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Contemporary methods of solid phase extraction

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Product Manager Separation Technology

Novi Sad, Serbia, September 9th, 2009

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OUTLOOK

- J.T.Baker Solid-Phase Extraction Products
- Freon replacement – ISO-9377-2 (2000)
- Environmental Testing – Application examples

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Principles of spe

SPE is an extraction process whereby, an aqueous sample is filtered through a thin bed of sorbent particles, the analytes of interest are removed from the sample matrix, and concentrated onto the sorbent. Once concentrated, the analytes are removed by an eluting solvent.

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What are the Benefits of SPE?

- ✓ SPE uses less solvent than LLE
- ✓ SPE is faster (at least 5 times)
- ✓ High capacity (2-8 %)
- ✓ Total SPE costs are considerably less than LLE
- ✓ SPE typically provides more accurate data than LLE
- ✓ High selectivity: broad choice of bonded phases and solvents
- ✓ Automation much easier

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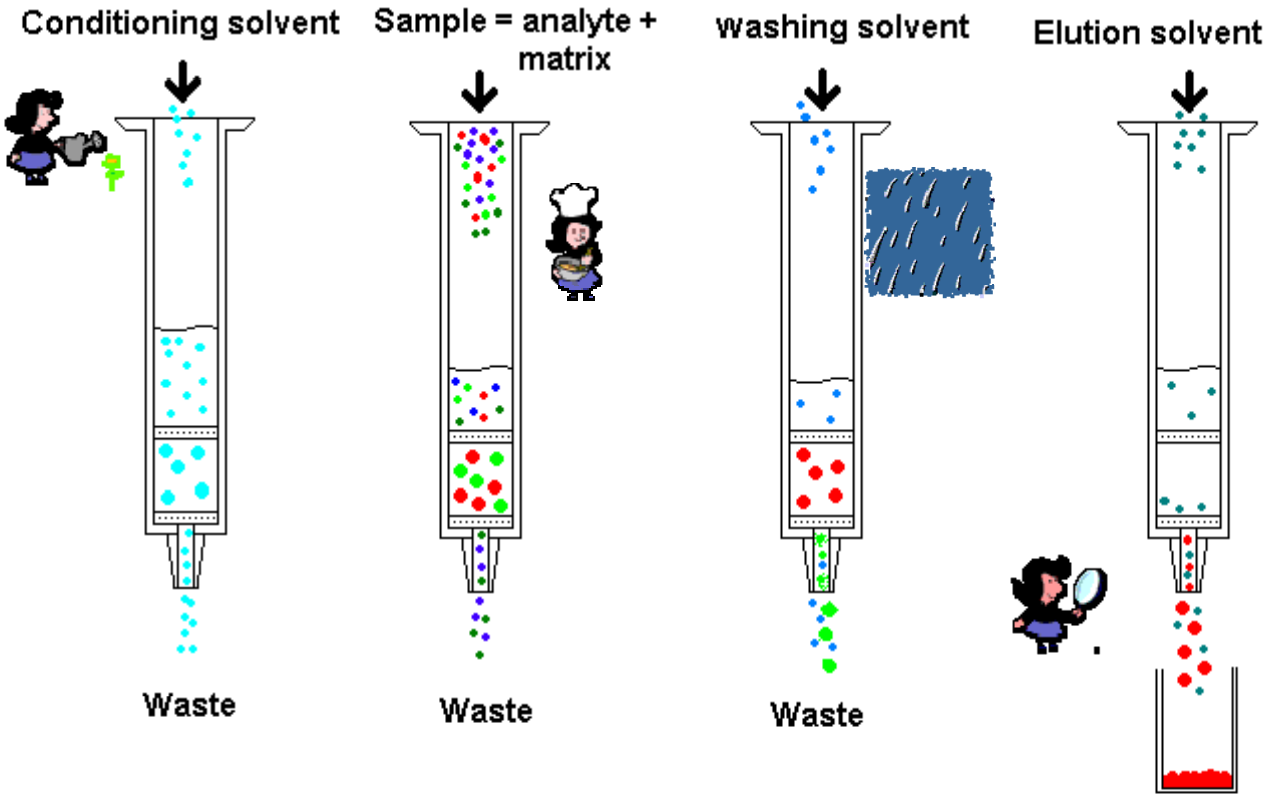
The 4 Basic Steps in SPE



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Solid-Phase Extraction Flash Presentation

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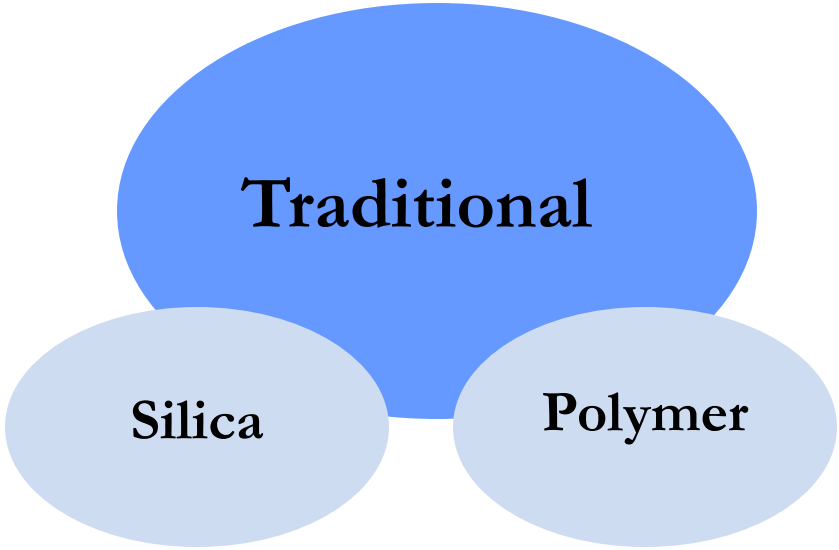
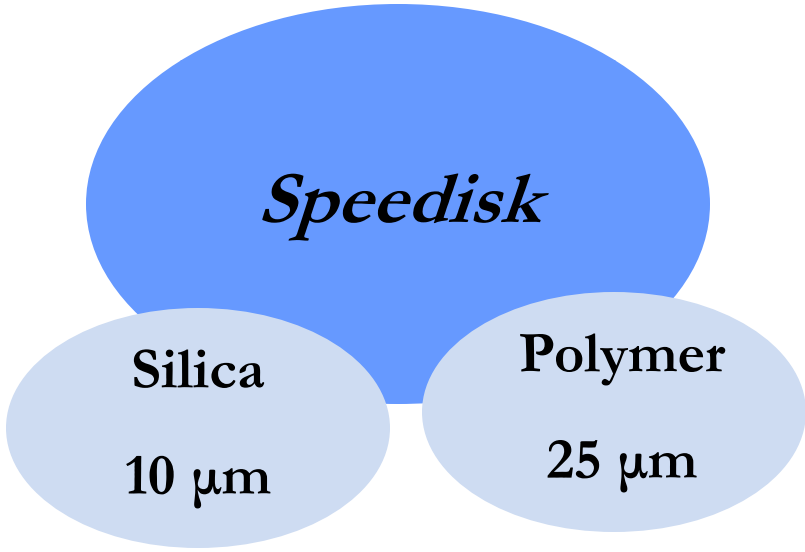
J.T. Baker SPE sorbents portfolio

