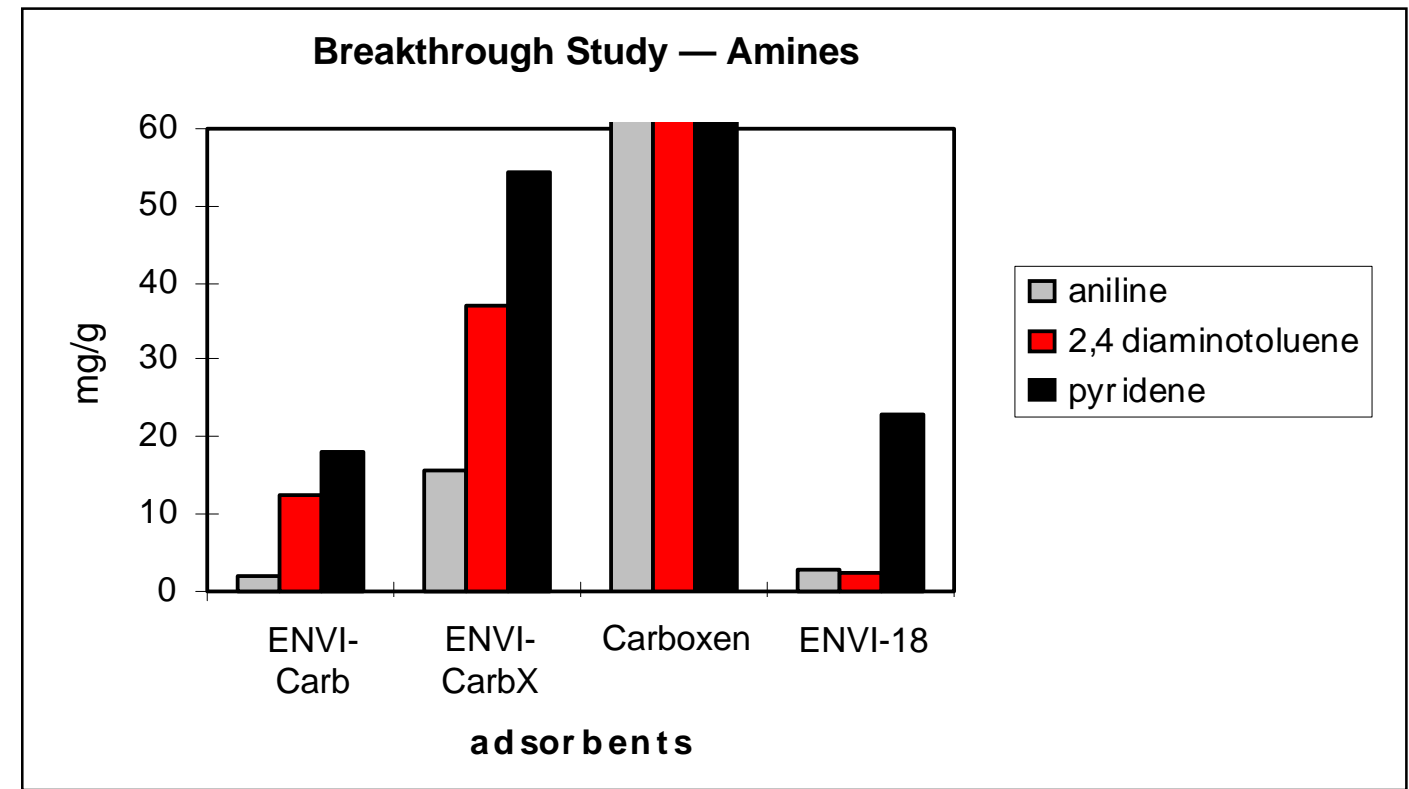
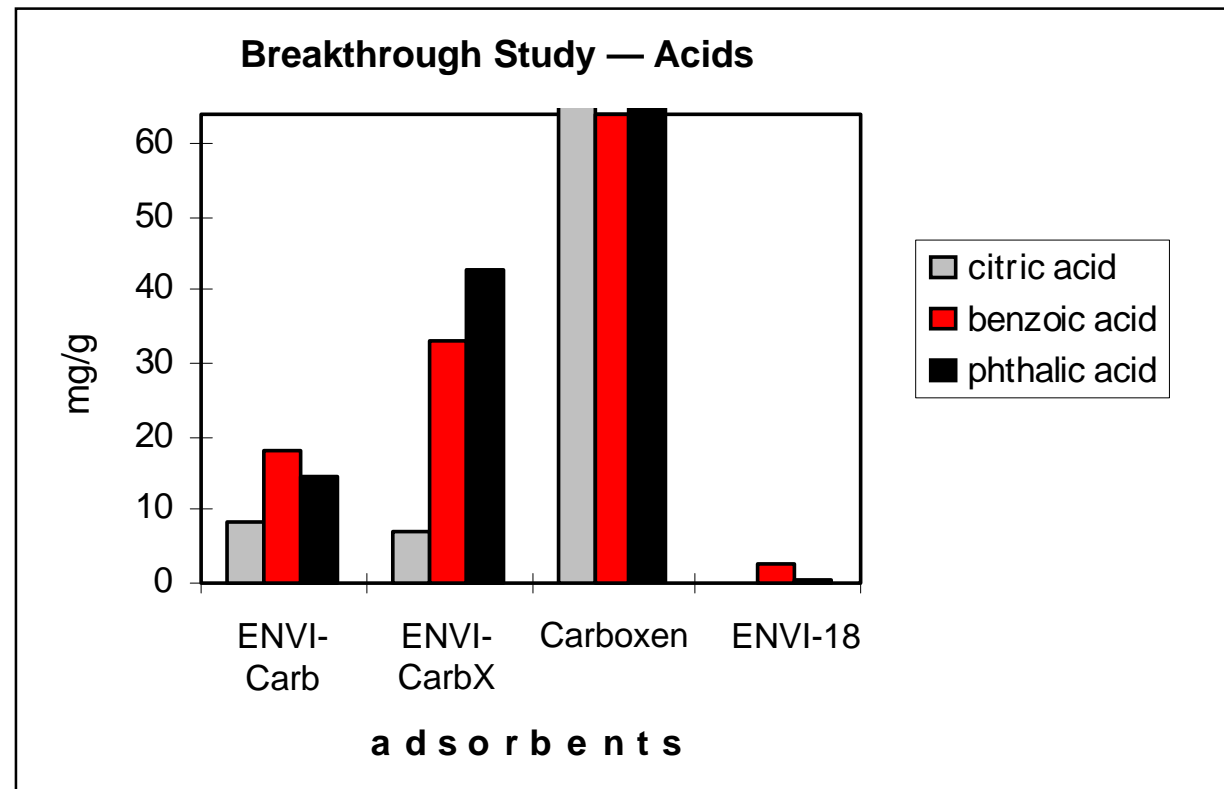
Figure A. Dynamic LC Testing System



