

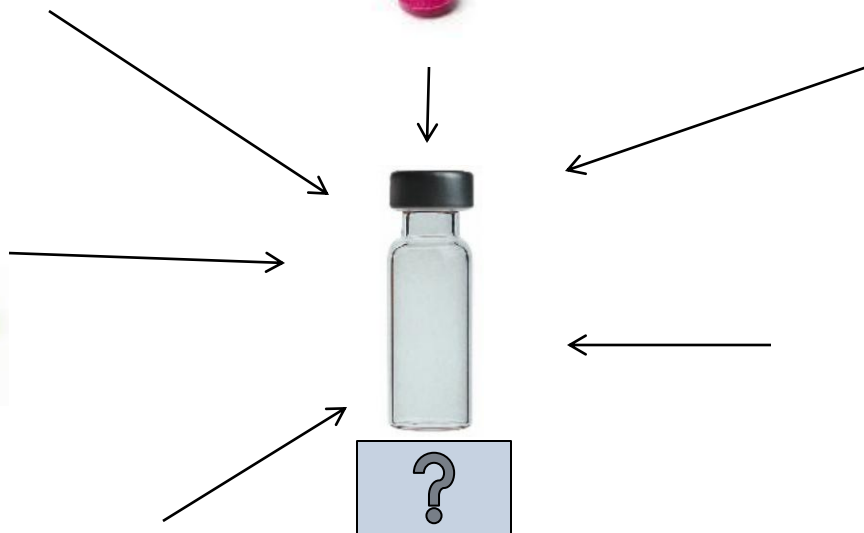


**Increasing Extraction Efficiency of Wet
Samples Using a Novel New Polymer
During Accelerated Solvent Extraction**

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The Challenge for Analysis



1.5 mL GC / LC Vial

How do we get analytes out of these samples?

For Solid and Semi-solid Samples

Thermo Scientific™ Dionex™ ASE™ 150 and 350 Accelerated Solvent Extractor System

Dionex ASE 150 System

- Low-end system
- Ideal for low-throughput labs
- Smaller footprint that is economically priced
- Fast and efficient extraction of a single sample



Dionex ASE 350 System

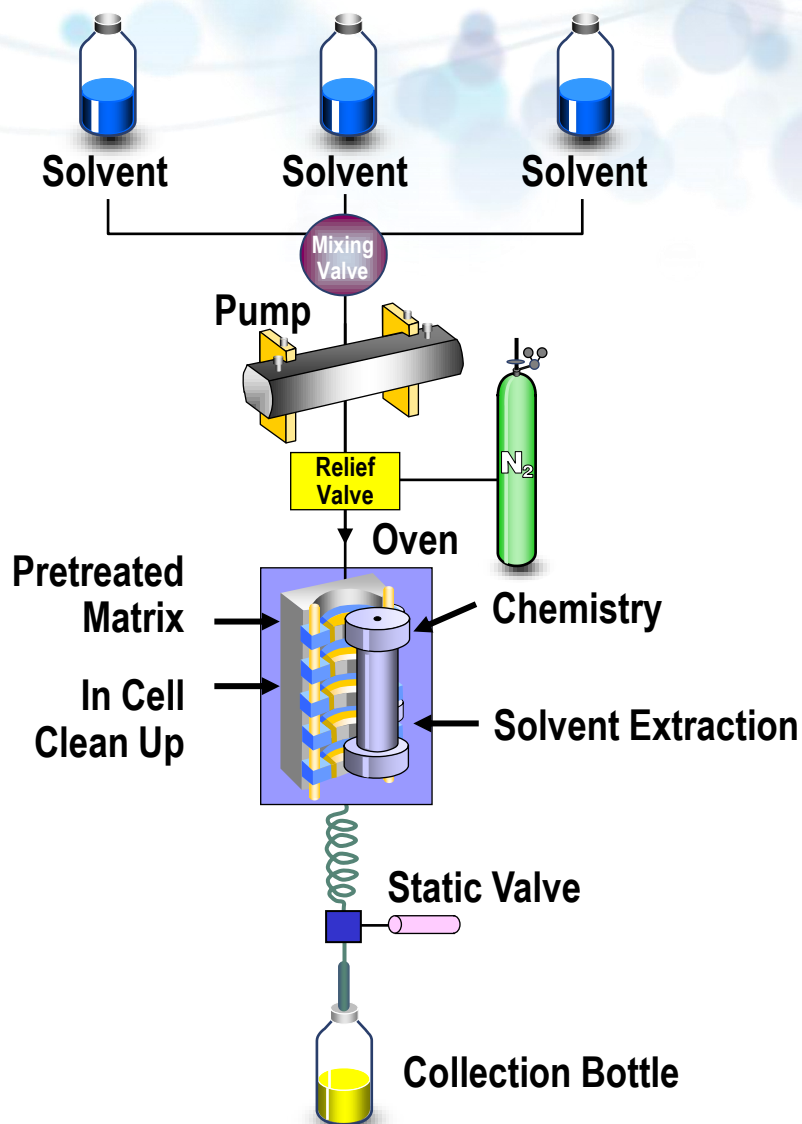
- High-end system
- Ideal for high-throughput labs requiring automation
- Unattended extraction of up to 24 samples
- Mixing or selection of three different solvents for complex extractions

