Solid Phase Extraction for Water Analysis

presented by

Dr. Bernd Thierfelder

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Outline

1. Introduction in SPE
2. Retention Mechanisms / Sorbent Selectivity
3. strata™-X for Water Analysis
4. Applications of Water Analysis

1. Introduction in SPE

What is Solid Phase Extraction (SPE)?

It‘s a very selective and effective sample preparation method.

A day in the life of a scientist …

Collect Specimen

⇓

SAMPLE PREPARATION

⇓

Analysis (HPLC, GC, ...)

⇓

Data Handling

- Homogenization
- Dilution
- Weighing
- Settling and Decanting
- Centrifugation
- Filtration
- Enzymatic Hydrolysis
- Evaporation
- Protein Crash / Precipitation
- Liquid / Liquid Extraction
- *Solid Phase Extraction*

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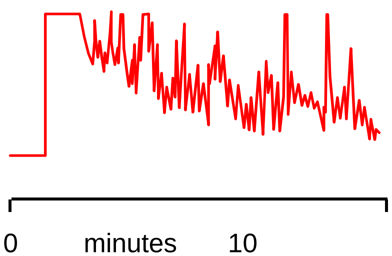
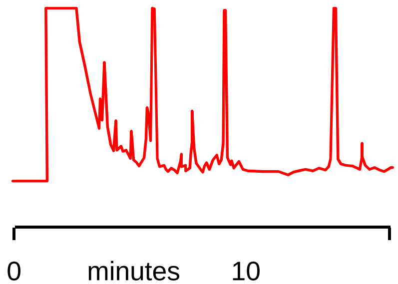
Three Goals of SPE