Summary of Capacity Study

Analyte	Breakthrough Capacity (mg/g)			
	ENVI-Carb	ENVI-Carb X	Carboxen 1002	ENVI-18
Citric acid	8.5	7.2	>171	0.1
Benzoic acid	18.2	33.1	>64.1	2.5
Phthalic acid	14.7	43	>171	0.6
Phenol	8.2	30.7	>100	4.6
Catechol	14.8	31.9	>100	1.4
Aniline	2.2	15.9	>175	2.8
2,4-Diaminotoluene	12.3	37	>127	2.5
Pyridine	18.2	54.2	>154	23.1

Breakthrough Capacities



Adsorbent Extractables/GC-FID Backgrounds

Figure B shows typical GC-FID backgrounds of extracts from the ENVI-Carb and ENVI-18 sorbents. 1mL of either methanol or methylene chloride was passed through unconditioned 250mg ENVI-Carb or 500mg ENVI-18 adsorbents, and was collected and analyzed by GC-FID. Although there was a difference in bed weights used for the experiments, the extracts from the carbonaceous adsorbent look significantly cleaner than those from the bonded silica.

Figure B. Adsorbent Extractables/GC-FID Background Chromatograms

Column: PTA-5, 30m x 0.25mm ID, 0.5 μ m film

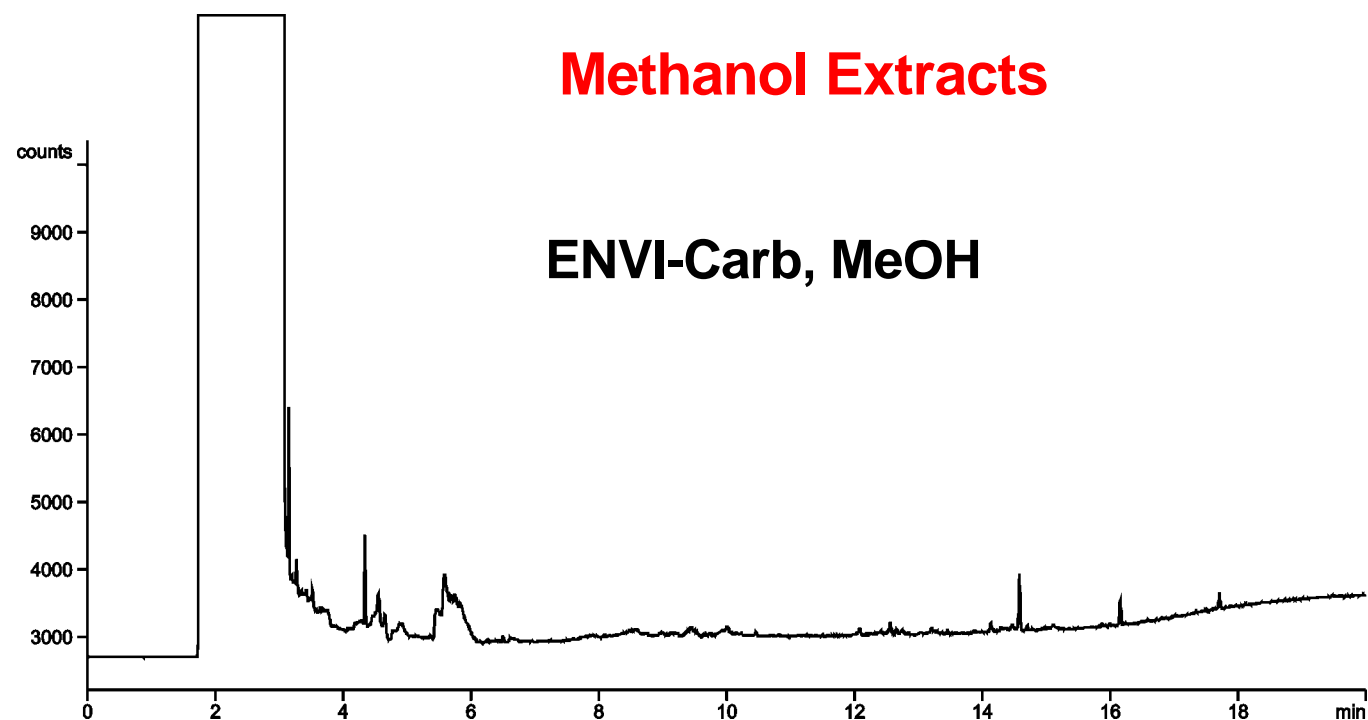
Oven: 50°C (2 min) to 280°C at 15°C/min (2.67 min)

Carrier: He, 0.7mL/min (set at 200°C)