Accelerated Solvent Extraction Technique

- Extraction of solid or semi-solid samples by a solvent at elevated temperatures (40 - 200 °C) and pressure (1500 psi)
- Use of elevated temperatures and pressures accelerates the extraction process
- Elevated Temperature
 - Increased solubility
 - Increased diffusion rate
 - Decreased viscosity of solvent
- Elevated Pressure
 - The boiling point of the solvent increases as the pressure increases
 - Solvent remains as a liquid
 - Forces liquid into the pores

Thermo Scientific Dionex ASE 350 Extraction Process

Load Cell	0.5
↓	
Smart Run™ System® Detects Cell Size	
↓	
Fill, Heat, and Pressurize	5-7
↓	
Static Extraction	5
↓ ↑	
Rinse with Fresh Solvent	0.5
↓	
Purge with Nitrogen	1-2
↓	
Extract Ready	Total (min) 12-14



Pre-Treatment Of Wet Samples

- Water can interfere with the extraction efficiency
- Co-extracted water may introduce interferences in the analysis step
- Solvent evaporation can preferentially concentrate the analyte into the aqueous phase and make the analysis challenging
- Examples of wet samples that need pre-treatment:
 - Wet soil
 - Wet sediment
 - Animal tissue
 - Fruits
 - Vegetables

How do we Currently Process Wet Sample?

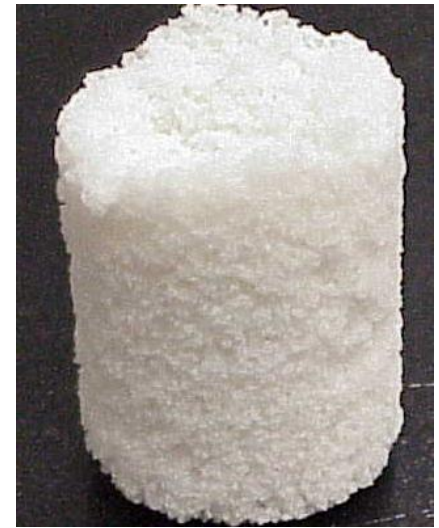
- Pre-extraction drying
 - Air drying; time consuming
 - Oven drying; not suited for volatile or semi-volatile compounds
 - Freeze drying; time consuming
- Post-extraction drying
 - Drying the solvent after extraction using sodium inorganic salts
 - Drying using super absorbent polymers

Moisture Removal by Inorganic Salt

- Sodium sulfate, calcium chloride, magnesium sulfate, calcium sulfate are used for moisture removal
 - Associate with water molecules and form hydrated salts
- Sodium sulfate is not suitable for in-cell moisture removal and extraction
 - Dissolves in hot solvent and precipitates downstream clogging the outlet frit, tubes and valves
- Sodium sulfate aggregates to a hard lump

