



Empore™ Extraction Disks

General Guidelines for Applications

February 1996

Empore™ Extraction Disks with Chelating Resin (Iminodiacetate Functionalized Poly [styrenedivinylbenzene])

Empore Chelating Resin Disks provide a mechanism to selectively remove multivalent metal cations from solutions by simply passing the solution through the porous membrane. The selectivity can be used to concentrate either the metals from “large” volumes of matrix or to selectively isolate them from a complex organic or inorganic matrix. If the intent is to quantify the ionic metals, the chelating resin is eluted and the eluate analyzed. In the reverse application, the chelator could be used to purify a solution when the metals are the source of problems in an application. In this case, the purified filtrate is now ready for use, and the metal ions are bonded to a solid support which can be disposed in an environmentally acceptable manner.

Summary

The disk consists of a polymer support (cross-linked poly[styrenedivinylbenzene]) functionalized by bonding at the nitrogen atoms to iminodiacetic acid groups. The functional group exhibits differing ionic charges depending on the pH of the solution. For instance, at a pH of 2, the carboxylate groups will be neutral; however, the nitrogen will have a net positive charge and the molecule a weak anion exchange capability. Increasing the pH ionizes the carboxylate groups and at pH ≥ 5 both are negatively charged. As the pH approaches neutral, the molecule functions as a cation exchanger or metal cation chelator as described herein.

In general, a chelating agent, or ligand, contains two or more electron donor atoms that can form coordinate bonds to a single metal ion; and with successive donor atoms, creates a ring containing the metal ion. The ring structure is referred to as a chelate, the name deriving from the Greek word *chela* for the great claw of the lobster. Stability of the chelate complex is strongly dependent on the relationship between the size of the metal ion and that of the opening within the crown or crypt. Mercury (Hg^{2+}), for example is extracted efficiently from solution; however, is extremely difficult to elute from the sorbent.

This iminodiacetate chelator has an affinity for multivalent (primarily 2+ and 3+) transition elements; and it will bind better with alkaline earth than alkali metal ions. Relative selectivity roughly follows the EDTA formation constants: $\text{Pb} > \text{Cu} > \text{Cd} > \text{Co} > \text{Fe} > \text{Ca} > \text{Sr}$. Capacity is relatively high and is dependent on the matrix pH (higher at about pH ≥ 5) and which ions are present in solution. Elution is accomplished with an acid solution such as 3 molar(M) nitric or hydrochloric acid.

Product Information

Particle Size:	8 microns
Composition:	90% Iminodiacetate functionalized SDB 10% PTFE
Thickness:	0.5 mm
Ionic form:	Sodium salt of iminodiacetic acid
Stability to Solvents:	Compatible with all organic solvents (it may swell in some solvents)
pH Stability:	Stable between 0 - 14
Flowrate:	3-10 min/ltr (47mm disk with DI water, 500 mm Hg @ 25°C)
Disk sizes:	25mm in syringe tip filter holder 47mm and 90mm for use with standard filtration glassware
Capacity¹:	Cu ⁺² = 0.45 millimoles @ pH 5
Breakthrough¹:	Cu ⁺² = 0.30 millimoles @ pH 5

Selectivity

Candidate metals in ammonium acetate buffer were evaluated in three groups to ascertain relative selectivities. Replicate experiments were done on 47mm disks with standard mixtures of the metals at either 5 or 20 ppm. The standards were applied sequentially in aliquots and each aliquot of filtrate analyzed by ICP.

As with ion exchange chemistry, higher selectivity cations will displace those of lower selectivity when near the capacity or breakthrough values. Based on the experimentation, the order of selectivity within each group is:

- Cu>Cd>Co>Mn>Ba>Ca>Sr
- Zn>Al>Cr>Sn
- Pb>Fe>Ni>Mg

Capacity/Breakthrough

Capacity determinations were done individually for Cu²⁺, Fe³⁺, and Pb²⁺; each in a pH 5 ammonium acetate buffer. Each 47 mm disk was loaded well past the point at which the metal was detected in the filtrate (breakthrough concentration) and both the amount retained on the disk (capacity) and the breakthrough concentration determined.

