Increasing Extraction Efficiency of Pesticides and Dioxins from Wet Samples Using a Novel Polymer During Accelerated Solvent Extraction

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Overview

Accelerated solvent extraction is a high-temperature, high-pressure extraction technique that is widely used for sample extractions in the environmental, chemical and food analysis industries. Extractions at higher temperatures and pressures allow faster extraction of analytes relative to conventional solid-liquid based extraction techniques such as Soxhlet. Typically the sample is mixed with a dispersant and loaded into a cell followed by extraction with a suitable solvent. Analyte recovery using this method of extraction for wet samples is always challenging, as the presence of water in the sample can interfere with the extraction efficiency. The analyte of interest may partition between the extracting solvent and the water phase. It is therefore desirable to dry the sample prior to extraction. Traditional drying techniques that involve mixing the wet sample with an inorganic salt that has a high affinity for the aqueous phase are unsuitable for in-cell extraction. This study presents the use of a novel new polymer for in-line drying of a wet sample for the analysis of organochlorine pesticides, and polyaromatic hydrocarbons (PAHs) in different matrices. Data showing recoveries for each of these target compounds in different matrices will be presented.

Introduction

Thermo Scientific™ Dionex™ ASE™ Prep MAP is a proprietary polymer designed to remove moisture and increase extraction efficiencies from wet samples including soils, tissues and food products. This unique formulation allows moisture removal under a variety of ionic strength conditions and accelerated solvent extraction conditions. It is useful for in-cell extractions of trace level organics from a variety of moisture containing samples such as soil, sediments, animal tissue, fruits, and vegetables with no additional pre or post extraction steps.

Methods

Sample Preparation

Moisture containing samples were used or a known amount of water was added to dry samples for Method A. The samples were then combined in a 1:1 ratio of Dionex ASE Prep MAP and Thermo Scientific™ Dionex™ ASE™ Prep DE prior to extraction. Oyster samples for Method B were prepared by blending or chopping to produce a uniform homogenate. A 2 g portion of the homogenate was then accurately weighed and mixed with 1 g of Dionex ASE Prep DE and 1 g Dionex ASE Prep MAP. Samples in both cases were transferred into extraction cells and extractions were performed according to the conditions listed in the table. In the case of spiked samples the spikes were added to the sample prior to extraction.

ACCELERATED SOLVENT EXTRACTION CONDITIONS		
	Method A	**Method B**
Oven Temperature	100 ˚C – 150 ˚C	100 ˚C
Pressure	1500 psi	1500 psi
Oven Heatup Time	5 min	5 min
Static Time	5 -10 min	5 min
Static Cycles	1-3	3
Rinse Volume	60%	60%
Solvent	Hexane or 1:1 Acetone/Dichloromethane	Hexane/Acetone (1:1, v/v)

Results

The moisture removal polymer, by itself, can remove up to 5 g of water per gram of the polymer at room temperature. The addition of Dionex ASE Prep DE, when used in an accelerated solvent extraction cell configuration results in improved removal of water under accelerated solvent extraction conditions. The water absorbing ability of the polymer increases with decreasing temperature. For example, at 100 °C 4 gm of Dionex ASE Prep MAP and 4 gm of Dionex ASE Prep DE can remove roughly 10 gm of water where as at room temperature about 2 gm of the polymer is adequate for this application.

Moisture Removal Formats

In-Cell Moisture Removal Mode

This mode is designed for inline moisture removal with the Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor system. The moisture absorbing polymer is combined with the Dionex ASE Prep DE preferably in a 1: 1 ratio to aid moisture removal. In this mode after the extraction is complete the collected solvent is expected to be free of moisture. The amount of Dionex ASE Prep MAP required can be estimated from the expected moisture content of the sample. Typically this mode is recommended for all samples where the extraction method is run at 125 ˚C and below. The benefit of this mode is that there is no need to remove the moisture post extraction.