Moisture Removal by Polymeric Material

- Commercial polymers - super absorbent polymers
- The most common polymer is the sodium salt of polyacrylic acid
- Limitations
 - Water absorbing capacity decreases as the ionic strength increases
 - Poor water absorbing property under high temperature conditions
 - Form a hard plug inside the extraction cell
 - Difficult to clean the extraction cell



Thermo Scientific Dionex ASE Prep MAP Moisture Absorbing Polymer

- Designed to remove moisture from wet samples (in-cell, in-line) as well as from the extract (in-vial, off-line)
- The polymer is a free flowing white granular material that can be easily mixed with Thermo Scientific™ Dionex™ ASE™ Prep DE (diatomaceous earth) dispersant and used for the moisture removal applications under accelerated solvent extraction conditions
- Thermo Scientific™ Dionex™ ASE™ Prep MAP polymer replaces the use of sodium sulfate
- Mode-of-use
 - In-cell, in-line
 - In-vial, off-line
 - Combination



Thermo Scientific Dionex ASE Prep MAP Polymer

- Key Advantages
 - Not sticky and processing is easy
 - Maintains its particulate form even after absorbing moisture



Moisture Removal Capacity of Thermo Scientific Dionex ASE Prep Map (in-cell)

- Dionex ASE Prep MAP and Dionex ASE Prep DE (1:1)
- Accelerated solvent extraction conditions:
100 °C, 5 min heat, 5 min static, 3 cycles, flush 30%, purge 120 s, hexane

Water Present in Cell (g)	Dispersant	Water Observed in Collection Bottle (g)
8.26	8 g Dionex ASE Prep MAP	0.13
8.00	8 g Dionex ASE Prep DE	0.07
8.22	4 g MAP and 4 g DE	0.0

In-Cell Moisture Removal at Varying Temperatures

Temperature (°C)	Amount of Polymer Required per g of Water	Amount of Dionex ASE Prep DE Required per g of Water
100	0.4 g	0.4 g
125	0.8 g	0.8 g
150	1.0 g	1.0 g

In-Cell Water Removal of Different Matrices

- Accelerated solvent extraction conditions:
100 °C, 5 min heat, 5 min static, 3 cycles, flush 30%, purge
120 s, hexane

Temperature (°C)	Sample	Amount of water in the sample (g)	Dispersant, (polymer and DE)	Water Observed in Collection Bottle (g)
100	Soil	7.00	4 g each	No
100	Apple	8.49	4 g each	No
100	Carrot	8.79	4 g each	No
100	Pear	8.49	4 g each	No

Moisture Removal Under High-Ionic Strength Conditions

- Moisture removal capacity of the Dionex ASE Prep MAP and polyacrylate based polymers were compared at ambient temperature
- The water containing salt concentration ranging from 0-26.5% NaCl

	Grams of Polymer Needed to Absorb per g of Water	Grams of Polymer Needed to Absorb a g of 2.91% NaCl Solution (sea water level)	Grams of Polymer Needed to Absorb a g of 26.5% NaCl Solution (saturation level concentration)
Dionex ASE Prep MAP	0.20	0.19	0.18
Polyacrylate based Commercial Polymer	0.04	0.08	0.27

Extraction of Phenolic Compounds from Environmental Samples

Application Example 1

- Important contaminants present in the environment - used in industrial processes to manufacture chemicals like pesticides, explosives, drugs and dyes
- They also are used in the bleaching process of paper manufacturing
- Phenolic compounds have substantial applications in agriculture as herbicides, insecticides and fungicides



Recovery of Phenolic Compounds

	Analytes	In-Cell Moisture Removal (% Recovery)
1	2, 4-Dinitrophenol	81.01
2	Phenol	89.99
3	P-Toluidine	86.72
4	4-Nitrophenol	96.05
5	2-Chlorophenol	92.33
6	4-Ethylaniline	92.82
7	4-Chloroaniline	94.44
8	2-Nitrophenol	93.83
9	2, 4- Dichlorophenol	97.50
10	2, 4, 6- Trichlorophenol	97.51