1. Purification/Clean up

Before SPE

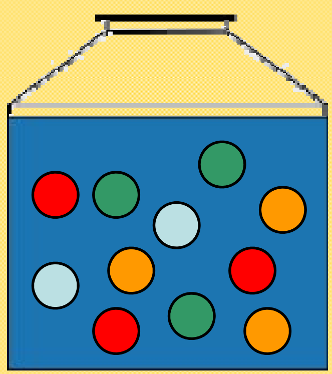


After SPE

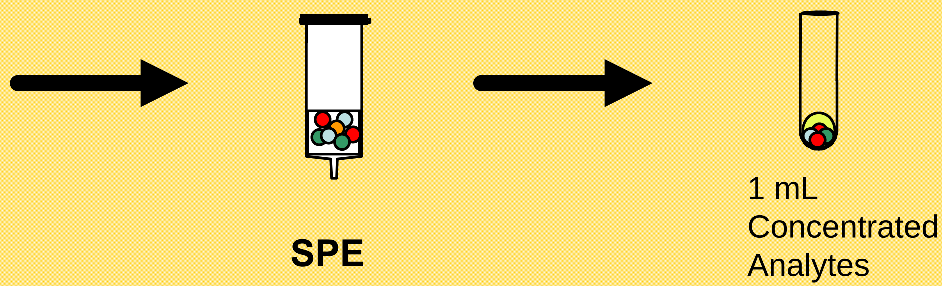


2. Concentration, e.g. from 1 Liter to 1 mL

3. Solvent Switch, e.g. from water to MeOH



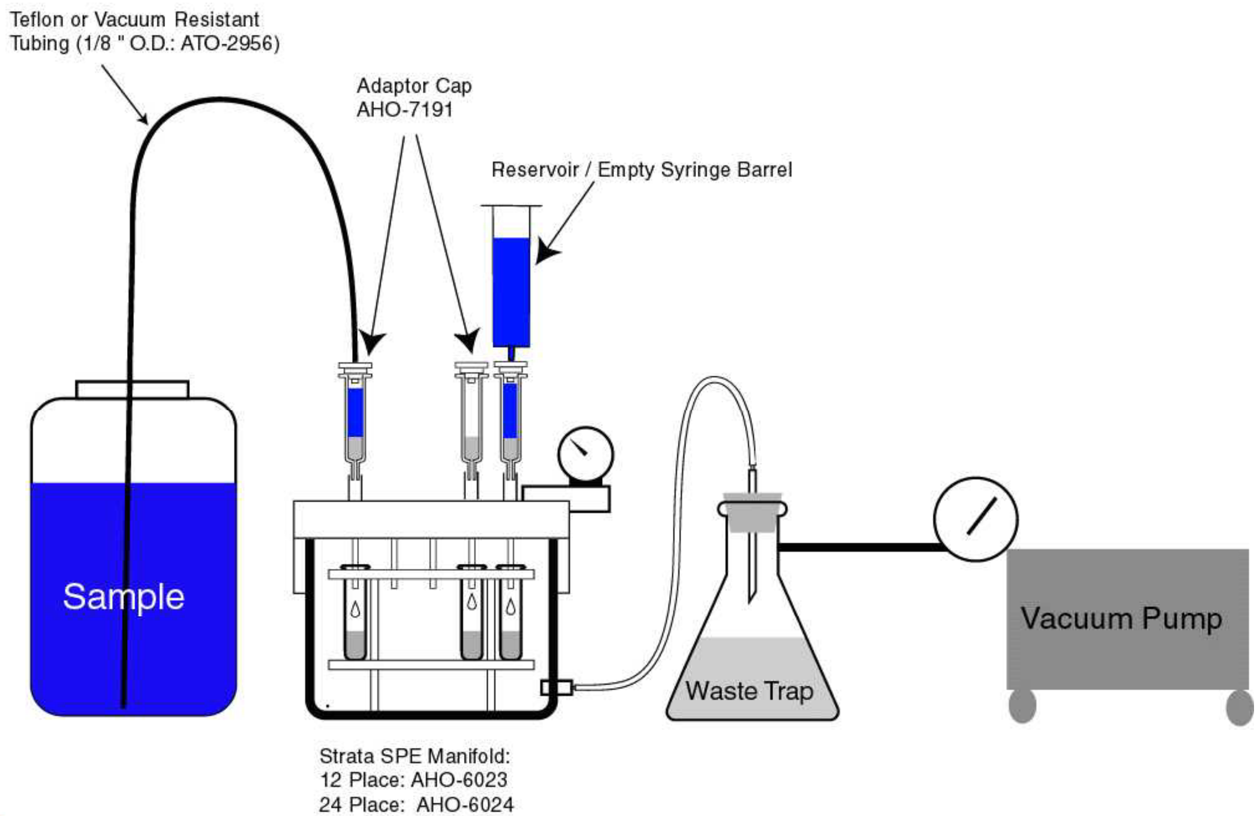
1 Liter Dirty Water



Processing Samples

with a Vacuum Manifold, a pump and a waste trap

Sample reservoir is connected to cartridge by a tubing and adaptor cap. Atmospheric pressure pushes water sample through cartridge and flow is controlled by stopcocks between cartridge and cover of manifold.



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SPE of Aqueous Samples

<u>Example:</u> A green sample containing a blue (non-polar) and yellow (polar) dye can be separated with SPE.

Sample Matrix | Contaminants | Target Analyze(s)

green dye | yellow = hydrophilic (polar) | blue = hydrophobic (non-polar)

Steps of SPE

1a. Condition

1b. Equilbrate

The two steps remove air and wet phase; phase is extended to its max. level.

2. Load sample

Analytes are retained by the sorbent.

3. Wash

Contaminants are washed off the phase.

4. Elute

Analytes are eluted from the phase.