Det.: FID, 300°C

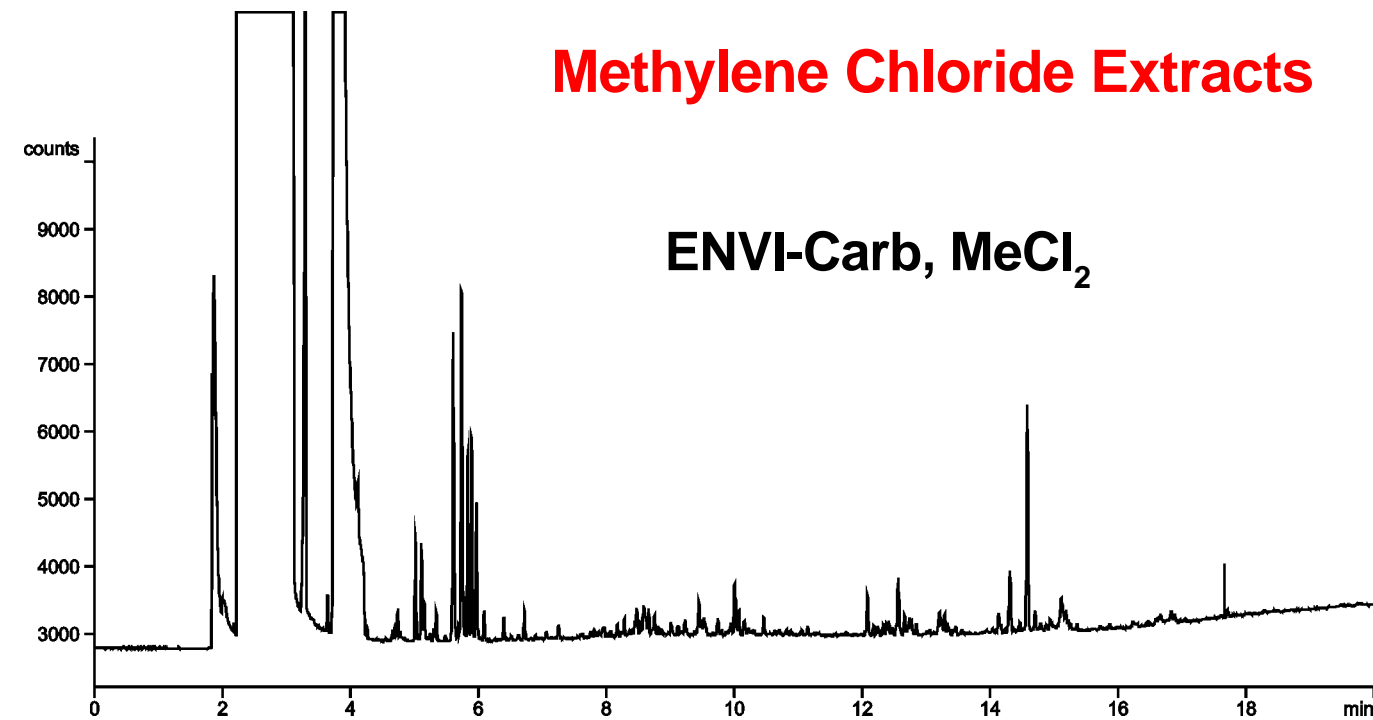
Inj.: 1 μ L, splitless, 175°C

Methanol Extracts



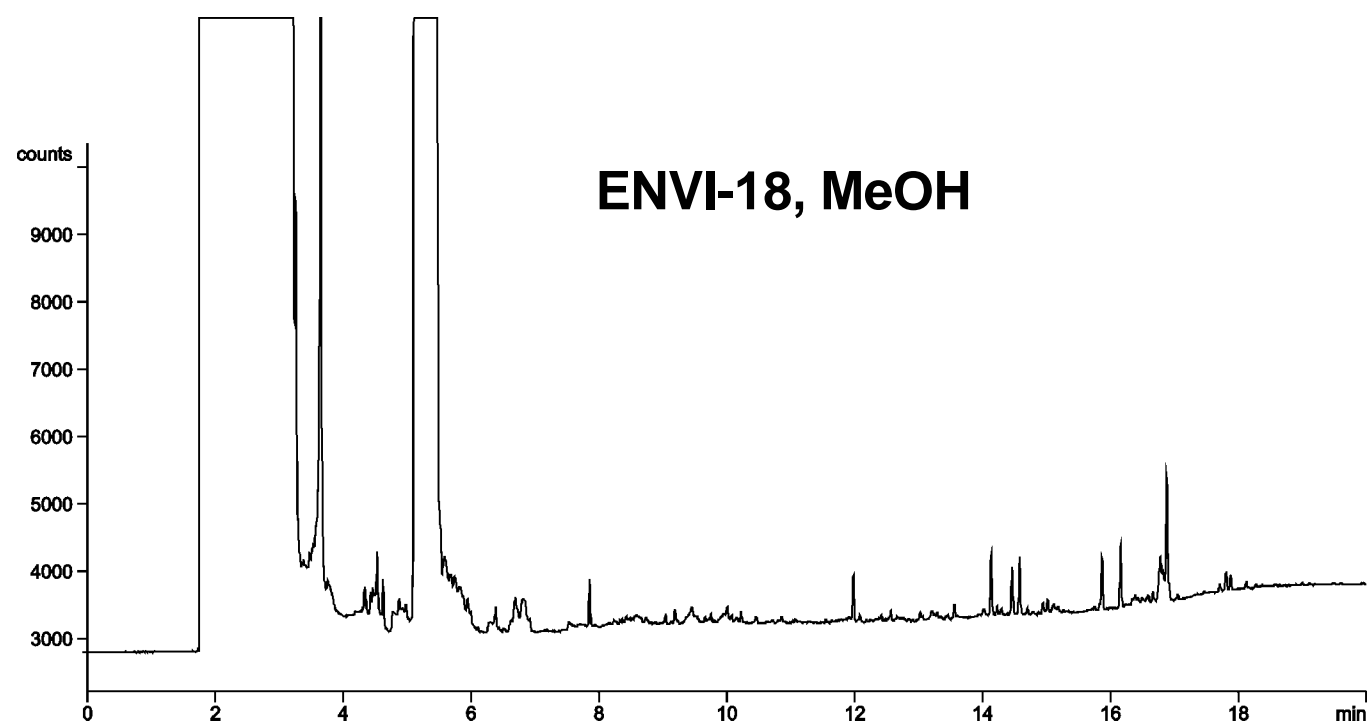
ENVI-Carb, MeOH

Methylene Chloride Extracts

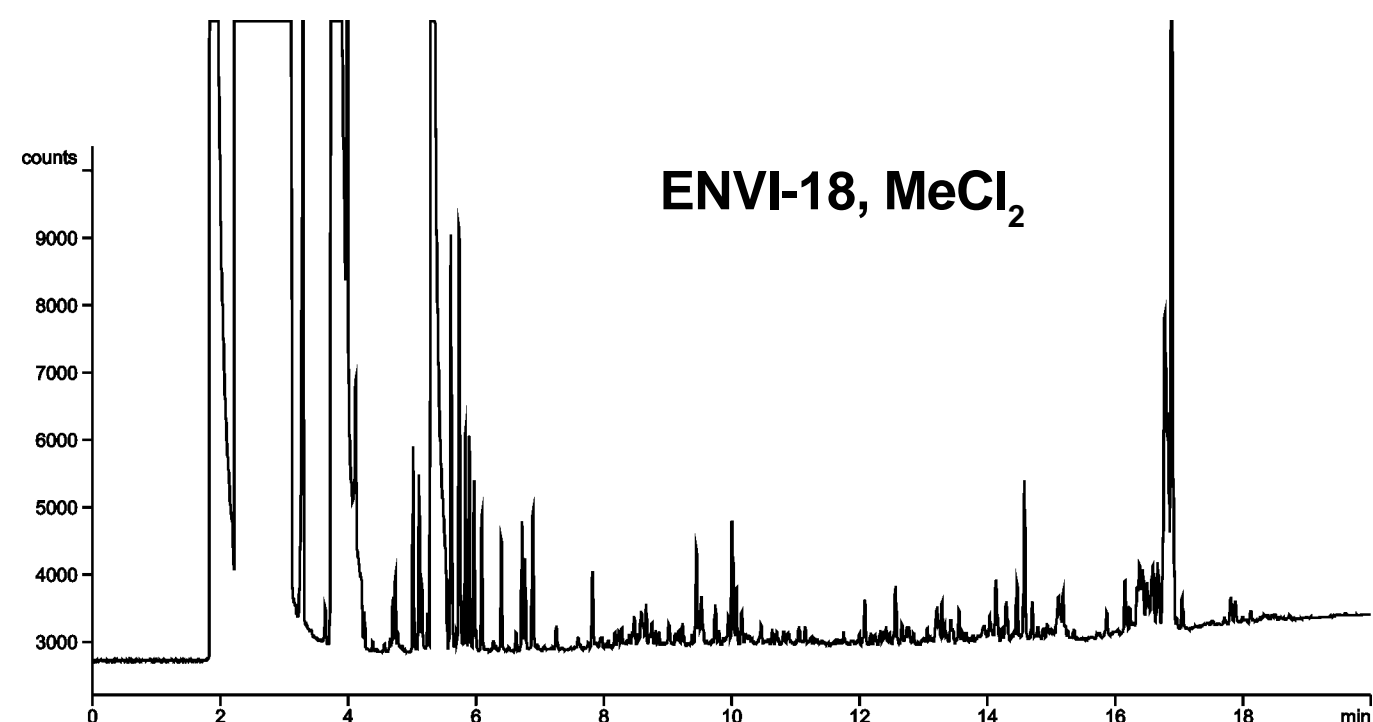


ENVI-Carb, MeCl₂

ENVI-18, MeOH



ENVI-18, MeCl₂



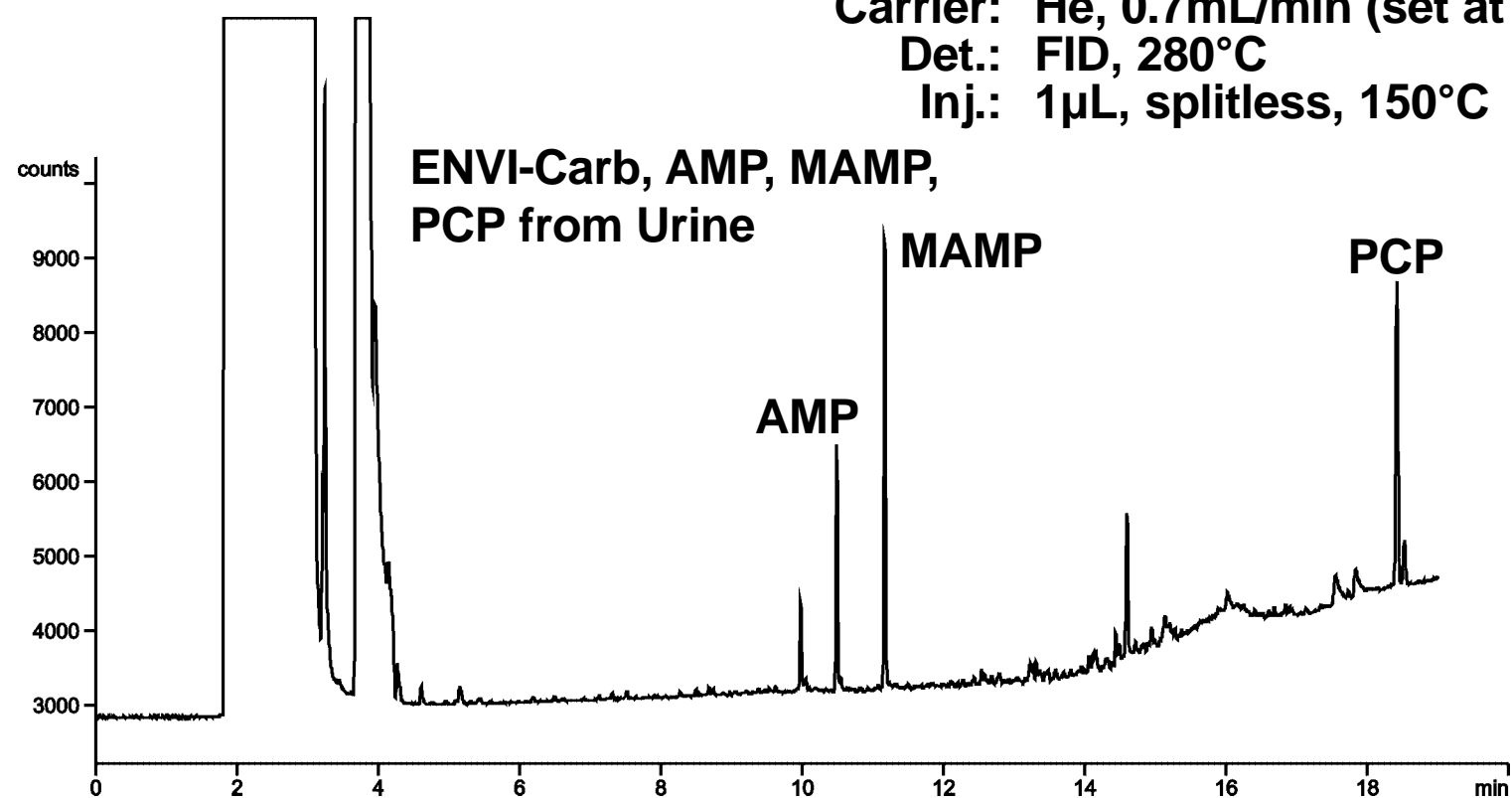
SPE Procedure for Extracting Amphetamine (AMP), Methamphetamine (MAMP), and Phencyclidine (PCP) from Urine

- 1. Condition the ENVI-Carb tube (3mL, 250mg packing) or the ENVI-18 tube (3mL, 500mg packing) with 2mL methanol, then 2mL buffer (76:24 0.05M K_2HPO_4 :0.05M K_3PO_4 , pH ~11.0).**
- 2. Pass 2mL of urine (diluted 1:1 with the same buffer, and adjusted to pH 11.0-11.3 with 10M KOH), spiked with AMP, MAMP, and PCP.**
- 3. Rinse the tube with 2mL buffer, then 2mL deionized water.**
- 4. Dry the tube with clean nitrogen for 10 minutes.**
- 5. Pass 2 x 1mL 80:20 methylene chloride:methanol aliquots through the tube. Collect both aliquots in the same vessel. Evaporate to 1mL and inject onto GC.**