"Dry packed" 40 µm



"Slurry packed"



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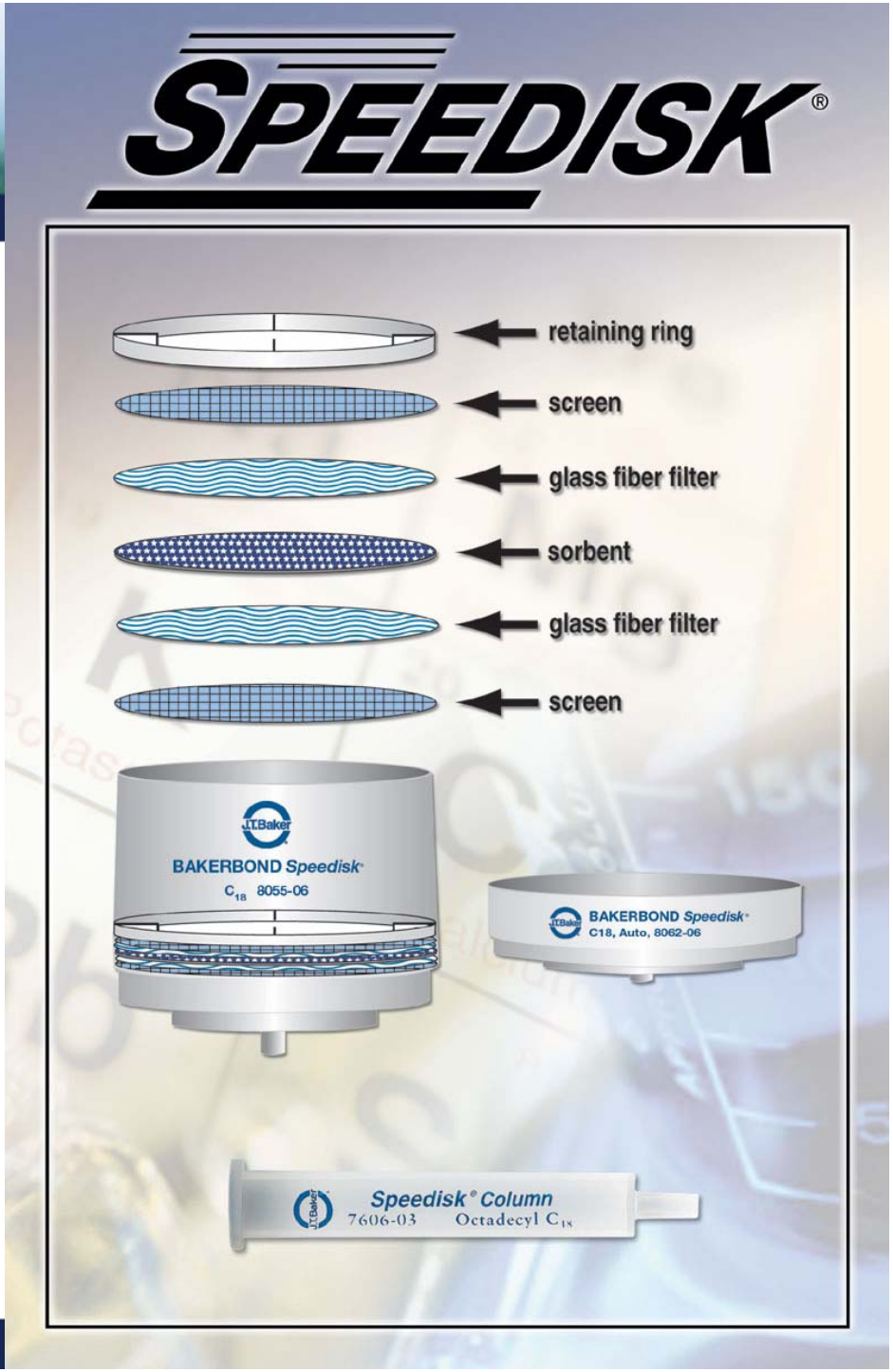
Sorbents and configurations for BAKERBOND spe

	spe™	*Speedisk* ®		
• Silica				
• Polymeric				 

Pre-cleaned housing

BAKERBOND *Speedisk*™ Products are Protected by U.S. Patent No. 5,595,653



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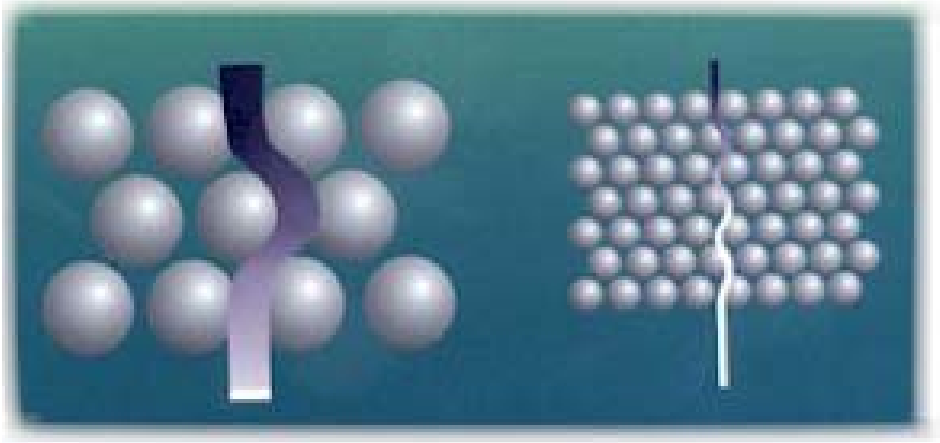
Benefits of *Speedisk*® configuration