2. Retention Mechanisms / Sorbent Selectivity

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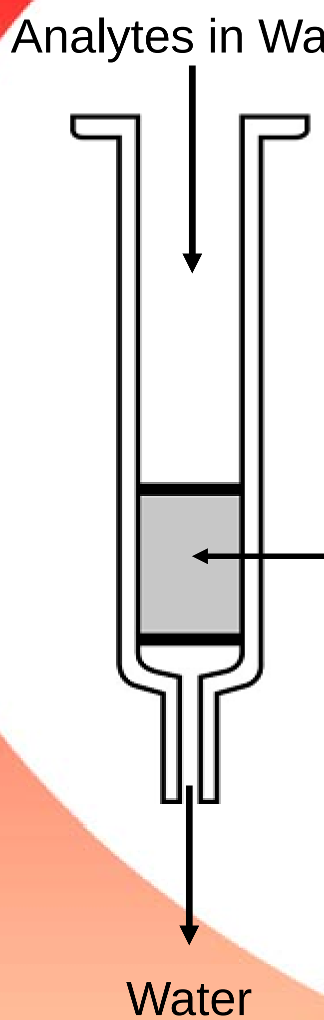
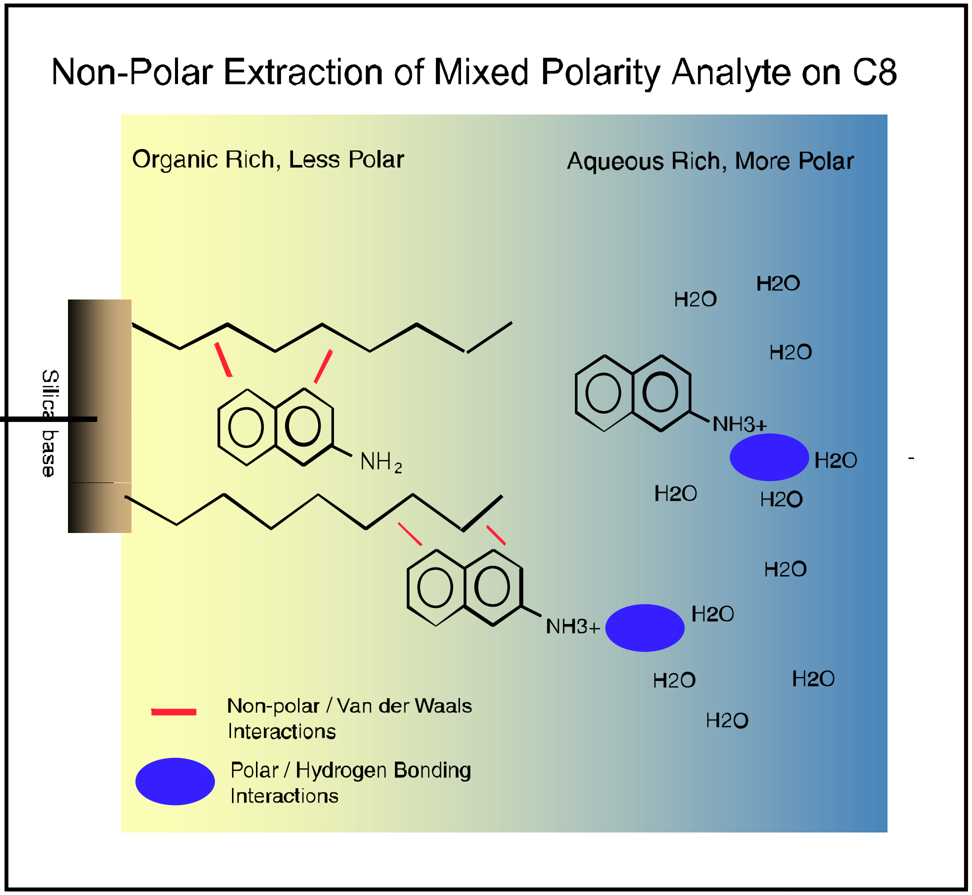
SPE of Analytes from Water

SPE Phase must have a high retentivity towards analytes.

Interactions must be stronger than analyte's solubility in water.





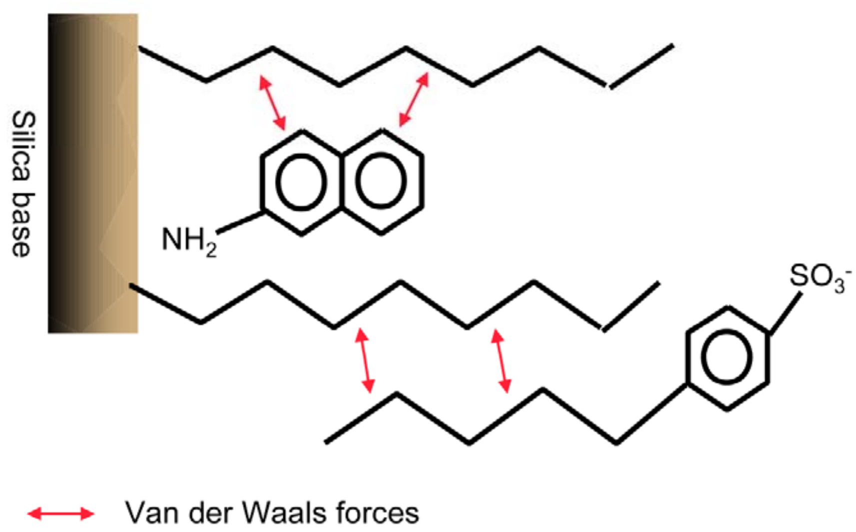
Retention Mechanism

Hydrophobic / Non-Polar / Reversed Phase

Typical phases: C18, C8, Phenyl, Polymers (i.e. PSDVB, strata-X)