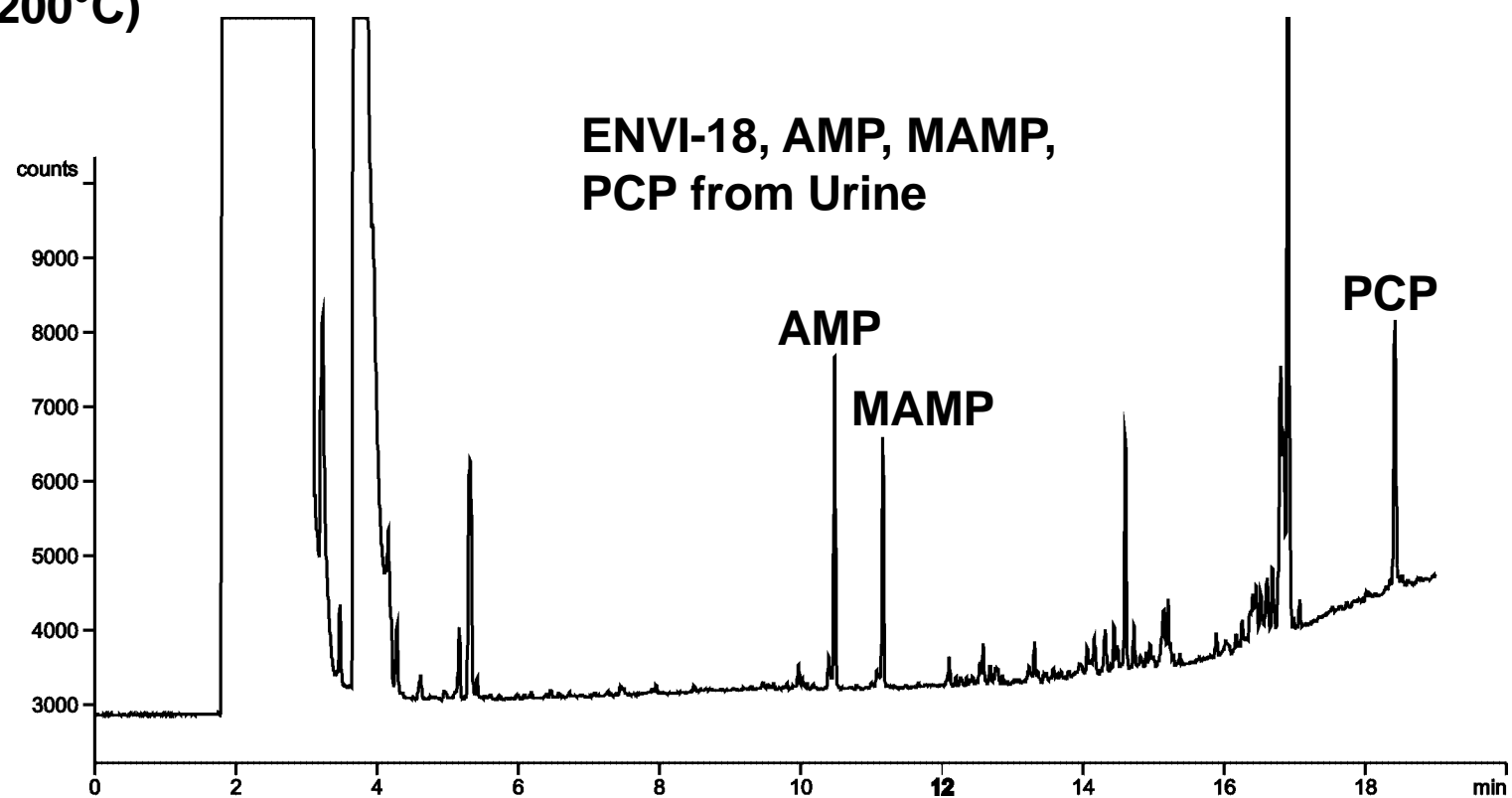
Figure C. Amphetamine (AMP), Methamphetamine (MAMP), and Phencyclidine (PCP) from Urine

Column: PTA-5, 30m x 0.25mm ID, 0.5 μ m film
Oven: 50°C (2 min) to 280°C at 15°C/min (1.67 min)
Carrier: He, 0.7mL/min (set at 200°C)
Det.: FID, 280°C
Inj.: 1 μ L, splitless, 150°C