<u>Laminar</u> BAKERBOND *Speedisk*®

- High flow rate
- High capacity
- Minimum of clogging



40 µm Conventional flow pattern

10 µm *Speedisks*® flow pattern

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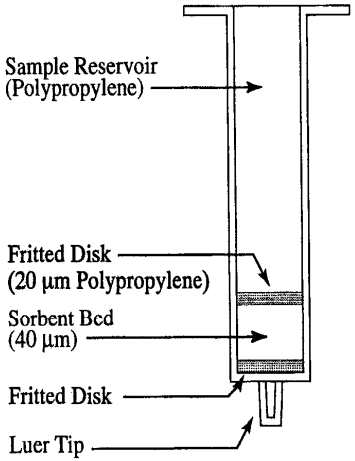
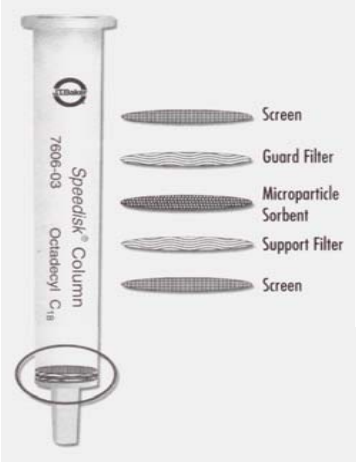
Conventional spe

VS *Speedisk* ®





Sorbent Weight	100 mg (40 µm) / 1 cc	10 mg (10 µm) / 1 cc
Sample Volume	2.0 ml	1. 0 ml
Conditioning solvent	2.0 ml (20 sec)	0.5 ml (5 sec)
Sample addition	2.0 ml (100 sec)	1.0 ml (50 sec)
Wash solvent	1.5 ml (15 sec)	0.4 ml (5 sec)
Eluting solvent	2.0 ml (20 sec)	0.3 ml (3 sec)
Evaporation/reconst.	3 – 10 min	not necessary

ハイパフォーマンス固相抽出 — 従来のSPEとの比較 —

Speedisk®

concept

1 Speedisk Column は高流速での処理が可能

従来品(SPE Column)では流速を上げるとバンド幅が大きく広がっているが
SpeediskColumnにはその影響がほとんど見られない。
(サンプル：メチルオレンジ 1mg/ml)

流速 1ml/min

従来品
充填剤量500mg

Speedisk Column
充填剤量100mg

流速 3ml/min

2 Speedisk Column の大きい保持量

従来品
充填剤量500mg

Speedisk Column
充填剤量100mg

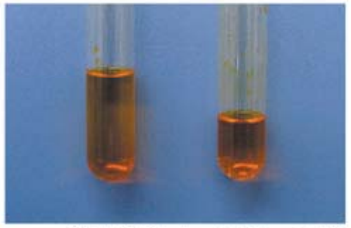
メチルオレンジを共に5mlづつ添加した。SpeediskColumn
はバンドがシャープな為、サンプル添加時にサンプルをロス
する事なく多くのサンプルを保持できる。

3 Speedisk Column の高い濃縮効果

メチルオレンジを同量づつ添加し、メタノールで100μl刻みにメチルオレン
ジの色が落ちるまで溶出させた。

従来品
充填剤量100mg

Speedisk Column
充填剤量100mg



従来品溶出液　SpeediskColumn溶出液

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Disk and Column type configuration

Speedisk® Disk type

- ✓ Large Volume Samples
- ✓ Environmental Applications

Speedisk® Column type

- ✓ Low Volume Samples
- ✓ Biological/Pharmaceutical Applications

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Speedisk® silica based product range

- C_{18}, C_{18} Light Load, C_{18} Polar Plus
- C_8, C_8 Polar Plus
- Phenyl
- C_4
- C_2
- Cyano (CN)
- Amino (NH2)
- Diol (COHCOH)
- CBx WP, PEI WP, Butyl WP, HI Propyl WP (biotechnology)
- Silica (SiOH)
- Quaternary Amine (N+)
- Aromatic Sulfonic Acid (C_6H_5-SO_3H)
- Carboxylic Acid (COOH)
- narc-1, narc-2 (for drugs of abuse analysis)

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Some typical *Speedisk* ® Application

Environmental

- - PAH ‘s from water and soil
- - PCB‘s from oil
- - Explosives in soil
- - Pesticides from water/soil
- - Phenoxy acid herbicides from water

Food/Feed/Beverages

- - Aflatoxine from corn meal
- - Caffeine from di-caffeinated diet cola
- - Vitamin E from juice

Pharmaceutical/Clinical/Biological

- - Benzodiazipines from serum
- - Anabolic Steroids/Urine
- - Aflatoxine from liver

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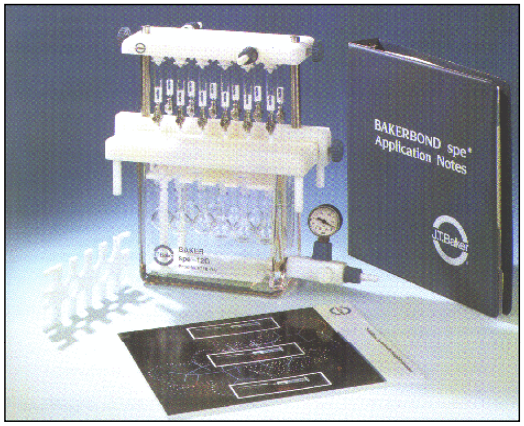
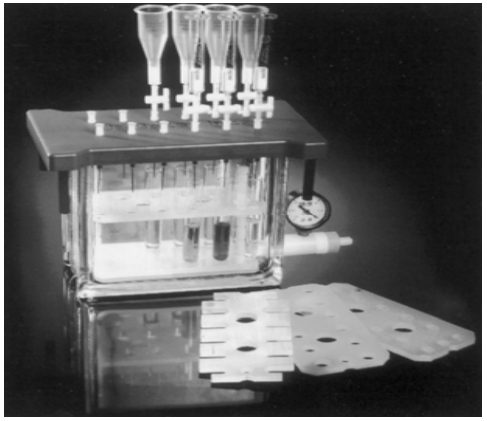
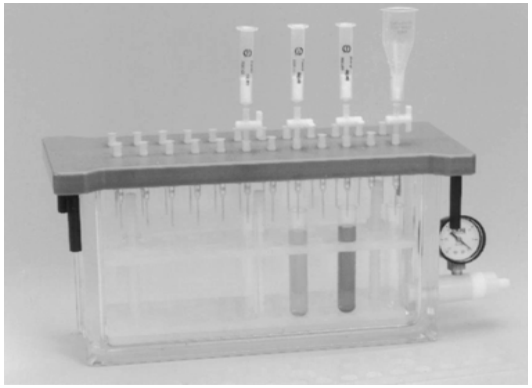
Accessories….