Most common for aqueous samples / Huge difference in polarity between phase and water. Organic compounds interact with organic solid phase due to their organic frame.

Hyrdrophobic / Non-Polar / Reverse Phase
Interactions wtih C8 Functional Groups



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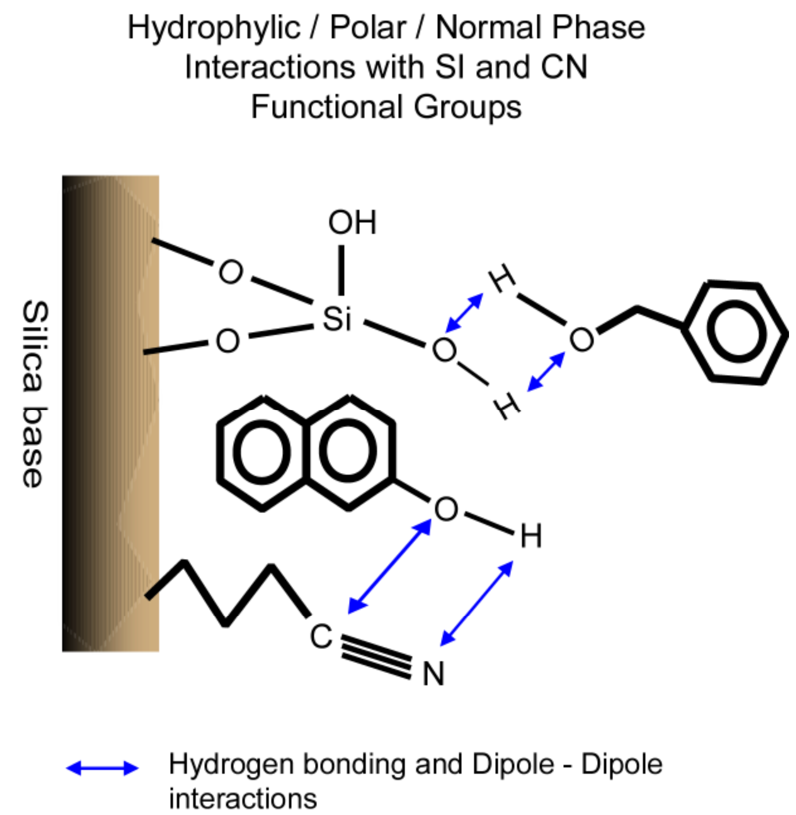
Retention Mechanism

Hydrophilic / Polar / Normal Phase

Typical phases: Silica, Florisil®, NH_2, CN

In most cases used for strong organic and non-aqueous environmental samples like hexane.



