

Advances in Sample Preparation for Accelerated Solvent Extraction

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Overview

Purpose: To demonstrate the utility of a new polymeric material as a water absorbent consumable for extraction applications.

Methods: Water absorption at room temperature was measured by mixing the water with the polymer. The in-cell water removal was performed in an extraction setup in an accelerated solvent extraction instrument at high temperature and pressure. Analytes in the extract were measured by high-pressure liquid chromatography.

Results: The in-cell method with the water absorbing polymer can remove moisture when mixed with wet sample. A simple addition of a small amount of polymer in the collection bottle can also result in complete water removal from the collected extract.

Introduction

Analyses of organic pollutants are becoming increasingly important, and the emphasis has been being able to isolate and analyze trace organic compounds from a variety of matrices such as soil, sediment, fruits, and vegetables. In this regard, sample pretreatment constitutes an important step prior to analysis. The purpose of the sample pretreatment step is to selectively isolate or concentrate the analytes of interest from matrix components and present a sample suited for routine analysis by established analytical techniques such as gas chromatography or high-pressure liquid chromatography. Typical sample pretreatment steps include techniques such as solid phase extraction, liquid-liquid extraction, solid-liquid extraction, dilution, evaporation, distillation and the like. Accelerated solvent extraction (ASE) is a technique used for extracting the analytes of interest from a solid, semisolid or liquid sample by performing extraction using an organic solvent at elevated temperature and pressure. The elevated pressure also elevates the boiling temperature of the solvent, thereby allowing faster extraction to be conducted at relatively higher temperatures. The benefit of higher temperature extraction is primarily speed; this extraction process is significantly faster than traditional methods such as soxhlet extraction.

In some samples containing moisture or water such as soil samples or food samples (fruits, vegetables etc.) an additional step may be needed either before the extraction to remove the moisture from the samples or post extraction to remove the moisture from the extracted solvent (containing the extracted analytes). Sample drying can be accomplished in several ways such as air drying and oven drying prior to extraction. However, these approaches are not suited when analyzing volatile or semi-volatile components as they would be removed from the sample prior to extraction or analysis.

Another common method for moisture removal is by using salts such as sodium sulfate, calcium chloride, magnesium sulfate, calcium sulfate and the like. These salts tend to associate to water molecules to form hydrated salts. Sodium sulfate for example tends to clump together when water is present.

Sodium sulfate is not suitable for in-cell moisture removal and extraction in ASE. Sodium sulfate can dissolve in hot solvent to a certain extent and can precipitate downstream in some instances clogging the outlet frit, tubes and valves. Moreover, sodium sulfate becomes an aggregate hard lump upon water absorption and is not easy to process during sample preparation for in-cell moisture removal and extraction.

Polymers have been used for moisture removal such polymers have been designated super absorbent polymers. The most common polymer is the sodium salt of polyacrylic acid. Although this polymer removes water by absorbing it into the polymer matrix, the water absorbing capacity decreases as the ionic strength increases. Another limitation of the polymer is poor water absorbing property under high temperature conditions. Yet another limitation of this polymer is that it becomes a hard plug inside the extraction cell (1). The present research solves these issues.

Here, the authors synthesized water absorbent polymer comprising a copolymer of a basic monomer with an acidic monomer. This combination is suitable for moisture removal under high ionic strength conditions. Results shown here also demonstrate that when the polymer is mixed with diatomaceous earth (DE) absorbent the water removal efficiency increases significantly. Different formats of using the polymer such as in-cell, in-vial and a combination of the two are discussed.

Methods

Polymer used

A proprietary water absorbent polymeric material used here.

Sample preparation

Sample containing moisture was used or a spiked sample with water was added to the polymer or polymer and DE and loaded into the Thermo Scientific Dionex ASE cell for the extraction in ASE.

Extraction in ASE

Sample extraction at high temperature and pressure was performed using the Dionex ASE 350

ASE 350™ extraction condition:

Pressure: 1500 psi
Temperature: 100 °C- 150 °C
Static time: 5-10 min
Cycles: 1-3
Flush: 10-75%
Purge: 120 sec
Solvent: Hexane or 1/1 Acetone/Dichloromethane

Measurement of moisture removal capacity at room temperature

Known amounts of water were spiked as the sample and was mixed with the polymer to measure the water removal capacity at room temperature in the presence of organic solvent. Similarly, water removal capacity of sodium sulfate was measured at room temperature for comparison purposes.

