

## Spherification: Experimenting with Food Gels, Polymers and Hydrocolloids

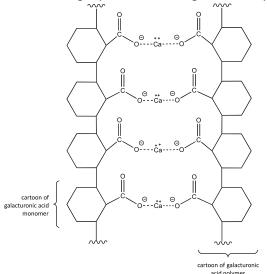
### Introduction:

This laboratory describes three types of molecular gastronomy style (aka modernist cuisine) food experiments. Gels and hydrocolloids are examples of food polymers. Many food polymers including complex polysaccharides, can bind a significant number of water molecules due to many polar bonds found their carboxyl and alcohol functional groups. Because these long polymers bind to shells of water and interact with each other (sometimes binding directly to each other called cross-linking), gels and hydrocolloids add a viscosity to a solution. At higher concentrations they form a semi-solid "gel" as the polymers will interact with each other. These long strands of polymers will tangle, can cross-link and have a tremendous water holding ability. This means the water is "held in place" by the intertwined gels and hydrocolloids. Altogether, this physical interaction creates a coherent liquid mass that is used for many purposes. A simple examination of food in the freezer section (frozen prepared



**Modern Chemistry in the Kitchen.** A. Mint direct spherification. B. Reverse or indirect spherification of liquid flavors. C. Students preparing their own creation of a direct spherification

foods and ice cream for just a few examples) will show you many of the gels and hydrocolloids (from simple starch to alginate, xanthene gum, gum arabic, etc.) that are used to maintain the viscosity of frozen foods. You will also find these additives in cheese, sauces and other items. While some of these additives seem strange, they are isolated from natural materials and sometimes slightly modified making them an important tool in the kitchen.



**Background:** In food, gels and hydrocolloids are an interesting way to deliver food and liquids in a unique and interesting way. Gels can be very rigid (agar gels) or elastic and flexible (think Jello). The formal definition of a gel is a colloid (particles dispersed in a continuous medium) where the viscous medium acts more or less like a solid. These molecules are primarily isolated from natural sources. Agar, alginate and carrageenan are complex carbohydrates from seaweed, locust bean gum is made from carob plant seed, fruit cell walls produce pectin and the cellulose found in all vegetative matter is used to produce methylcellulose.

We will be using a few different compounds in this laboratory: alginate, agar and locust bean gum. Take the time to look up the structure, composition and chemical behavior of each of these hydrocolloids to best understand how to use them.

An important step in spherification experiments is hydration. Hydration is the act of water binding, via hydrogen bonds to a large polymer causing the polymer to swell. When done properly, gels will bind to each other and absorb

water creating a mesh network (sometimes cross-linked, others not). How a gel hydrates can be tricky - some gels will bind a tight layer of water forming a shell that limits water access to gel particles trapped within a clump of solid non-hydrated powder. If you tried to add a thickener to make gravy you have likely already observed this phenomena. Think of a blob of cornstarch at the bottom of a pot with the thick impenetrable layer covering the rest of the dried cornstarch! Each gel will hydrate a little differently. In general, getting a good dispersion of the particles before or as they hydrate avoids lumps of gels. Sometimes this is done by mixing the gel with another solid, often table sugar before adding to water. This is done to limit the gel molecules from interacting until they hydrate. Sometimes they are pre-hydrated in corn-syrup or alcohol. The latter can interfere with some spherification experiments.



Turning a flavorful liquid into a sphere that pops in your mouth is an invention of modern kitchen *alchemy* that uses the principles of calcium crosslinking of polysaccharides such as the calcium crosslinking of pectins discussed in this section. In the process of *direct spherification*, a flavorful liquid is blended with sodium alginate powder. The alginate is a polysaccharide (similar to pectin) derived from seaweed. In direct spherification, the liquid-sodium alginate mixture is then dripped into a bath of calcium chloride. The calcium ions displace the sodium and crosslink the chains of alginate to make a thin, flexible solid around the sphere of liquid. The result is a liquid encapsulated in a calcium cross linked film of alginate. In *reverse spherification*, a calcium containing liquid is dripped into a bath of sodium alginate. Either method produces the liquid filled spheres. In many ways, the spheres resemble the roe or fish eggs used to make caviar. The spheres are an attractive way to decorate dishes and add bursts of flavor in unexpected ways

Two excellent reviews on foods and hydrocolloids are found in the freely accessed article by Saha and Bhattacharya. J Food Sci Technol 2010 Dec; 47(6): 587-598. PMCID: PMC3551143. Food Gels: Gelling Process and New Applications Banerjee and Bhattacharya. Critical Reviews in Food Science and Nutrition 2012, 52(4): 334-346.