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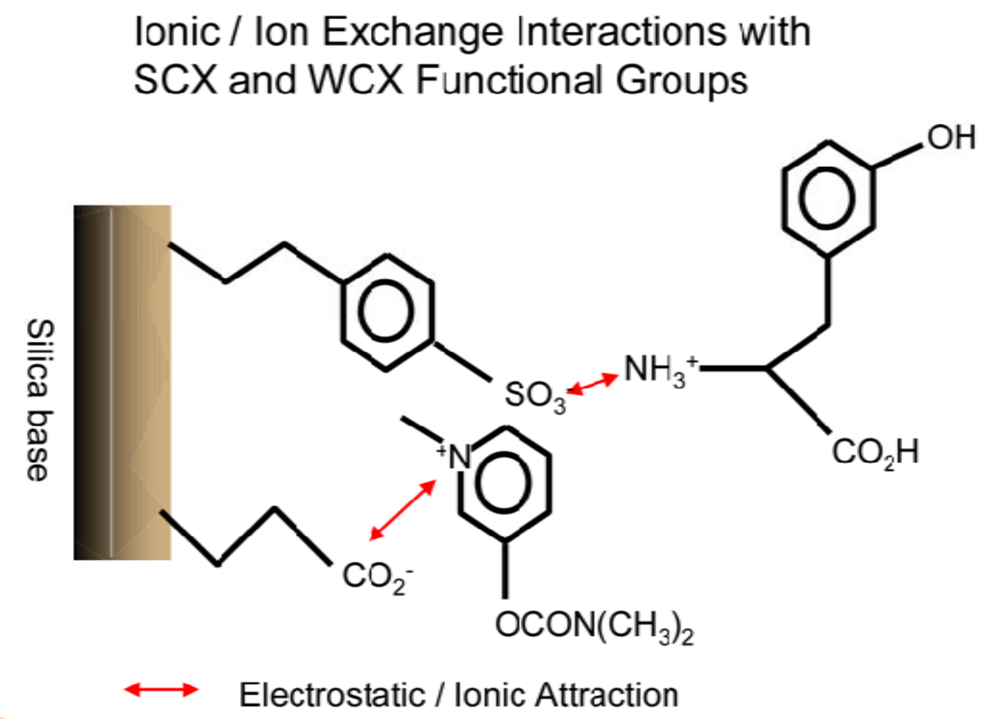
Retention Mechanism

Ion Exchange – Ionic interactions

Typical phases: SCX, WCX, SAX, WAX (NH_2), strata-X-C, -X-CW, -X-AW

Can be used for aqueous environmental samples if just a specific ionic class of analytes has to be extracted. Adjusting appropriate pH for load and elution step is necessary.



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Matrix

Polarity of sample and solid phase must be opposed.

Liquid Phase / Sample	Solid Phase
Aqueous: Water, biological fluids, aqueous homogenates	**Non-Polar** C18, C8, Phenyl, SDB, strata-X
Organic: Non-polar organic solvents	**Polar** Silica, Florisil®, NH_2, CN
Aqueous or Organic	**Ion Exchange** SCX, WCX, SAX, WAX, strata-X-C, -X-CW, -X-AW

Sorbent Selectivity

Selection of sorbent dependent on analyte and sample matrix.
These sorbents have a single retention mechanism.

Classic Sorbents

Most common RP phases:

- **SDB Polymer**
- **C18E**

- **C18U**
- **C8**
- **Phenyl**
- **CN**
- **NH_2**

Most common NP phases:

- **Si**
- **FL-PR**

- **SCX, WCX, SAX**

Non-polar

Reversed Phase Sorbents for organic compounds in aqueous environmental samples, e.g. surface water.

Polar

Normal Phase Sorbents for polar organic compounds in organic solvents e.g. organic soil extracts.

Ionic

IEX Sorbents for specific ionic compounds from aqueous or organic samples.

Sorbent Selectivity

Question: Can a sorbent have more than one retention mechansim?

Multiple Modes

Mixed Phases: Hydrophobic + Ion exchange

Typical phases: strata Screen C and strata Screen A

"Universal": Hydrophobic + Hydrophilic

Typical phases: modified polymers such as strata-X

"Universal": Hydrophobic + Hydrophilic + Ion exchange

Typical phases: modified polymers such as strata-X-C(W), -AW

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3. strata-X for Water Analysis

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Modern Polymer Sorbents
strata-X / strata-X-C(W) / strata-X-AW

strata-X:	hydrophobic and hydrophilic retention mechanism for neutral non-polar and polar compounds
strata-X-C:	strata-X + strong cation exchange for bases
strata-X-CW:	strata-X + weak cation exchange for strong bases
strata-X-AW:	strata-X + weak anion exchange for acids

33 µm and 100 µm particles with large surface area > $800 m^2/g$ / $500 m^2/g$

pH stability 1-14

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Advantages of strata-X Series

- Simplicity: One method approach
- High & reproducible recoveries for acids, bases and neutrals

  ⇒ Can be used for all kinds of environmental aqueous samples
- High pH stability (pH 1-14)
- High capacity → lower solvent consumption
- Resistant to de-conditioning
- Clean = LC/MS and GC/MS friendly