BAKER 12 G PTFE DESIGN



BAKER 12 G REGULAR DESIGN



BAKER 24 G REGULAR DESIGN

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Speedisk ® Multi-96 Well Plate

Speedisk ® 48 Processor:

- Positive Pressure Processsor for processing 1, 3, 6 ml columns in batches of 1 - 48 samples.

Speedisk ® 96 Processor:

- Positive Pressure Processor for processing 1 ml rimless columns in a 96 (8 x 12)microplate format

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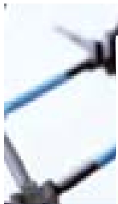
Special designed *Speedisk* extraction manifolds

- **Expanded Extraction Station 6-port**



Selection Guide for spe sorbents and solvents

Organic samples mw < 2000 (in solution)

This Sorbent Selection Guide is a systematic guide classifying samples according to polarity, ionizability and solubility in water or organic solvents. This information is useful in selecting the necessary components of a preliminary extraction method.

SAMPLE SOLUBILITY	Organic Solvent Soluble			Water Soluble: Ionic		Water Soluble: Non-ionic/ion-paired		
SAMPLE MATRIX	Organic Polar	Organic Moderately Polar	Aqueous Non Polar	Aqueous Anionic	Aqueous Cationic	Aqueous Non Polar	Aqueous Moderately Polar	Aqueous Polar
MECHANISM*	NPC	LSC	RPC	IEC	IEC	RPC	LSC	NPC
SPE PHASE RECOMMENDED**	H_2O-Philic DVB Cyano Diol Amino 1,2 Amino	H_2O-Phobic DVB H_2O-Philic DVB Silica gel Florisil Alumina	H_2O-Phobic DVB H_2O-Philic DVB SDB-1/SDB-2 Octadecyl Octyl Cyclohexyl Phenyl Cyano	H_2O-Phobic WA-DVB H_2O-Philic SA-DVB Amino 1,2 Amino Quaternary Amine	H_2O-Phobic SC-DVB H_2O-Philic SC-DVB Cyano Carboxylic Acid Sulfonic Acid	H_2O-Phobic DVB H_2O-Philic DVB SDB-1/SDB-2 Octadecyl Octyl Cyclohexyl Phenyl Cyano	H_2O-Phobic DVB H_2O-Philic DVB Silica gel Florisil Alumina	H_2O-Philic DVB Cyano Diol Amino 1,2 Amino
SOLVENTS***	Hexane Chloroform Dichloromethane Acetone Methanol	Hexane Chloroform Dichloromethane Ethyl acetate Methanol	Hexane Dichloromethane Acetone Acetonitrile Methanol Water	Acids, buffers	Acids, bases, buffers	Hexane Dichloromethane Acetone Acetonitrile Methanol Water	Hexane Chloroform Dichloromethane Ethyl acetate Methanol	Hexane Chloroform Dichloromethane Acetone Methanol

*Separation Mechanisms

LSC: Liquid Solid Chromatography (Adsorption)

NPC: Normal Phase Chromatography (Bonded Phase Partition)

RPC: Reversed Phase Chromatography (Bonded Phase Partition)

IEC: Ion-Exchange Chromatography (Bonded Phase Ion-Exchange)

*Bonded phases listed in order of increasing polarity

*Eluting solvents listed in order of increasing polarity

*Selective elution can be performed by combining two or more miscible solvents to achieve various degrees of polarity

**Solvents

9262 Hexane, ULTRA RESI-ANALYZED®

9257 Chloroform, ULTRA RESI-ANALYZED®

9264 Dichloromethane, ULTRA RESI-ANALYZED®

9260 Ethyl acetate, ULTRA RESI-ANALYZED®

9254 Acetone, ULTRA RESI-ANALYZED®

9253 Acetonitrile, ULTRA RESI-ANALYZED®

9017 Methanol, ULTRA RESI-ANALYZED®

4219 Water, ULTRA RESI-ANALYZED®

SDB: Styrene Divinyl Benzene

DVB: Divinyl Benzene

H_2O-Phobic WA DVB: Weak anion exchanger

H_2O-Phobic SC DVB: Strong cation exchanger

H_2O-Philic SA DVB: Strong anion exchanger

H_2O-Philic SC DVB: Strong cation exchanger

This Sorbent Selection Guide is also available on:

www.jtbaker.com/chromatography/SolidPhaseExtraction.asp

www.jtbaker.com

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Development of new products applicable to the quantitative determination of the mineral oil index (hydrocarbon index) according to ISO-9377-2 (2000)

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Determination techniques for Mineral Oil in Europe

Use of Infrared (IR) since 1951

NEN 6673 (1981), DIN 38409-H18 (1981), NEN 6675 (1989)

Tetrachloromethane > Freon > Tetrachloroethylene

From 1997 Gaschromatographic determination

NEN 5733 (1997), DIN-EN ISO 9377-4 (1999), **ISO 9377-2 (2000)**

Petroleum Ether, Iso-Hexane, Pentane, n-Hexane etc.

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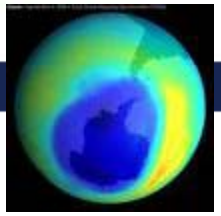

Table 2. Comparison of chlorofluorocarbon replacements to trichlorofluoromethane.

Compound	Intended use	ODP	GWP	Estimated atmospheric lifetime, years
Trichlorofluoromethane	Refrigeration, blowing agent	1	1	144
1,1-Dichloro-1-fluoroethane (HCFC-141b)	Blowing agent, solvent	0.1	0.12	11
1,1,1,2-Tetrafluoroethane (HFC-134a)	Refrigeration	–	0.4	14
Pentafluoroethane (HFC-125)	Refrigeration, fire extinguisher	–	0.84	41
1-Chloro-1,2,2,2-tetra-fluoroethane (HCFC-124)	Blowing agent, refrigeration	0.02	0.1	1.3
1,1,1-Trifluoro-2,2-dichloroethane (HCFC-123)	Refrigeration, blowing agent	0.02	0.02	1.6

Abbreviations: ODP, ozone depletion potential; GWP, global warming potential.

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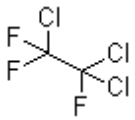
EXTRACTION SOLVENTS (IR-determination)

FREON

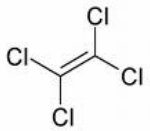
(1,1,2-Trichlorotrifluoroethane)



Freon is used as an extraction agent for mineral oil determination using IR-detection since 1951. Although new methods are developed utilizing a sophisticated GC apparatus, still a lot of laboratories deal with a straightforward IR analyser. Remark: Freon is almost fully prohibited from the European Market

Tetrachlorethylene

(Perchloroethylene) *product code 9360*



Tetrachlorethelyne is a largely used alternative for Freon. This solvent also acts as an extraction agent for the determination of the Hydrocarbon oil index, using IR detection. J.T. Baker's Ultra Resi Tetrachloroethylene suits to your existing Freon application.