In-Vial Moisture Removal Mode

This mode is designed for offline moisture removal such as with the collected solvent extract from the accelerated solvent extraction. The amount of polymer required can be calculated based on the estimated amount of moisture in the extract container. The amount of moisture absorbing polymer needed is 0.20 ± 0.05 g for absorbing one gram of water at room temperature. The extract can also dried by passing it through a bed of Dionex ASE Prep MAP placed on a filter paper. This mode is applicable to all accelerated solvent extraction methods independent of temperature.

Combination Mode

In this mode, the in-cell moisture removal is followed by in-vial moisture removal. If some break through of moisture is observed in the extract during extraction then addition of a small amount of polymer in the collection bottle can result in complete moisture removal. This mode is particularly useful for samples with unknown moisture content and for extractions occurring above 125 ˚C. The mode is also recommended for use with water containing solvents.

In-Cell Moisture Removal (Method A)

A combination of Dionex ASE Prep MAP and Dionex ASE Prep DE (1:1) was used to perform in-cell extractions on wet samples at various extraction temperatures and cell sizes, using hexane as the extraction solvent. Table 1 shows the results of this analysis. The water removal efficiency dropped as the temperature increases.

Table 1: In-Cell moisture removal using Dionex ASE Prep MAP and Dionex ASE Prep DE at various temperatures and cell sizes during accelerated solvent extraction.

Extraction Temperature °C	Total Water Present in the Cell (g)	Amount of Dionex ASE Prep MAP (g)	Amount of Dionex ASE Prep DE (g)	Cell Size (mL)
100	5.05	2	2	34
125	2.54	2	2	34
150	2.15*	2	2	34
100	10.0	4	4	66
125	5.05	4	4	66
150	2.09*	4	4	66
100	15.1*	6	6	100
125	8.14*	6	6	100
150	2.14*	6	6	100

*Maximum Water Removed

Table 2 shows the amount of polymer required for in cell moisture removal with accelerated solvent extraction under a variety of common temperatures. It is clear that as the temperature increases the water removal and the maximum water removal decreases.

Table 2: Polymer and Dionex ASE Prep DE amounts required for in-cell moisture removal at various temperatures.

Temperature °C	Amount of Polymer required per gm of water	Amount of Dionex ASE Prep DE required per gm of water
100	0.4 g	0.4 g
125	0.8 g	0.8 g
150	1.0 g	1.0 g

Moisture Removal Under High Ionic Strength Conditions

The moisture removal capacity of the Dionex ASE Prep MAP was measured at room temperature with and without added salt solution (Table 3). The moisture removal capacity was unaffected by the salt concentration. In contrast, the other commercially available polyacrylate-based polymer showed a lower moisture absorbing ability as the salt concentration increased. Additionally the polyacrylaye-based polymers are not suitable for extraction under accelerated solvent extraction conditions as they give out water. In contrast the Dionex ASE Prep MAP is ideal for moisture removal under accelerated solvent extraction conditions.

Table 3: Moisture removal capacity of the Dionex ASE Prep MAP compared to a polyacrylic acid based polymer.

Type of Polymer	Polymer needed to Absorb 1 gram of water (g)	Polymer needed to Absorb 1 gram of 2.91% NaCl solution * (g)	Polymer needed to Absorb 1 gram of 26.5% NaCl solution ** (g)
Dionex ASE Prep MAP	0.20	0.19	0.18
Commercial Polyacrylate-based Polymer	0.04	0.08	0.27

* Sea Water Concentration
** Saturation Level Concentration

Organochlorine Pesticide analysis of Oyster Samples Following In-Cell Moisture Removal (Method B)

Table 4. In-cell moisture removal of oyster sample using Dionex ASE Prep MAP and Dionex ASE Prep DE.