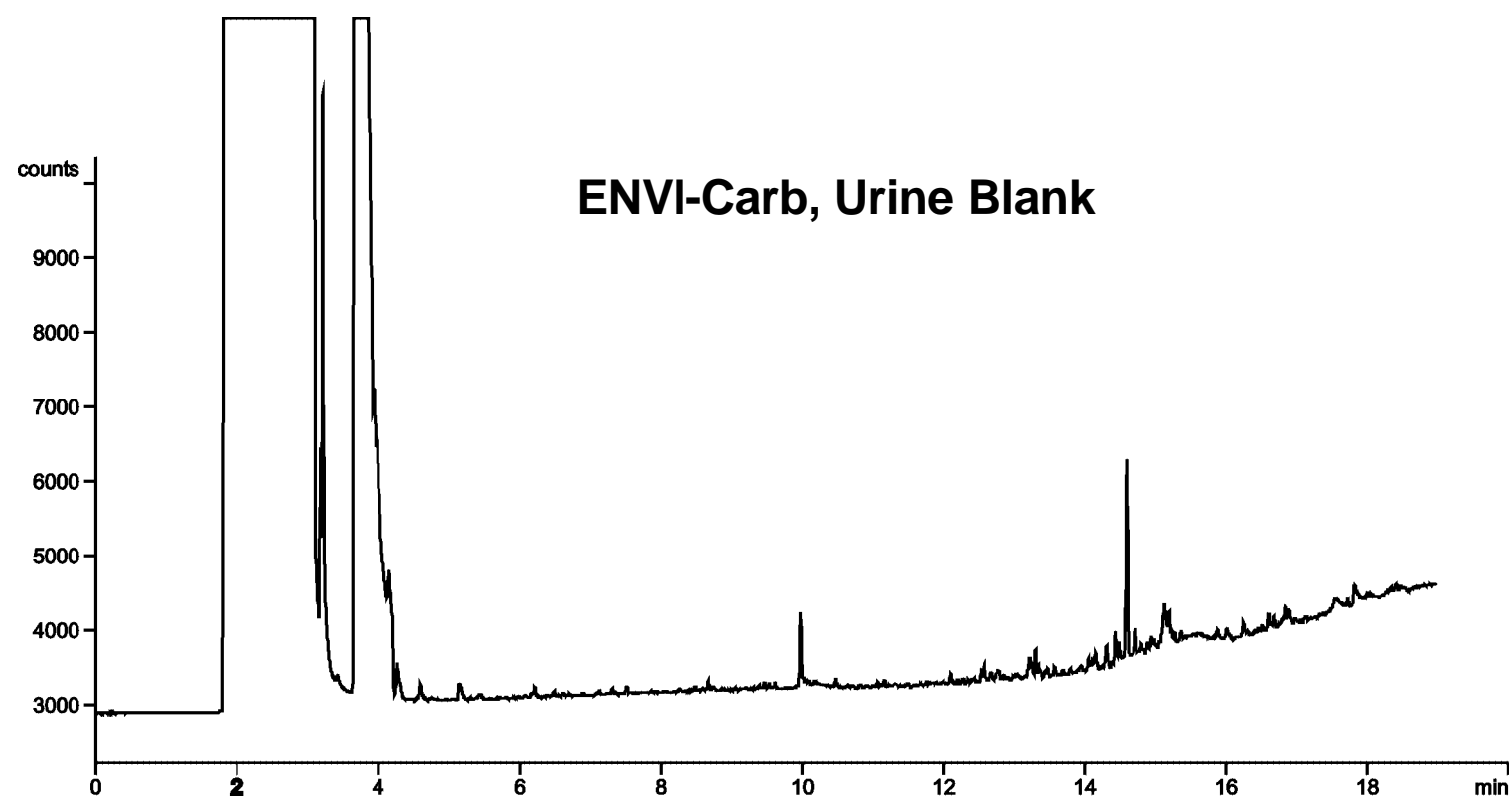
ENVI-Carb



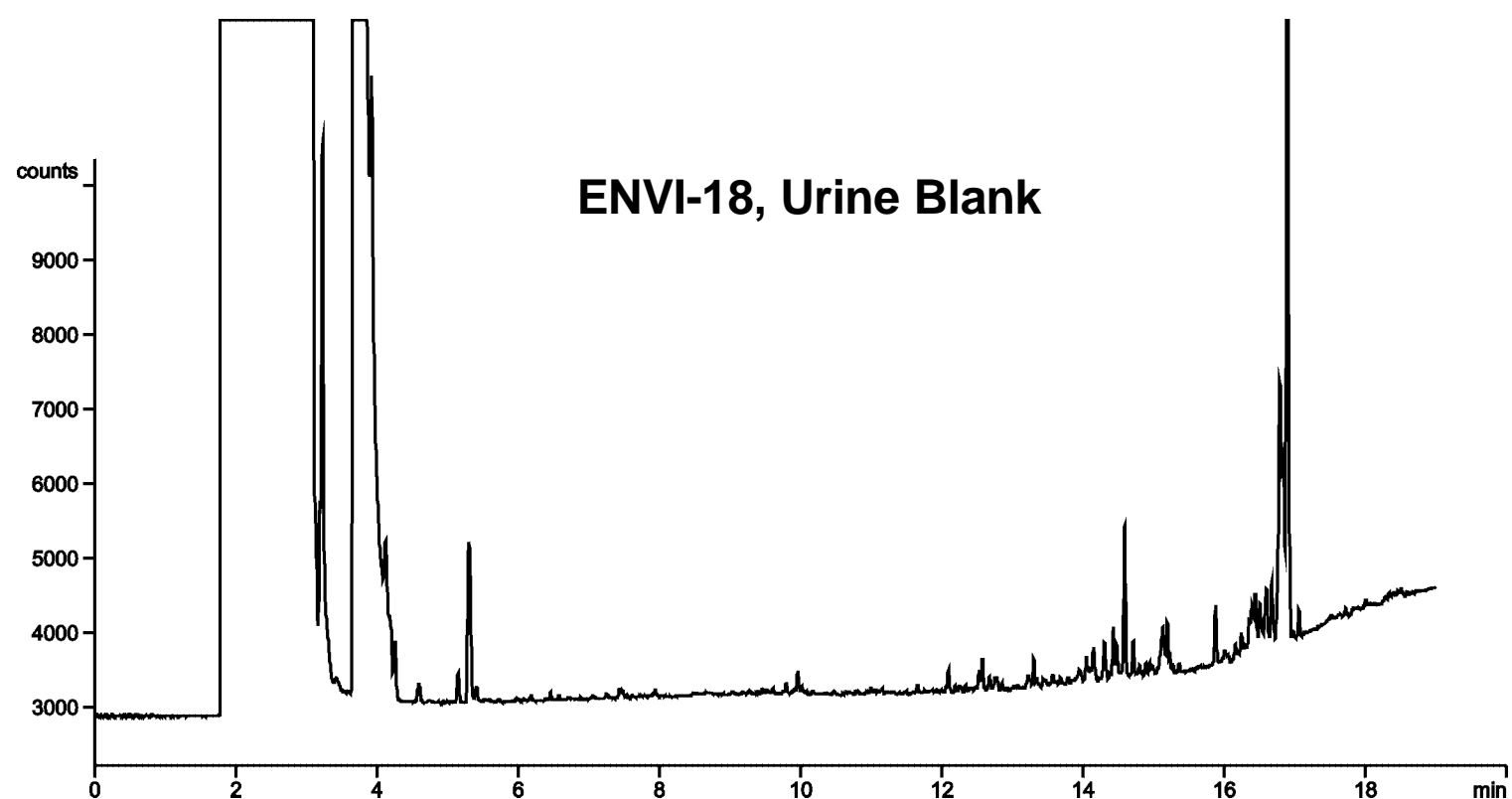
ENVI-18



ENVI-Carb, Urine Blank



ENVI-18, Urine Blank



Recoveries of Amphetamine (AMP), Methamphetamine (MAMP), and Phencyclidine (PCP) from Urine

Drug	ENVI-Carb % Recovery (\pm Std. Dev.)	ENVI-18 % Recovery (\pm Std. Dev.)
Amphetamine (AMP)	41.2 (\pm19.2)	62.3 (\pm9.6)
Methamphetamine (MAMP)	72.4 (\pm7.5)	49.2 (\pm9.4)
Phencyclidine (PCP)	96.2 (\pm23.2)	83.9 (\pm16.2)