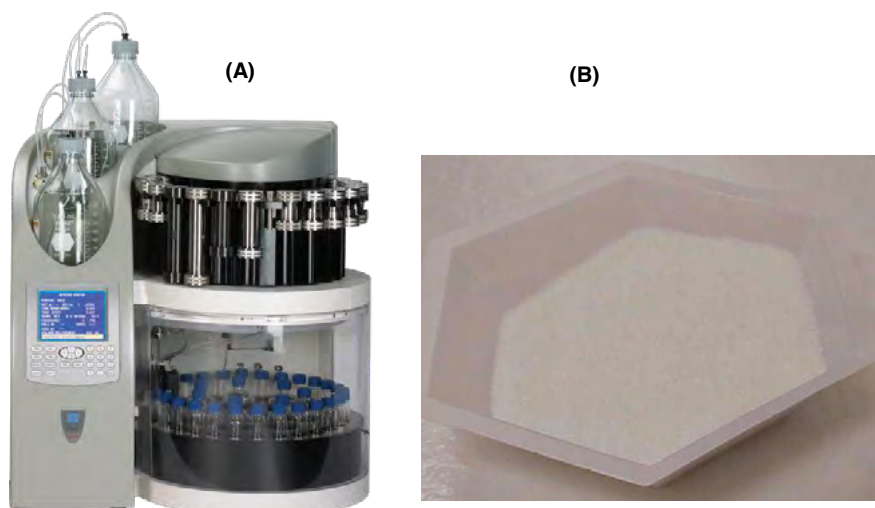
Water removal capacity of polymer and polymer-DE in Dionex ASE

The water removal capacity of the polymer was measured as the maximum amount of water present in the cell without any breakthrough of the water into the collection bottle.

Liquid chromatography

A P680 pump, PDA-100 photodiode array detector and a chromatographic oven were used for chromatographic separation. Thermo Scientific Dionex Chromeleon 6.8 chromatography data system software was used for data acquisition. The separation column was a Thermo Scientific Acclaim Polar Advantage C16 5µm 4.6 x 150 mm, flow rate was 1.0 mL/min. Separation was based on gradient elution of A comprising 25 mM acetic acid/ammonium acetate and B comprising of acetonitrile where composition of B changed from 25% to 70% over 17.5 min. Detection wavelength was 280 nm.

FIGURE 1. (A) The Dionex ASE 350 System; (B) The water absorbent polymer



Results

Water-absorbent polymer capability

The amount of water-absorbing polymer needed is approximately 0.20 g for absorbing one gram of water at room temperature.

The moisture removal formats

a) In-cell moisture removal:

The water-absorbing polymer can remove moisture when mixed with wet sample for in-cell moisture removal and extraction. For improved flow characteristics and improved moisture removal the polymer is used in conjunction with Thermo Scientific ASE Prep DE (diatomaceous earth). Dionex ASE Prep DE is normally used with the sample when pursuing ASE extraction, therefore adding the polymer to this setup maintains the customer's current practices.

Under the high-temperature extraction conditions of the ASE the water-absorbing ability of the polymer decreases with increasing temperature. For example, at 100 °C a 4 g polymer and 4 g DE can remove roughly 10 g of water completely where as at room temperature only 2 g of the polymer is adequate. The polymer can be used by itself when pursuing in-vial moisture removal or extractions. Note: Sodium sulfate should not be used to remove water in the in-cell configuration.

b) In-vial moisture removal:

The amount of water-absorbing polymer needed is 0.20g for absorbing one gram of water at room temperature. A simple addition of a small amount of polymer (proportional to the amount of water present) in the collection bottle can result in complete water removal from the extract. In comparison the amount of sodium sulfate needed is 4g to absorb one gram of water. Further there is no need to add the polymer in an aliquot basis.

c) Combination Mode:

In this mode, the in-cell moisture removal (in-line) is followed by in-vial moisture removal (off line). If some breakthrough of water is observed in the extract then addition of a small amount of polymer in the collection bottle can result in complete moisture removal. In fact a small amount in the collection vessel always ensures that there would be no moisture present in the samples. This mode is particularly useful for samples with unknown moisture content.

In-cell moisture removal

The polymer was tested for in-cell water removal using a Dionex ASE 350 system at various extraction temperatures. Hexane was used as the extraction solvent. Results are shown below in Table 1. The polymer retained its conformation and could be used by itself or in conjunction with DE. The water removal efficiency dropped as the temperature increased, nevertheless practical water removal was still feasible even at 150 °C. The maximum water removal was 4.0g using only polymer at 100 °C. When the polymer is mixed with DE, water removal efficiency increases significantly due to improved flow characteristics. The water removal capacity of this combination (polymer and DE) will be tested at higher temperatures (125-150 °C) in the near future.

Table 1. In-cell water removal capacity of the polymer and polymer-DE at different temperatures in ASE.