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ISO-9377-2 (2000)

Since October 2000 an alternative method, to replace Freon, has been directed by the EC (ISO-9377-2)

- Single hydrocarbon or a mixture of hydrocarbons, both with a Boiling range between 36-69°C, replaces Freon

- The extraction is followed by cleanup for removal of polar substances (using Activated Florisil®) and Gas Chromatographic (GC) separation with on-column injection (including large volume injection (LVI) technique) and Flame Ionization Detection (FID).

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ISO-9377-2

Hydrocarbon oil index

Sum of concentrations of compounds extractable with a hydrocarbon solvent with boiling point between 36 °C and 69 °C, not adsorbed on Florisil® and which may be chromatographed with retention times between those of n-Decane (C10H22) and n-Tetracontane (C40H82)

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Procedure ISO 9377-2 (2000)- Summary

- **Water sample (1L) is extracted with 50 ml extracting agent**
  - 'Single Hydrocarbon Solvent with boiling range 36 °C - 69 °C'
- **Water is removed with Sodium sulfate, anhydrous**
  - 'Na_2SO_4 has to dried before use'
- **Polar substances are removed by clean-up on Florisil**
  - 'Florisil has to be activated by heating to 140 °C for 16 h'
- **Preconcentration step with evaporation apparatus**
  - 'To enhance the limit of detection'
- **Final analysis of hydrocarbon index with on-column GC-FID / Large Volume Injection Technique**

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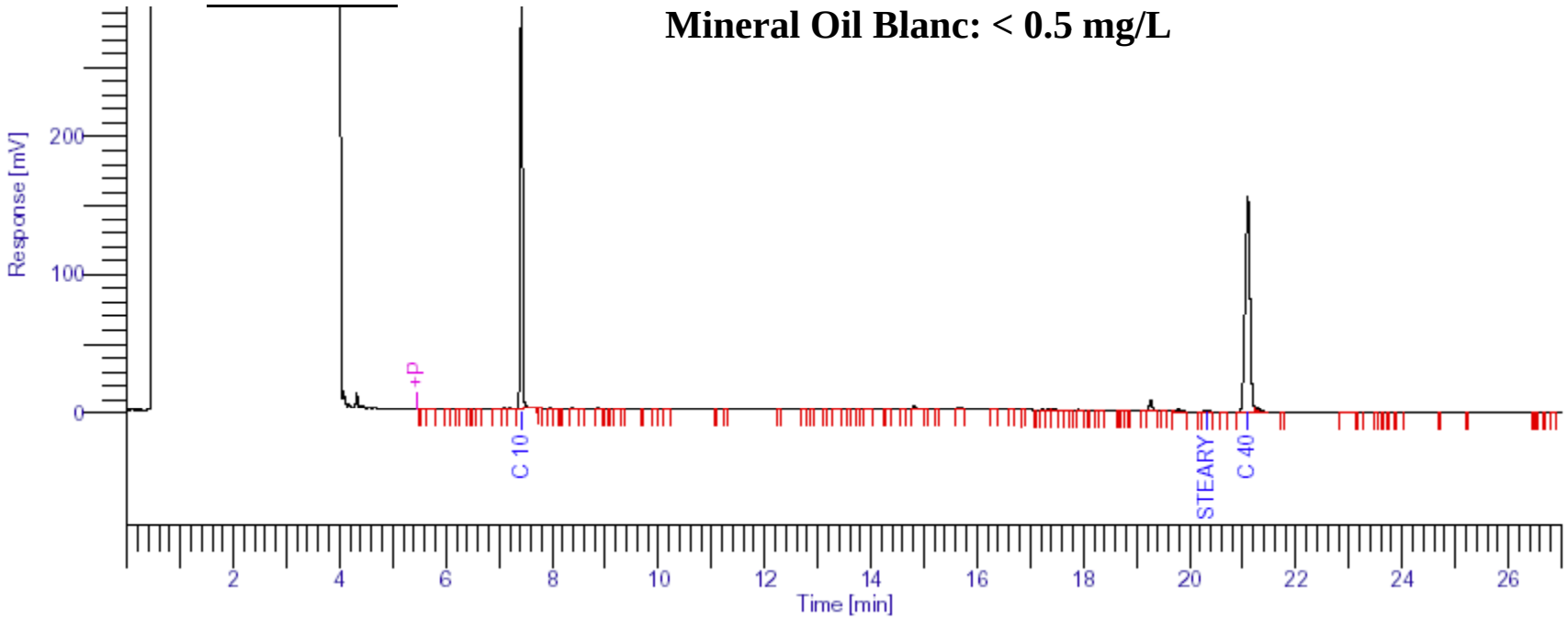
Mineral Oil Blanc: < 0.5 mg/L



Ultra Trace GC Large Volume Injection of Iso-Hexane inclusive C10/C40 internal standards, injectionvolume 100 µl (by kind permission of Interscience B.V.)

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Products for Mineral Oil Determination according to ISO 9377-2 (2000)

9266 Petroleum Ether

9267 Iso-Hexane

- *total peaks between n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$)…max. 0.5 mg/L*

7061-00 Florisil, activated

- *(16 h at 140 °C)*

3377-00 Sodium Sulfate, anhydrous

7495-18 SPE Column Ready to use with 2 g Sodium Sulfate / 2 g Florisil

7495-04 SPE Column Ready to use with 0.5 g Sodium Sulfate / 0.5 g Florisil

For use in Large Volume injection techniques

0252 Sand "washed and ignited"

Used as blank sample

0168 Magnesium Sulfate Heptahydrate

Agent to avoid formation of emulsions

Info Bulletin

Adobe Acrobat 7.0 Document

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Application Examples – Environmental

- Pesticides (Triazines, Organchlorines etc)
- Polychlorinated Biphenyls (PCBs)
- Polycyclic Aromatic Hydrocarbons (PAH's)
- Acrylamide
- Pharmaceuticals
- Endocrine disruptors

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SPE Application Notes Examples-Environmental

Extraction and determination of pharmaceutical residues and related polar contaminants in water samples	Adobe Acrobat 7.0 Document
Clean up procedure with Florisil®/Sodium Sulfate for Hydrocarbon Index determination according to ISO 9377-2.	Adobe Acrobat 7.0 Document
Multiresidue Analysis Method of Triazines, Organochlorine Pesticides and Polyaromatic Hydrocarbons in Drinking Water (adapted from the method E.P.A. 525.2.)	obe Acrob 0 Docume
Extraction of Polycyclic Aromatic Hydrocarbons in water	Adobe Acrobat 7.0 Document
Extraction of steroid hormones, hormone conjugates and macrolide antibiotics in influents and effluents of sewage treatment plants	Adobe Acrobat 7.0 Document

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SPE Application Lists

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SPE and Speedisk Applications

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Evaluation Purpose Only

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Deventer Applications

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Zanob Applications

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QUESTIONS?