## Pre-Laboratory Concepts:

- 1. Perform a web search for spherification. Read some of the background material and watch a video or two. What is spherification? Answer in general simple terms AND follow with a specific scientific description of spherification.
- 2. What is the difference between direct (sometimes called basic) spherification and reverse spherification?
- 3. There are two key components for all spherifications besides the flavorants (food juice). What are these two components? Describe them in terms of chemistry. What KIND of molecule are they?
- 4. How do these two molecules work together for direct and indirect spherification. Do not explain how you will use them (mix one with the other and wait..) but the science that makes these two components useful in spherification.

**Procedures:** Gels and Polymers are easily found from a number of suppliers including Molecular Gastronomy, Will Powder, and Molecular Pantry. Several of these suppliers have kits to expand your experiments.



## Food Gels – Fruit Juice Noodles.

- 1. Prepare an ice water bath large enough to cool the gel in the tubes.
- 2. Gather four, food grade PVC flexible tubing (10-12 inches long, 1/8 to 1/4 inch diameter). Often found in hardware stores or wine and beer homebrew suppliers.
- 3. One 20 ml syringe with catheter tip. Match the inside diameter of your tube to the tip of the syringe. The fit must be tight enough to push hot liquid through without leaking.
- 4. Select a fruit juice or prepare a purée. Jumex brand Mango Juice will work well. If the juice is not very sweet, dissolve 15 g of table sugar into the juice or puree. Prepare a puree by blending the fruit into a minimal volume of solution to get 1-2 cups worth of juice. Add sugar to your puree to make a sweet tasting puree. Strain solids from the juice before using.
- 5. Determine the density of your juice. Carefully determine the mass of 10 ml of juice. One way to do this is to subtract the mass of an empty syringe from the mass of your syringe after carefully drawing 10 ml of juice into the syringe. Calculate how many ml (or convert the volume to cups) of juice you need to make 150 g of juice.

### Basic "recipe"

150 g (about ½ cup) of fruit juice or clarified fruit purée.
1/2 tsp Lemon juice (2.5 g)
1.0 g agar
1.2 g locust bean gum

#### Procedure:

- 1. Using an immersion blender or whisk add juices, then blend agar and locust bean gum.
- 2. Allow hydrocolloids to begin to hydrate for 5 min at room temperature.
- 3. Transfer to a small pot and slowly bring to a simmer while stirring.
- 4. Maintain at a high simmer to low boil for 5 min.
- 5. Fill a syringe with the gel and fill a food safe tube with the heated gel. Ensure you clean out the syringe before the gel can solidify.
- 6. Place the filled tube in the ice water bath for 5-15 min, keeping the ends out of the water bath.
- 7. Once the gel has solidified, use air in the syringe to expel the gel from the tube onto a clean container.
  - Examine and record your description of the physical nature of the gel. How durable and thick is the gel? Gels are described as firm, brittle, flexible, soft, elastic, sliceable... How do these terms apply to your gel?

Experimental Ideas: Locust bean gum is used as a thickener. Agar acts as a more rigid gel.

- Agar and xanthan Gum have very different uses. As mentioned above agar makes a solid rigid but fragile gel while xanthan gum is often mixed with locust bean gum to make a hot flexible gel. Locus bean gum is often used at 0.1 1.5% (w/w). Mixed with agar at 0.1 1.0% (w/w) or xanthan gum at 0.2-0.8% (w/w) or kappa carrageen at 0.1-0.5% (w/w).
- As a class, discuss an experiment using the scientific process to create a hypothesis and an experimental design to how to make different types of gel noodles. Create a table of the percent of each food polymer with a prediction. Prepare the gel and analyze the physical properties of the gel.
- Gels and hydrocolloids that form into tight well cross linked structures with less associated water form tighter more brittle gels. Investigate the structure of the polymers you've used to explain your results. Consider the size, polarity, charges, ability to hydrogen bond with water when analyzing your results.