Temperature, °C	Maximum water present in the cell, g	Polymer/Dispersant	Water observed in the collection bottle, g
100	4.0	4g polymer	No
110	3.5	4g polymer	No
125	2.2	4g polymer	No
150	1.5	4g polymer	No
100	10.05	4g polymer and 4g DE	No

Analyte recovery for in-cell moisture removal and in-vial moisture removal

Analyte recovery from the Dionex ASE extraction using the polymer was studied using a mixture of phenols. An in-cell extraction was pursued in the presence of 8 g of the polymer and a spike with a standard solution that contained 1.5 mL standard solution in acetonitrile and 8.5 mL of water. The spiked polymer sample was then extracted using the Dionex ASE 350 instrument and a 1:1 ratio of dichloromethane: acetone solvent at an extraction temperature of 100^o C. The extract was evaporated to 10 mL under nitrogen stream at 40^oC. The spike level was 30 µg/mL for a 10 mL extract.

The 10 mL extract was analyzed using high-pressure liquid chromatography (HPLC) instrument. The results from the above experiment are shown in Table 2. The per cent recovery data showed acceptable performance of the polymer for these test analytes based on an acceptance criteria of ± 30%. Moreover, it also indicates that there is no detrimental effect of using this polymer for in-cell extraction for these test analytes.

Analyte recovery for in-vial moisture removal at room temperature was studied using same concentration level of analytes in a 10 mL solvent. A known amount of water (5 mL) was spiked into the 10 mL solvent. The water was removed either by polymer or by sodium sulfate. The results are shown in Table 2. Comparable recoveries were obtained for in-vial moisture removal by the polymer compared to sodium sulfate.

Table 2. Recovery of analytes for in-cell moisture removal at 100 °C by polymer, in-vial moisture removal at room temperature by polymer and sodium sulfate .

	Analytes	Total spike level in 10 mL	In-cell moisture removal by polymer	In-vial moisture removal by polymer	In-vial moisture removal by sodium sulfate
		µg	% recovery	% recovery	% recovery
1	2, 4-Dinitrophenol	300	81.01	82.96	86.79
2	Phenol	300	89.99	88.58	88.41
3	P-Toluidine	300	86.72	95.03	93.88
4	4-Nitrophenol	300	96.05	90.96	88.93
5	2-Chlorophenol	300	92.33	87.45	87.16
6	4-Ethylaniline	300	92.82	89.47	88.02
7	4-Chloroaniline	300	94.44	88.39	87.51
8	2-Nitrophenol	300	93.83	92.64	87.39
9	2, 4-Dichlorophenol	300	97.50	93.25	89.58
10	2, 4, 6-Trichlorophenol	300	97.51	95.20	91.02

Water removal capacity with and without added salt solution

The water removal capacity of the polymer from the present study and sodium polyacrylate polymer were compared with and without added salt solution. The water removal capacity of the in-house polymer was substantially unaffected by the salt concentration and roughly similar amount of polymer was sufficient for absorbing 1 g of water independent of the salt matrix. In contrast, the polyacrylate polymer was affected by the matrix. The in-house polymer is suitable for moisture removal even under high ionic strength conditions.

Table 3. Water removal capacity of the polymer versus a commercial polyacrylic acid-based polymer at room temperature.

	Grams of polymer needed to absorb per g of water	Grams of polymer needed to absorb per g of 2.91% NaCl solution (sea water concentration)	Grams of polymer needed to absorb per g of 26.5% NaCl solution (saturation level concentration)
Polymer	0.20	0.19	0.18
Polyacrylate polymer	0.04	0.08	0.27

In-cell moisture removal with fruit and vegetable samples

The moisture removal capacity of the polymer-DE was tested in-cell using fruits and vegetable samples. Homogenized fruits or vegetable (10 g) sample mixed with 4g polymer and 4g DE and loaded into Dionex ASE cell for the extraction. The ASE extraction was pursued at 100 °C. Hexane was used as extraction solvent. The results on Table 4 indicated that the polymer and DE combination produced excellent results with real life samples.

Table 4. In-cell water removal of the polymer-DE at 100 °C using fruit and vegetable samples.

Temperature, °C	Sample, g	Total water present in the cell, g	Dispersant	Water observed in the collection bottle, g
100	10g Apple	8.49	4g polymer and 4g DE	No
100	10g Carrot	8.79	4g polymer and 4g DE	No
100	10g Pear	8.49	4g polymer and 4g DE	No

Conclusion

- The utility of a new water absorbent polymer for removing moisture from wet samples as well as from a collected extract is shown here.
- The new polymer is designed to work with accelerated solvent extraction and is intended for in-cell (in-line) moisture removal, in-vial (off line) moisture removal such as from the Dionex ASE collection vial and a combination of both in-cell and in-vial.
- The unique formulation of the polymer allows moisture removal under ASE extraction conditions and is not affected by the sample ionic strength. The polymer is a free-flowing white granular material that can be easily mixed with Dionex ASE Prep DE and used for the moisture removal applications. Additionally the polymer can be easily removed from the Dionex ASE cell after the high-temperature extractions are complete.
- The polymer overcomes the limitation of sodium sulfate for in-cell moisture removal and extraction.
- Details investigations are underway to expand the applicability of this polymer with various samples/applications.

References

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