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THANK YOU FOR YOUR ATTENTION!

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BAKERBOND™

Activated Carbon

BAKERBOND™ ACTIVATED CARBON PRODUCTS

A. **BAKERBOND™ Activated Carbon**

B. **specially developed for the extraction of Acrylamide from surface and drinking water**

C. **German standard method (DIN 38 413 - P xx)* for the determination of acrylamide in water (e.g. drinking water, surface water) by high performance liquid chromatography with mass spectometric detection (HPLC MS/MS)**

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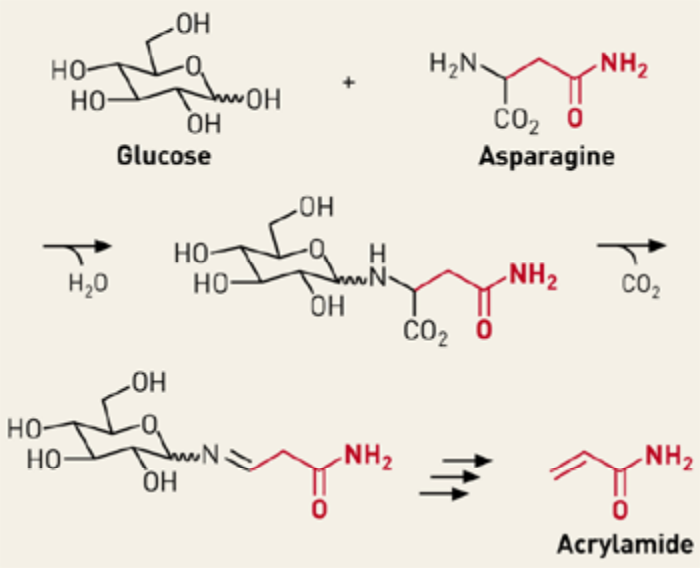
Acrylamide



- One of the contaminants in 1st Priority List of FDA, WHO and EPA
- Formed during the cooking of carbohydrate rich food

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Solid-phase extraction

- Fried, baked, or roasted food
- Present in breads and cereals

- Preparation of polyacrylamide or its copolymers
- Polyacrylamide used in purification of drinking, waste and process water

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Solid-phase extraction

PHYSICAL PROPERTIES OF BAKERBOND™ ACTIVATED CARBON

BAKERBOND™ Carbon	
Appearance	**Black Spheres**
Particle Size (by Laser Scanning in Water Suspension) d_{10} [µm] d_{50} [µm] d_{10} [µm]	 **210 – 240** **300 – 330** **405 – 435**
Specific Surface Area (by Nitrogen Adsorption (BET-method), m^2/g)	**Typical 1300 !!!**
Porosity **Microporosity (cm^3/g)** **Mesoporosity (cm^3/g)**	 **typical 0.75** **typical 0.50**
Loss on drying (%)	**1.40 – 1.60**
Bulk density (g/ml)	**typical 0.40**

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Solid-phase extraction

BAKERBOND™ Activated Carbon

Sorbent

PN 7532-00 – 100 gr of Activated Carbon

SPE columns

PN 7575-06 – 6 ml PP / 500 mg

PN 7575-07 – 6ml PP / 1000 mg

Microsoft Word Document

Sales Tools

Microsoft Word Document

Organophosphorous Pesticides Application

Microsoft Word Document

Acrylamide Application

Microsoft Word Document

Acidic Herbicides Application

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Solid-phase extraction

BAKERBOND™ Carbon-Amino Double Phase Column

Clean-up of Pesticides and Insecticides from Food and Feed

Microsoft Word Document

Sales Tool

Microsoft Word Document

Application

Pesticide residue analysis in agricultural products
Organophosphates, Carbamates, Pyrethroids

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Solid-phase extraction

BAKERBOND™ SDB-1

Extraction of Chlorphenoxyacid Herbicides from Water
Extraction of Phenols from Water
Extraction of Carbamates from Water
Extraction of Explosives and Metabolites from Water
Extraction of Organophosphorus Pesticides from Water
Extraction of Pesticides from Water using
Extraction of Pesticides from Soil and Urine

Microsoft Word Document

Sales Tool

Microsoft Word Document

Instructions for use

Microsoft Word Document

ISO norm : *Final Draft ISO/CD 18857-2 „Water quality – Determination of selected alkylphenols, alkylphenol ethoxylates and bisphenol A-Method for non filtered samples using solid-phase extraction and gas chromatography with mass selective detection* - to be ready soon!

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SPE Application Examples – Pesticides

Pesticide class	ED Chemicals in the Group
Carbamates	Aldicarb, Carbaryl, Methomyl, Baygon (propoxur), Bendiocarb, Oxamyl
Organochlorines	Aldrin, Chlordane, Endosulfan, Endrin, Nonachlor, Oxychlordane
Linuron, diuron, and derivatives/metabolites	Ethylene Thiourea (ETU), Linuron (Lorox) Diflubenzuron, Diuron
Organophosphates	Malathion, Ethylmalathion, Methylmalathion, Chlorpyrifos, Acephate, Chlorfenvinphos, Diazinon, Dichlorvos, Dimethoate, Fenthion, Glufosinate, Mevinphos, Parathion, Phosphamidon, Quinalphos,
Triazines and triazoles	Amitrol, Atrazine, Biteranol, Cyanazine, Simazine, Terbutryn, Triadimefon, Triadimenol, Triazines

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SPE Application Examples – Pesticides

HTML Document

EXTRACTION OF EPA METHOD 8081A OR 8082 ANALYTES ORGANOCHLORINE PESTICIDES OR POLYCHLORINATED BIPHENYLS USING H2O-PHOBIC DVB EXTRACTION DISK (GC-ECD)

HTML Document

EXTRACTION OF ORGANOCHLORINE PESTICIDES, HERBICIDES, AND ORGANOHALIDES FROM DRINKING WATER EPA METHOD 508.1 (*Speedisk* C_{18} High Capacity Extraction Disk, GC-ECD)