Capacity determinations for all three metals tested were similar and averaged 0.45 millimoles metal/47mm disk as listed in the product description section. Relative standard deviations for replicates of each metal were less than 5.

Some general comments on capacity:

- Capacity of the disk differs for the same metal as the pH increases. For instance, at pH 3 versus pH 5, the average capacity for Cu⁺² increased from 26 to 32 mg/disk.
- When nearing the breakthrough concentrations, the more strongly bonded metals (Cu, Pb, Fe) will displace those less strongly bonded.
- When capacity is of concern, the concentrations of other cations present in the matrix must be considered as they may compete for the sites.
- Chelation may not occur if the metal ion of interest is complexed with another anion in the matrix.

¹ Capacity is the absolute amount of copper retained by the disk after sequential addition of copper in aliquots and was determined by mass balance calculation following the analyses of filtrate aliquots. Breakthrough is the point in the sequential addition at which some copper was detected in the filtrate. Both values were determined for 47mm disks in standard extraction glassware.

General Procedure for Extracting Liquid Samples

The instructions herein are intended as guidelines only. Sample volume, pH, complexing agents, etc. may be changed to selectively extract specific multivalent metal ions. Additional assistance is available from 3M Empore Technical Service at (800) 328-5921.

1. All glassware should be precleaned according to your lab protocols for glassware used in metals analysis. Plasticware is acceptable. Do not use metallic or PTFE-coated metallic disk supports. Kel-F supports are available for the 3M Empore Extraction Glassware. Contact your distributor representative for ordering information. ***Always use metal-free reagents with the chelator disks.***
2. Center the chelator disk on the base of the extraction glassware. If the matrix to be extracted is solvent-based, wet the disk with about 2 mLs of a metal-free solvent such as methanol to preswell the polymer. The sorbent is a polymeric resin which will swell when wetted with solvent. Therefore, a prewash with a metal-free solvent prior to assembling the extraction glassware will prevent cosmetic wrinkles from forming. Seat the glass reservoir and clamp in place.
3. **Prewash/Condition.** The glassware and disk by adding 20 mLs 3 molar nitric or hydrochloric acid (select an acid compatible with your instrumentation) to the reservoir. Allow it to soak for a minute, then draw the acid through. To eliminate any residual acid, wash the reservoir and disk twice with about 50 mLs metal-free DI water. The chelator disk is a hydrophilic sorbent; therefore, methanol conditioning is not necessary.
4. **Convert to ammonium form.** The chelator is shipped as a sodium salt of iminodiacetic acid. The ammonium form is the most active. To convert the disk to the ammonium form, add about 100 mLs of a 100mM ammonium acetate buffer at pH 5.3. Allow the disk to soak for a minute then draw the buffer through using a vacuum. Optionally, 20 mLs of 2M ammonium hydroxide can be used.
5. **Sample Extraction.** Add the sample (pH \geq 5) to the reservoir and apply the vacuum to draw the entire sample through. When the extraction is complete, rinse the disk with 20 mLs DI water.
The liquid sample matrix pH should be about 5 for extracting most common transition metals. The matrix can be aqueous- or solvent-based. The SDB particle is stable in commonly used organic solvents; it may, however, swell when wetted with some solvents. If the sample contains high levels of particulates, it may be advantageous to prefilter prior to extracting.
6. **Elution.** With an elution vial in the receiver, elute the chelator by adding 10 mLs of 3 molar nitric or hydrochloric acid to the reservoir. Allow it to soak for a minute, then draw through with a vacuum. Repeat the elution with a second 10 mL aliquot of acid. NOTE: Elution efficiency studies focused on number of aliquots but did not vary aliquot volume, hence the 10 mL aliquot size herein. The use of two aliquots was shown to effectively elute >95% of bound analytes. Elution volume may be optimized to stay within a target final volume so as to proceed directly to the instrumentation.
7. Adjust the final volume of the eluate to the desired volume and proceed to ICP or AA analysis as appropriate.

IMPORTANT NOTICE TO PURCHASER:

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