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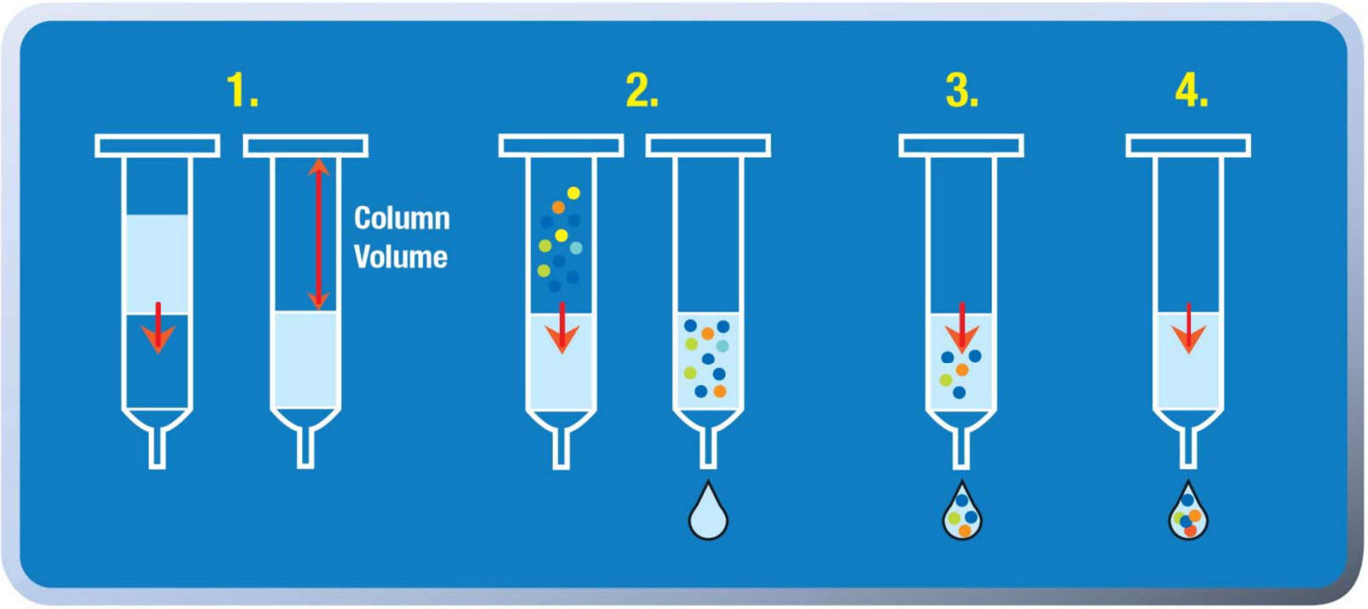
strata-X simplifies Method Development



Step 1	Step 2	Step 3	Step 4
Condition 5mL of methanol. Equilibrate with 5mL water	Load sample	Wash impurities with 5mL of a 5% methanol solution in water	Elute analyte with 3-5mL of methanol!

Method based on a 200mg sorbent bed mass

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4. Applications of Water Analysis

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Multiresidue solid phase extraction of 16 pesticides from groundwater coupled with high-performance liquid chromatography *

SPE Method

Sorbent: strata-X, 200mg/6mL

Conditioning: 10mL dichloromethane
10mL acetontrile
10mL water

Load: 1L water sample

Wash: water/methanol (95:5 v/v)

Elution: 5mL acetonitrile
5mL methanol

Pesticide	R% Strata X	LOQ ($\mu g\,l^{-1}$)
Desysopropylatrazine	82(2)	0.009
Desethylatrazine	92(3)	0.009
Aldicarb	71(4)	0.14
Simazine	85(5)	0.009
Carbofuran	97(5)	0.06
Metalaxyl	100(4)	0.06
Atrazine	90(4)	0.009
2,4-D	113(4)	0.07
Metazachlor	90(4)	0.06
Dicloran	84(5)	0.03
Phenmedipham	66(2)	0.05
Linuron	93(2)	0.05
Iprodione	71(3)	0.05
Procymidone	74(6)	0.07
Fenitrothion	97(1)	0.15
Vinclozolin	88(10)	0.1

* Talanta 71 (2007) 25–30, Angelo Antonio D'Archivio, Maria Fanelli, Pietro Mazzeo, Fabrizio Ruggieri
Universit`a degli Studi di L'Aquila, Dipartimento di Chimica, Ingegneria Chimica e Materiali,
Via Vetoio, 67010 Coppito, L'Aquila, Italy