HTML Document

EXTRACTION OF PESTICIDES FROM WATER USING SDB-1 or *Speedisk*® H_2O-Phobic DVB Column (HPLC)

HTML Document

EXTRACTION OF PESTICIDES FROM WATER USING C_{18} POLAR PLUS®

(GC or HPLC)

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SPE Application Examples – Pesticides

HTML Document

EXTRACTION OF CARBAMATES FROM WATER USING SDB-1 OR *Speedisk*® H_2O-Phobic DVB Column (HPLC)

HTML Document

EXTRACTION OF TRIAZINE HERBICIDES FROM SOIL (SIMAZINE, ATRAZINE, PROPAZINE) – (Aromatic Sulfonic acid SPE, HPLC)

HTML Document

EXTRACTION OF TRIAZINES AND URONES FROM WATER USING C18 POLAR PLUS® (HPLC)

HTML Document

EXTRACTION OF TRIAZINES FROM WATER USING C18 POLAR PLUS® (HPLC)

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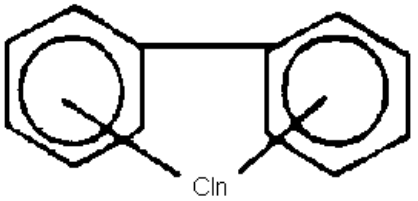
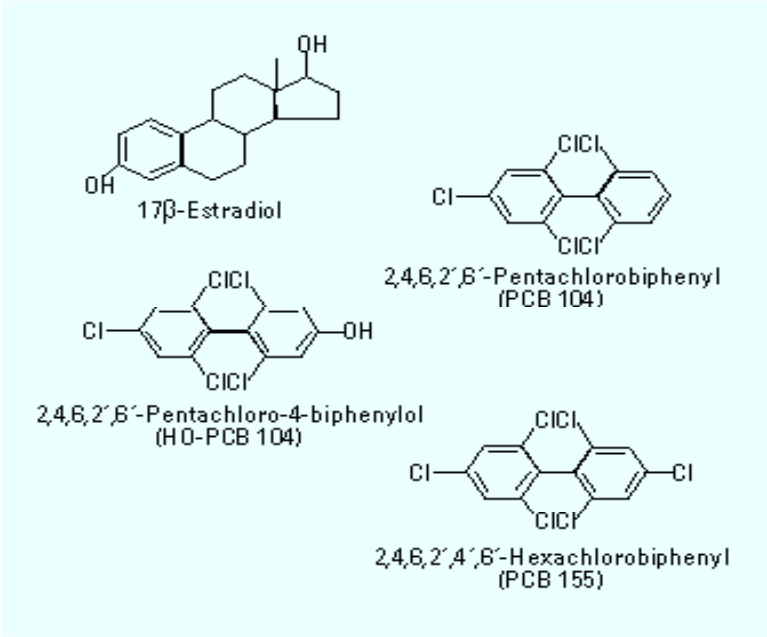
PolyChlorinated Biphenyl's – PCBs

- Class of organic compounds characterized by two benzene rings linked by a C-C bond



- Very resistant to degradation (oxidation, acids, bases, themperature)



- Soluble in most of the common organic solvents, slightly soluble in water

-Used as cooling/isolation fluids and fire retardants

- Accumulated - high stability under environmental conditions

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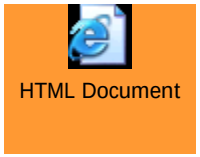
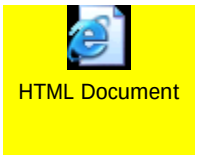
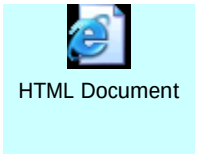
SPE Application Notes Examples – PCBs



EXTRACTION OF POLYCHLORINATED BIPHENYLS (PCBs) FROM WATER– *Speedisk* C_{18} (GC/MS determination)



EXTRACTION OF POLYCHLORINATED BIPHENYLS (PCBs) FROM WASTEWATER EPA Method 1668– *Speedisk* C_{18} (GC/MS determination)



EXTRACTION OF PCBs FROM TRANSFORMER OIL –

Florisil (GC/MS determination)

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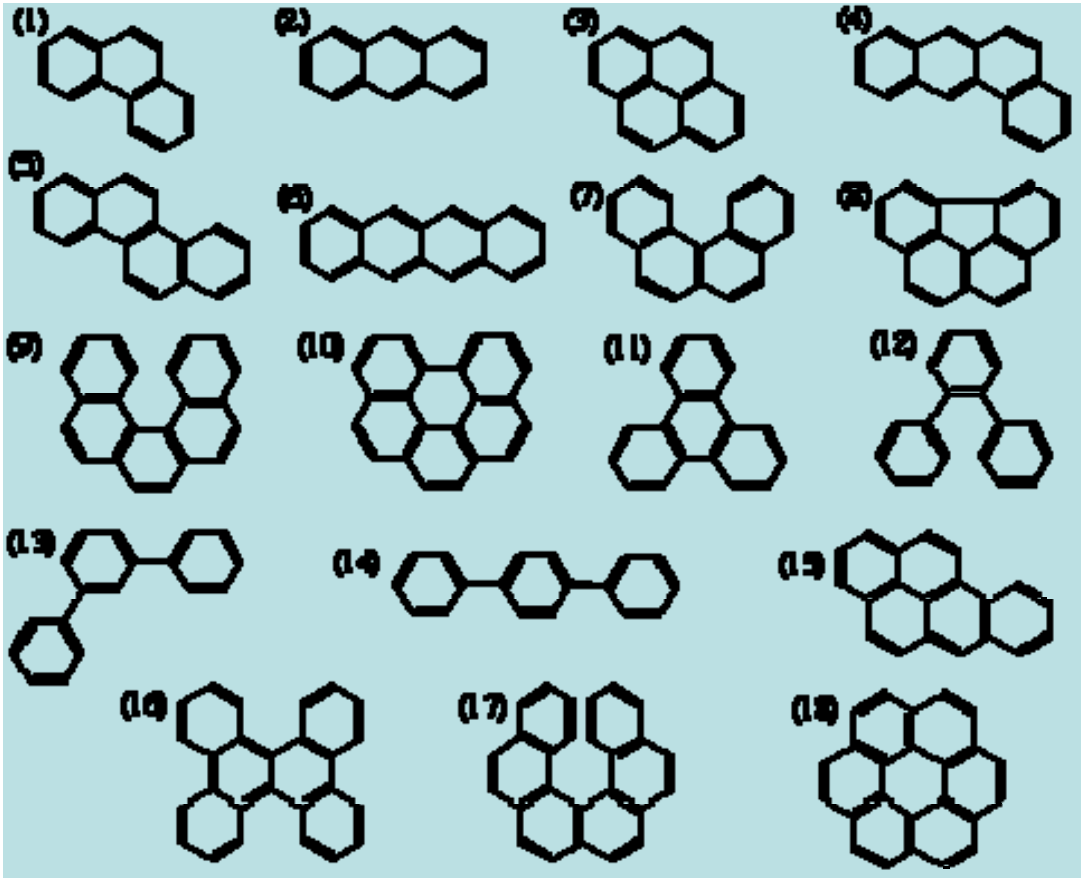
Polycyclic Aromatic Hydrocarbon's – PAHs