Spherification Lab



# **Reverse Spherification**

- 1. Prepare two water baths, one for rinsing and another to hold the finished spheres. Use distilled water not tap water to avoid calcium)
- 2. Prepare the fruit purée
  - A. 1 cup water
  - B. 2 tbsp sugar
  - C. 3-4 cups sliced (fresh or frozen) strawberries
- 3. Blend until smooth. Optional strain to remove seeds and solid mass or keep as is.
- Use pH paper to ensure the pH is above 3.5.
  If it is too acidic, titrate in sodium citrate (not citric acid).
  Do not add too much or you the citrate will bind and sequester the calcium.
  If the body is thin, add 1/4 tsp xanthan gum (optional)
- 5. Weigh the purée and add 2% Calcium Lactate Gluconate (2g solid per 100 g of liquid)
- 6. Prepare a third bath of sodium alginate dissolved in water (2.5 g per 500 g of cold distilled water)
- 7. Getting the alginate into solution without air bubbles is key to achieving good spheres.
  - A. Mix alginate with ~2 tablespoons of sugar and slowly add to cold water using a hand blender
  - B. Tap water contains calcium that will cause the gelling of alginate in the water bath
  - C. Disperse the solid in cold water to limit clumping. Use a hand blender. If needed, the solution can be heated slowly in a microwave for 1-2 min at a time to warm solution and drive out air bubbles.
  - D. Incubate the solution overnight or subject the solution to vacuum treatment (food saver or lab vacuum) will help this step.
  - E. Alternative approach is to leave overnight, covered at 4°C (refrigerator).
  - F. The solution is ready when clear and free of bubbles.
- 8. Use a spoon to slowly add the frozen fruit mixture to the alginate bath. Gently stir the bath to ensure an even exposure of the fruit sphere with the bath. Hold the spoon just above the surface of the alginate bath. A deeper bath helps give the sphere time to form as the liquid falls to the bottom of the bath. The longer the sphere is in the alginate bath the thicker the shell will become. Leave the sphere in the bath for ~ 30 seconds. Experiment with different times and check your results.
- 9. Remove the spheres and place into the rinse (water only) bath to wash away unreacted alginate. Stir and transfer to the third bath (water only).



# **Direct Spherification – Carrot Caviar**

- 1. Prepare Juice
  - A. 2-3 cups of sliced carrots
  - B. <sup>1</sup>/<sub>2</sub> -1 cups water
  - C. Minced fresh ginger root (about the size of your thumb)
- 2. Blend until smooth and strain through a fine sieve. Retain the juice.
- 3. Transfer approximately 1 cup of strained ginger carrot juice
- 4. Determine the mass of the ginger-carrot juice and calculate the mass of sodium alginate needed to make the final alginate 0.8%
- 5. Blend and remove bubbles by straining or vacuuming in a food saver container.
- 6. Optional Add a small amount ~less than a 1/4 tsp of xanthan gum to give enough body to a thin juice for a solution to form
- 7. Prepare Baths
  - a. Calcium Chloride 2 g per 200 ml water b. Rinse water only bath.

#### **Forming Spheres**

- 1. Draw the ginger carrot juice into a syringe and drop just above the calcium bath. High enough for a drop to form, not so high that the juice is splashed around before the drop can solidify.
- 2. Timing is critical. The point is to create a thin but stable shell and keep the center liquid. Residual calcium will continue to diffuse through the alginate solidifying the caviar.
- 3. Transfer the caviar to the water only bath to rinse the caviar transfer to a small dish for sampling!
  - A. The longer the time in the calcium bath the more thick the shell will become.
  - B. Carefully stir the calcium bath to avoid clumping and to ensure the entire juice drop is exposed to the calcium bath.

#### Experimental Ideas (reverse and direct):

- Another method to help reverse (indirect) spheres to form is to freeze the fruit & calcium mixture. Ensure the air bubbles are removed prior to freezing to avoid floating frozen spheres.
- The type of calcium salt can impact the taste of the spheres. Two alternative baths are to try is 1) calcium Lactate 2 g per 200 ml water or 2) calcium Lacate Gluconate 4 g per 200 ml water. Note the importance of which solution has calcium. Experiment with other fruit or juice sources. Which have calcium at low or high concentrations?
- Most labels use the USDA recommended daily allowance to describe the calcium content. How would you calculate the concentration of calcium using this information?
- Interested in making a caviar from a fruit or other food that has calcium? An alternative method uses agar to make spheres in a cold oil in place of alginate and a calcium water bath. A mixture of fruit, vegetable puree, or other liquid (for example a 50:50 mixture of hot sauce and soup stock) dissolved by boiling in a 1.5% agar preparation is dropped into an ice cold solution (olive or other) to form spheres. The container should be tall enough to cool down the agar as they spheres drop to the bottom. Rinse in water and enjoy.



Spherification Lab

#### Post laboratory thoughts:

- 1. Mango Gels. Describe the chemical characteristics of the two hydrocolloids used in making the noodles.
- 2. Why didn't we add calcium to the mango noodles?
- 3. How long did you leave the reverse spheres in the bath? Did you observe a difference in timing?
- 4. After rinsing the carrot caviar, did you notice a difference in the caviar made with any of the baths? Should you have expected to notice a difference?
- 5. Describe the role (chemical terms) that calcium plays in forming a solid with alginate.