Recovery of Phenolic Compounds using Dionex ASE Prep MAP with extraction followed by HPLC

Recovery of Phenolic Compounds

	Analytes	In-Vial Moisture Removal by Polymer (% Recovery)	In-Vial Moisture Removal by Sodium Sulfate (% Recovery)	
1	2, 4-Dinitrophenol	82.96	86.79	Recovery of Phenolic Compounds Using Dionex ASE Prep MAP for post extraction followed by HPLC
2	Phenol	88.58	88.41	
3	P-Toluidine	95.03	93.88	
4	4-Nitrophenol	90.96	88.93	
5	2-Chlorophenol	87.45	87.16	
6	4-Ethylaniline	89.47	88.02	
7	4-Chloroaniline	88.39	87.51	
8	2-Nitrophenol	92.64	87.39	
9	2, 4- Dichlorophenol	93.25	89.58	
10	2, 4, 6- Trichlorophenol	95.20	91.02	

Extraction of PAHs from Soil

Application Example 2

- Polycyclic aromatic hydrocarbons are found naturally but they can also be man-made in their purest form
- PAHs are created when coal, oil, gas, and garbage are burned incompletely.

• Although PAHs can exist in over 100 different combinations The following PAHs are listed individually on EPA's Priority Chemical list.

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo(g,h,i)perylene
- Fluorene
- Phenanthrene
- Pyrene



Extraction of PAHs from Soil

- A 5 g clean soil sample was spiked with PAHs and deliberately moistened with water to contain 30% moisture
- The spiked wet soil sample was mixed with 2 g of Dionex ASE Prep MAP and 2 g of Dionex ASE Prep DE and loaded into a 34 mL Dionex ASE cell
- Extraction Conditions: 1:1 ratio of dichloromethane: acetone at an extraction temperature of 100 °C
- The extract was concentrated to a volume of 1 ml - final spike Concentrations 20 µg/mL

Recovery of PAHs

	Analytes	In-Cell with Dionex ASE Prep MAP-DE (% Recovery)
1	Naphthalene	77.8
2	Acenaphthene	93.9
3	Acenaphthylene	74.5
4	Phenanthrene	100.7
5	Anthracene	103.1
6	Fluoranthene	102.3
7	Pyrene	98.8
8	Benzo(a)anthracene	96.8
9	Chrysene	93.3
10	Benzo(b)fluoranthene	96.2
11	Benzo(k)fluoranthene	97.2
12	Benzo(a)pyrene	85.3
13	Indeno((1,2,3,c,d)pyrene	98.1
14	Dibenzo(a,h)anthracene	109.7
15	Benzo(g,h,i)perylene	105.9

Recovery of PAHs Using Dionex ASE Prep MAP with extraction followed by GC-FID

Recovery of PAHs

	Analytes	In-Vial Moisture Removal using Dionex ASE Prep MAP (% Recovery)	In-Vial Moisture Removal using Sodium Sulfate (% Recovery)
1	Naphthalene	100.8	96.2
2	Acenaphthene	99.3	97.5
3	Acenaphthylene	97.0	95.7
4	Phenanthrene	103.1	98.6
5	Anthracene	103.3	99.8
6	Fluoranthene	110.1	101.0
7	Pyrene	109.4	100.6
8	Benzo(a)anthracene	116.4	108.1
9	Chrysene	117.3	104.0
10	Benzo(b)fluoranthene	120.3	103.7
11	Benzo(k)fluoranthene	119.2	106.4
12	Benzo(a)pyrene	118.0	106.0
13	Indeno((1,2,3,c,d)pyrene	112.1	105.5
14	Dibenzo(a,h)anthracene	110.9	105.1
15	Benzo(g,h,i)perylene	112.5	107.3

Recovery of PAHs Using Dionex ASE Prep MAP for post extraction followed by GC-FID