Compound	% Recovery Oyster dried with Dionex ASE Prep MAP and Dionex ASE Prep DE* (n = 3)	Recovery % Oyster dried with sodium sulfate** (n = 3)
Lindane	91	81
Heptachlor	93	64
Aldrin	94	66
Dieldrin	105	75
Endrin	106	70
DDT	114	69
Total	101	71

* Data is courtesy of Department of Toxicology, Texas Tech University, Lubbock, TX, USA

** In-cell drying with sodium sulfate is not recommended using the ASE instrument.

The spiked oyster samples were either treated with Dionex ASE Prep MAP and Dionex ASE Prep DE (1:1) or by using sodium sulfate as the drying agent prior to in-cell extraction in the Dionex ASE 350 system. The extraction was pursued at 100 °C using hexane: acetone (1:1) as solvents. The extracts were analyzed by GC-ECD. The results in Table 4 shows recoveries ranging from 91% for Lindane to 114% for DDT when the extractions are done using the Dionex ASE Prep MAP and Dionex ASE Prep DE and the recoveries for extractions done with sodium sulfate are considerably lower ranging from 69% for DDT to 81% for Lindane. The data shows that Dionex ASE Prep DE is an effective drying agent for wet oyster samples with excellent recoveries for the six OCPs. In contrast the sodium sulfate treated sample showed poorer recoveries.

Soil samples of 5 g each were spiked with known concentrations of PAHs. Following spiking with PAHs the soil samples were moistened with known amount of water (30% moisture). Each of the spiked wet soil samples were mixed with 4 g of 1:1 polymer and Dionex ASE Prep DE and loaded into a 34 mL cell. The soil samples were then extracted using the Dionex ASE 350 system using Method A. The extracts were evaporated to 1 mL under nitrogen stream at 40 °C. The concentration of the final concentrates were calculated to be 20 µg/mL. The extracts were analyzed using GC-FID. Table 5 shows that PAH recovery using Dionex ASE Prep MAP in the In-Cell and In-vial format shows comparable results, with the exception of Acenaphthylene and Benzo (g,h,i) peylene. This indicates that the in-cell extraction conditions for these two analytes still need to be optimized; however the recovery values are still within the acceptable range of US EPA method 8270 (± 30%).

Table 5. PAH recovery using GC-FID.

Compound	In-Cell Moisture removal by Dionex ASE Prep MAP and Dionex ASE Prep DE	In-Vial Moisture removal by Dionex ASE Prep MAP and Dionex ASE Prep DE	In-Vial Moisture removal by Sodium Sulfate**
	% Recovery	% Recovery	% Recovery
Naphthalene	78	101	96
Acenapththyene	94	99	98
Acenaphthylene	75	97	96
Phenanthrene	101	103	99
Anthracene	103	103	100
Fluoranthene	102	110	101
Pyrene	99	109	101
Benzo(a)anthracene	97	116	108
Chrysene	93	117	104
Benzo(b)fluoranthene	96	120	104
Benzo(k)fluoranthene	97	119	106
Benzo(a)pyrene	85	118	106
Indeno((1,2,3,c,d)pyrene	98	112	106
Dibenzo(a,h)anthracene	110	111	105
Benzo(g,h,i)perylene	106	113	107

Conclusion

- Unique formulation of Dionex ASE Prep MAP allows moisture removal under a variety of ionic strength conditions and accelerated solvent extraction conditions.
- Useful for in-cell extraction of organochlorine pesticides in a variety of moisture containing samples. OCP recoveries in oyster samples range from 91% for Lindane to 114% for DDT when the extractions are done using ASE Prep MAP and ASE Prep DE. The recoveries for extractions done with sodium sulfate are considerably lower ranging from 69% for DDT to 81% for Lindane.
- Dionex ASE Prep MAP has a high-capacity for water removal and does not suffer from some of the limitations of clumping or precipitation observed in some of the traditional drying methods.

References

1. Burford, M. D., Hawthorne, S. B., Miller, D. J. *Evaluation of drying agents for off-line supercritical fluid extraction*, J. Chromatography A, **1993**, 657, 413-427.

2. Hirotake, O., Masahrio, O., Sachiko, K., Shinjiro, H. D*etermination of Acephate and Methamidophos in Foods Using Super-absorbent Polymer*, Analytical Communications, **1997**, 34, 253-256.

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