Automated Procedure for Extracting Pesticides from Groundwater

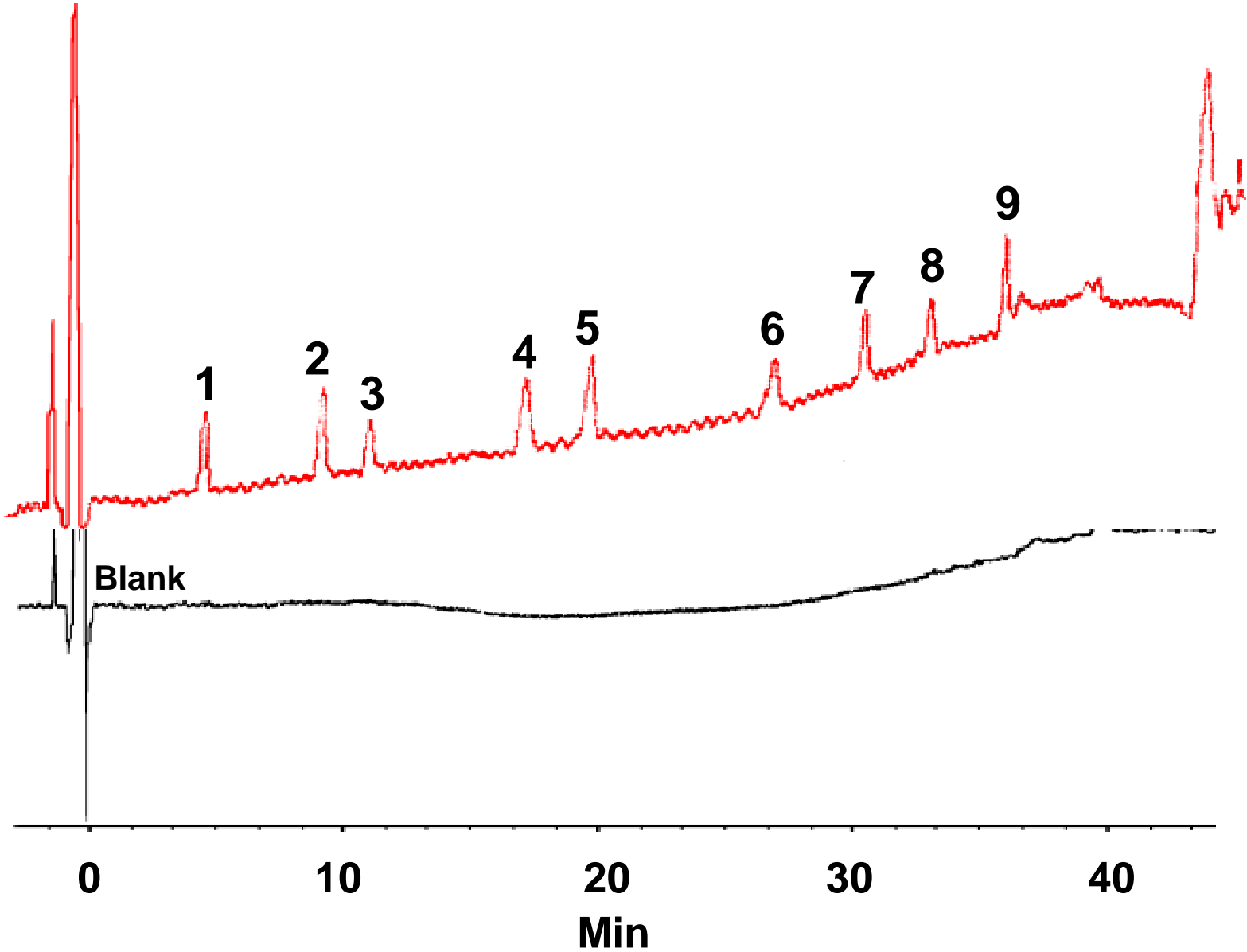
1. Condition ENVI-Carb SPE tube (3mL, 250mg packing) with 5mL methylene chloride:methanol, 4:1, then 2mL methanol, then 10mL 2% acetic acid.
2. Pass 400mL water sample through tube.
3. Rinse tube with 10mL water.
4. Dry tube with clean nitrogen for 5 minutes.
5. *Recovery of Base/Neutral Pesticides*
Pass 1mL methanol, then 2 x 2mL methylene chloride:methanol, 4:1 through tube. *Collect all 3 eluates (5mL total) in same recovery vessel.*
6. *Recovery of Acidic Pesticides*
Pass 2 x 2mL methylene chloride:methanol, 3:2 (made basic with 0.016mol/liter KOH) through same tube. *Collect both eluates (4mL total) in same recovery vessel. Add 350µL 2% trifluoroacetic acid in water to neutralize.*
7. Dry recovered eluates, then reconstitute each with 1mL methanol. Filter. Analyze by RP-HPLC.

Procedure provided by C.L. Ritland, S. Cohen, C.J. Mason, Nevada Div. Agriculture, Reno, Nevada, USA.

Figure D. Base/Neutral Pesticides in Water

Column: octadecylsilyl reversed phase, 25cm x 4.6mm ID, 3µm particles
Mobile Phase: gradient, A = water, B = acetonitrile
Flow Rate: 1.0mL/min
Det.: photo diode array, monitor 225nm
Inj.: 20µL of extract (see procedure) (spiking level: 3x est. detection limit)

Gradient Program	
Time (Min)	% B
0.20	20
32.00	40
48.00	70
54.00	70
54.01	100
60.00	100
60.01	20



- 1. Dimethoate
- 2. Tebuthiuron
- 3. Simazine
- 4. Pirimicarb
- 5. Diuron
- 6. Methidathion
- 7. Pronamide
- 8. Metolachlor
- 9. Parathion