Extraction of Organochlorine Pesticides

Application Example 3

- A class of chemicals used to control insects since the 1940s
- Persistent in the environment, and known for accumulating in sediments, plants and animals
- Organochlorines have a wide range of both acute and chronic health effects, including cancer, neurological damage, and birth defects
- Many organochlorines are also suspected endocrine disruptors
- Pesticides are regulated by the EPA
- Maximum EPA contaminant level for OCPs
 - 0.2 $\mu\text{g}/\text{L}$ for lindane
 - 2 $\mu\text{g}/\text{L}$ for endrin

Extraction of Organochlorine Pesticides

- In-Cell Moisture Removal
 - Sample size = 5 g (25% moisture content)
 - 4 g MAP:DE (1:1)
 - Hexane:Acetone (1:1)
 - ASE Parameters (ASE 100)
 - 1500 psi
 - 100° C
 - 3 x 5 minute static cycles
 - 60% flush
 - 120 second purge
- Test substances:
Lindane, Heptachlor, Aldrin, Dieldrin, Endrin, DDT

Extraction of Organochlorine Pesticides from Silt Loam Soil

- Loam is soil composed mostly of sand and silt, and a smaller amount of clay (34% sand, 54% silt, 12% clay, and 5% organic carbon)

pH = 7

Pesticide	% Recovery Using Sodium Sulfate	% Recovery Using ASE Prep MAP: DE
Lindane	73%	82%
Heptachlor	83%	88%
Aldrin	85%	94%
Dieldrin	87%	102%
Endrin	95%	123%
DDT	93%	111%
Overall	86 ± 8%	100 ± 15%



* Data courtesy of Department of Toxicology, Texas Tech University, Lubbock

** In-cell drying with sodium sulfate is not recommended using the Dionex ASE system

Extraction of Organochlorine Pesticides from Whole Shrimp

- High water and Lipid content



Pesticide	% Recovery Using Sodium Sulfate	% Recovery Using ASE Prep MAP: DE
Lindane	65%	96%
Heptachlor	62%	94%
Aldrin	58%	95%
Dieldrin	77%	106%
Endrin	79%	119%
DDT	85%	123%
Overall	71 ± 11%	106 ± 13%

* Data courtesy of Department of Toxicology, Texas Tech University, Lubbock

** In-cell drying with sodium sulfate is not recommended using the Dionex ASE system

Extraction of Organochlorine Pesticides from Oysters

- High in water and Lipid Content

Pesticide	% Recovery Using Sodium Sulfate	% Recovery Using ASE Prep MAP: DE
Lindane	81%	88%
Heptachlor	67%	83%
Aldrin	66%	91%
Dieldrin	75%	99%
Endrin	70%	104%
DDT	69%	94%
Overall	71 ± 6%	93 ± 7%



* Data courtesy of Department of Toxicology, Texas Tech University, Lubbock

** In-cell drying with sodium sulfate is not recommended using the Dionex ASE system

Total Fat Extraction from Animal Tissues

Application Example 4

- Industrial food processors are concerned with the reduction of total fat, saturated fat, and cholesterol
- The FDA Nutrition Labeling and Education Act of 1990 (NLEA) requires that all nutrient content claims be verified (i.e., 'low fat')
- In-cell moisture removal and fat extraction

Animal No.	% Fat Extracted by Current Freeze Drying Method	% Fat Extracted Using Dionex ASE Prep MAP	Difference
111	8.5	9.0	0.55
83	4.1	4.4	0.25
26	9.5	9.6	0.02
112	8.4	8.9	0.50



* Data courtesy of Processed Foods Research Unit USDA

- Conditions: Temp: 60C; preheat 5 min; Static: 10 min; Cycle: 1; rinse vol: 60%; purge: 120 sec; solvent: 100% of 3:2 Hexane/IPA
- A time-savings of three days when compared to the currently used freeze drying method

Conclusion

- Dionex ASE Prep MAP polymer is designed for in-cell (in-line) or in-vial (off-line) moisture removal
- Unique formulation allows moisture removal under a variety of ionic strength conditions
- Polymer overcomes the limitation of sodium sulfate for in-cell moisture removal and extraction
- Drying is faster than air drying, oven drying, and freeze drying
- Moisture removal was successfully demonstrated for a variety of solvent, temperature and matrices under accelerated solvent extraction conditions

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