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Solid phase extraction of pesticides from surface water *

SPE Method

Sorbent: strata-X, 200mg/6mL

Conditioning: 3x 1mL MeOH/ACN (1:1, v/v)

3x 2mL water

Load: 1L water sample (+ 0.5g NaCl)

Dry: 1h nitrogen stream

Elution: 3x 1mL MeOH/ACN (1:1, v/v)

Pesticides	Recovery [%]	RSD [%] n = 4	Set value [ng/l]
Desethylsimazin	85	5,8	100
2,6-Dichlorbenzamid	84	5,9	100
Ethidimuron	86	4,9	200
Chloridazon	86	3,6	50
Desethylatrazin	87	6,5	100
Desethylsebuthylazin	84	4,9	100
Bromacil	77	5,1	200
Simazin	84	7,1	100
Metribuzin	76	7,9	200
Desethylterbuthylazin	82	6,7	100
Metabenzthiazuron	82	5,4	50
Chlortoluron	83	4,5	50
Atrazin	82	9,0	100
Diuron	81	5,6	100
Isoproturon	81	5,5	100
Metazachlor	78	6,7	100
Terbumeton	77	9,1	100
Sebuthylazin	83	5,5	50
Propazin	79	10,3	50
Dimefuron	79	1,9	100
Terbuthylazin	78	9,0	100
Triadimenol	84	0,9	100
Epoxiconazol	80	2,6	200
Terbutryn	77	6,3	100
Metolachlor	71	16,2	200
Propiconazol	81	4,1	200
Kresoxim-methyl	79	3,5	100

* By courtesy of Mr. Cornelius Schmidt-Leistner from the „Bayerisches Landesamt für Wasserwirtschaft“ in Munich.

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Determination of selected human pharmaceutical compounds in effluent and surface water samples by high-performance liquid chromatography *

SPE Method

Sorbent: strata-X, 200mg/6mL

Conditioning: 3x 2mL methanol

3x 2mL water

3x 2mL water, pH 3

Load: 1L water sample, pH 3

Dry: vacuum aspiration

Elution: 3x 2mL methanol

Compound	SPE column recoveries[a]	
	Strata X R.S.D. (%)	LOD[b] ($ng\,l^{-1}$)
Acetyl-sulfamethoxazole	56 (5.4)	50
Clofibric acid	83 (7.0)	50
Dextropropoxyphene	63 (3.9)	20
Diclofenac	62 (20)	20
Erythromycin	73 (30)	10
Ibuprofen	117 (22)	20
Lofepramine	4.2 (35)	10
Mefenamic acid	24 (7.9)	50
Paracetamol	75 (6.9)	50
Propranolol	45 (5.6)	10
Sulfamethoxazole	120 (16)	50
Tamoxifen	42 (40)	10
Trimethoprim	123 (2.5)	10

* Journal of Chromatography A, 1015 (2003) 129–141, Martin J. Hilton, Kevin V. Thomas
Centre for Environment, Fisheries and Aquaculture Science (CEFAS), Burnham Laboratory, Remembrance Avenue, Burnham on Crouch, Essex CM0 8HA, UK

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Quantification of β-lactam antibiotics in urine and wipe samples from environmental and biological monitoring by SPE and LC-MS/MS

Institute of Energy and Environmental Technology (IUTA), D-47229 Duisburg, Germany

Table 2 Retention times (RT), recoveries and limits of detection (LOD) for wipe sample extracts (water) and urine samples

	RT [min]	Recovery Strata X [%][a]		LOD water [µg/L]	LOD urine [µg/L]
Cefotiame (**1**)	2.02	75		27	5.0
Amoxicillin (**2**)	2.81	78		0.8	20
Ampicillin (**3**)	7.02	74		0.5	0.4
Cefazoline (**4**)	9.32	71		0.9	11
Cefuroxime (**5**)	9.87	80		0.3	2.2
Piperacillin (**6**)	11.79	63		0.2	2.8
Penicillin G (**7**)	12.26	81		0.2	0.7
Penicillin V (**8**)	13.02	67		0.3	0.4

[a] n = 1; [b] n = 3

Thank you

for your attention

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