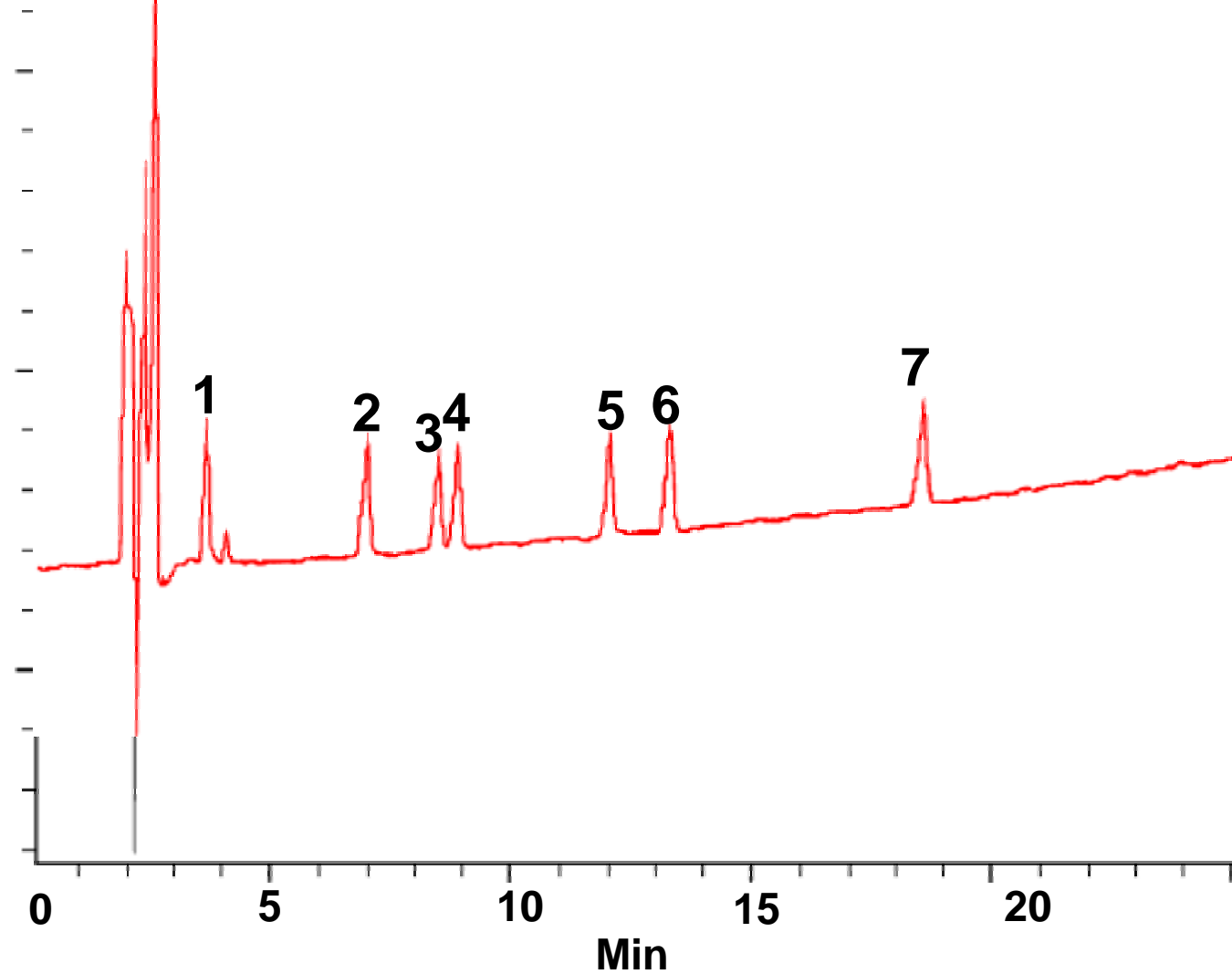
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Figure provided by C.L. Ritland, S. Cohen, C.J. Mason, Nevada Div. Agriculture, Reno, Nevada, USA.

Figure E. Acidic Pesticides in Water

Column: octadecylsilyl reversed phase, 30cm x 3.9mm ID, 4 μ m particles
Mobile Phase: gradient, A = water/0.05% trifluoroacetic acid
B = acetonitrile/0.025% trifluoroacetic acid
Flow Rate: 1.0mL/min
Det.: photo diode array, monitor 230nm
Inj.: 20 μ L of extract (see procedure) (spiking level: 3x est. detection limit)

Gradient Program	
Time (Min)	% B
0.10	35
23.00	65
23.01	90
25.00	90
25.01	35



- 1. Picloram
- 2. Dicamba
- 3. Bromoxynil
- 4. MCPA
- 5. 2,4,5-T
- 6. MCPB
- 7. Acifluorfen

796-0413, 0415

Figure provided by C.L. Ritland, S. Cohen, C.J. Mason, Nevada Div. Agriculture, Reno, Nevada, USA.

Recovery of Acidic and Base/Neutral Pesticides, Using ENVI-Carb SPE Tubes

Analyte	Concentration (µg/L)		Recovery (%)	Mean % RSD
	EDL	Sample		
Dimethoate	5.0	15.0	89.2	8.0
Tebuthiuron	2.5	7.5	88.7	8.3
Simazine	0.1	0.3	86.2	7.4
Pirimicarb	1.3	3.7	83.4	9.4
Diuron	1.3	3.7	94.9	6.2
Methidathion	1.3	3.7	86.0	18.4
Pronamide	0.8	2.3	85.3	11.9
Metolachlor	0.8	2.3	88.4	18.8
Parathion	2.5	7.5	71.8	13.3
Bromacil	1.3	3.7	98.5	14.1
Cyanazine	0.2	0.6	93.9	18.9
Atrazine	0.2	0.6	95.1	17.4
Prometon	0.3	0.7	98.8	18.1
Chlorpropham	0.4	1.2	50.7	36.9

3x Estimated Detection Limit

*n = 8, all others n = 9.

Analyte	Concentration (µg/L)		Recovery (%)	Mean % RSD
	EDL	Sample		
Alachlor	1.7	5.2	84.5	17.9
Dacthal	1.0	1.9	93.1	29.6
Picloram*	0.5	1.5	99.8	3.6
Dicamba*	1.3	3.7	128.8	12.0
Bromoxynil*	1.0	3.0	89.0	4.6
MCPA*	1.3	3.7	100.3	6.2
2,4,5-T*	1.5	4.5	102.0	6.2
MCPB*	1.2	3.6	93.8	5.4
Acifluorfen*	1.5	4.5	97.7	6.1
Bentazon	1.5	4.5	85.0	2.9
2,4-D	1.5	4.5	98.0	4.0
MCPP	1.3	3.7	92.3	3.2
2,4-DB	1.5	4.5	91.6	4.2
2,4,5-TP	1.5	4.5	95.7	4.0
Dinoseb	2.0	6.0	47.1	31.9

Data provided by C.L. Ritland, S. Cohen, C.J. Mason, Nevada Div. Agriculture, Reno, Nevada, USA.

Conclusions

Carbons are a new class of SPE packings.

Carbon adsorbents have been characterized for use in liquid extraction systems.

Breakthrough studies indicate that carbons are suitable alternatives to silica-based C18:

- Selectivity is based on molecular shape.**
- Retention is not compromised by analyte polar functional groups.**

Carbon adsorbents have less inherent extractables than silica-based C18, which improves chromatography of extracted samples.

Applications demonstrate carbon's versatility:

- Effective for many classes of drugs, pesticides, and herbicides.**
- Simultaneous extraction of nonpolar analytes and polar degradation products.**
- Fractionate acidic and base/neutral compounds.**