(1) Phenanthrene
(2) Anthracene
(3) Pyrene
(4) Benz[a]anthrecene
(5) Chrysene
(6) Naphthacene
(7) Benzo[c]phenanthrene
(8) Benzo[ghi]fluoranthene
(9) Dibenzo[c,g]phenanthrene
(10) Benzo[ghi]perylene
(11) Triphenylene
(12) o-Tephenyl
(13) Benzo[a]pyrene
(14) p-Tephenyl
(15) Benzo[a]pyrene
(16) Tetrabenzonaphthalene
(17) Phenanthro[3,4-c]phenanthrene
(18) Coronene

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Polycyclic Aromatic Hydrocarbon's – PAHs

- Large and heterogeneous group of organic contaminants
- Formed and emitted as a result of the combustion of organic material
- Lipophilic compounds (high affinity for organic matter)
- Differ substantially in their physicochemical properties
- Physico-chemical properties largely determine the environmental behavior

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SPE Application Notes Examples – PAHs

HTML Document

EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM WATER – *Speedisk* C18 (GC/MS determination)

HTML Document

EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM WATER - *Speedisk* C_{18} High Capacity (GC/MS determination)

HTML Document

EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM DRINKING WATER EPA Method 550.1 – *Speedisk* C_{18} High Capacity (HPLC-UV/FLU determination)

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Application Examples – Environmental

SORBENT	APPLICATION
C18	PAH's, Phthalates, Organochlorine pesticides, PCB's etc.
C18 XF	Extra filter for dirty samples
C18 Polar Plus	Phenols, Chlorophenoxy acids, Urones etc.
C8	Diquat, Paraquat
SAX	Haloacetic acids, Dalapon
H_2O Phobic-DVB (HC)	Chrorinated Acids,
H_2O Philic-DVB	Carbamates, Pharmaceutical residues from water
Oil & Grease	EPA 1664, Rev.A

XF= Extra filter

HC= High Capacity

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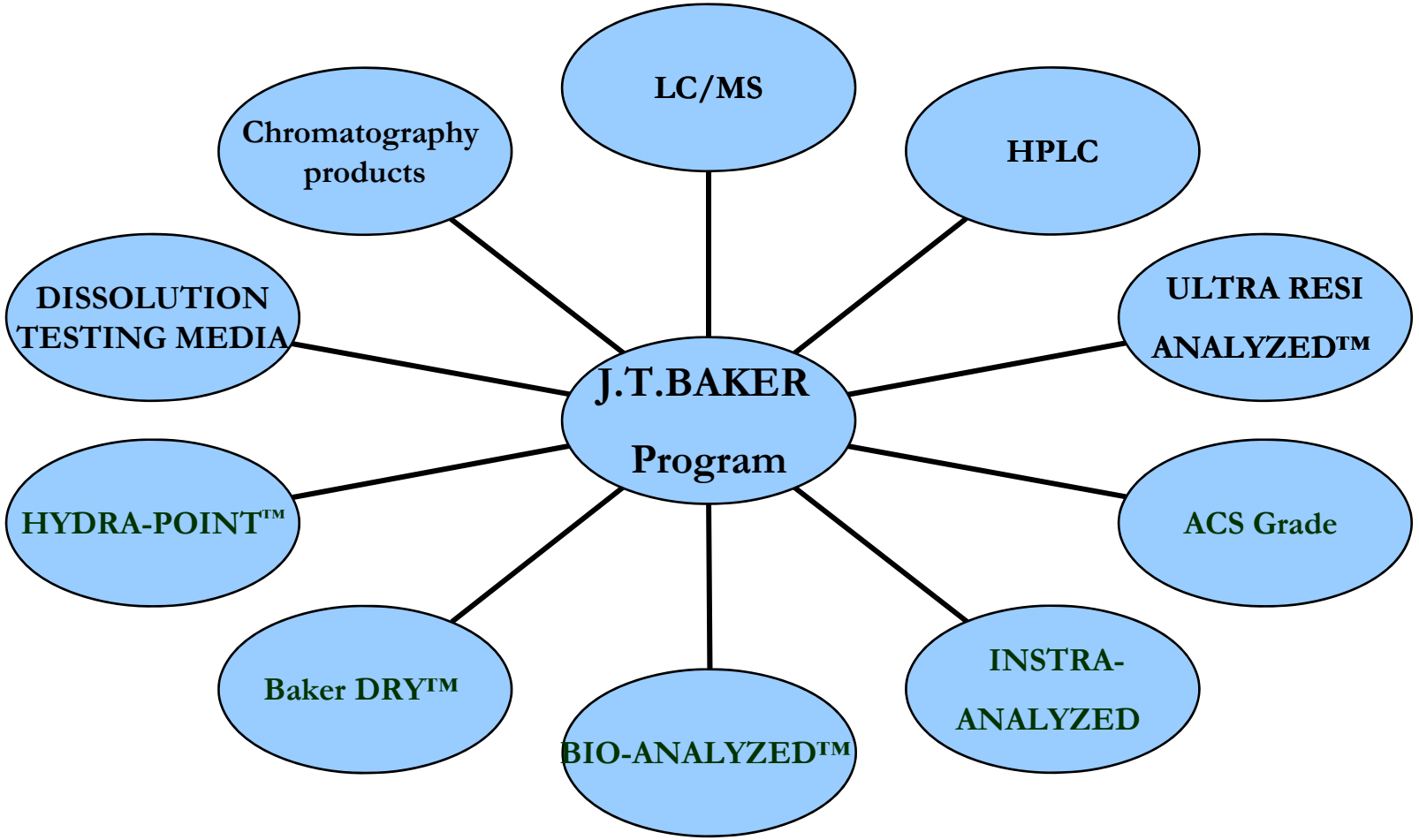
J.T.Baker Analytical BU program



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QUESTIONS?