[SQUEAKING] [RUSTLING] [CLICKING]

SARAH HEWETT: All right, good afternoon. We're going to get started because we have a lot to talk about for this one lab before a lot of you guys get to do it starting next week. So we are done for now talking about the essential oil lab, and you'll get one more lecture about that in the X-ray crystallography stuff coming up next week.

And for now, we're going to switch gears and talk about the ester lab. So before we get too far into it, the Ellen Swallow Richards reports are due next Wednesday and Thursday, the 16th and 17th. The TAs will be holding office hours and I will post those onto Stellar this afternoon. And then starting this Wednesday and Thursday, we're going be starting our next round of labs, so wherever you are standing, whichever bay you're in in the lab, that will determine which lab you are going to do next.

So A prime 2, center of the lab, you'll be doing essential oils, middle group, catalase, and then the people closest to the wall, you'll be doing the ester lab, which we're talking about today. If you're doing the catalase lab, and hopefully your TAs will remind you of this as well, but you need to bring a laptop. You'll be working in pairs, so if you don't have a laptop, then we can pair you up with somebody who has one.

But we need a good number of laptops to do that. That's how you'll be collecting your data, and we'll talk more about that starting on Thursday. But moving on to esters, so the structure of an ester, which hopefully you guys have seen before in your organic chemistry or maybe your gen chem classes, is something like this. You have an R group where this first R group can be a hydrogen, any alkyl group or an aromatic group.

Then you have your carbonyl, another oxygen and then a different R group. And this one can only be an alkyl or an aryl group. It has to have carbons. It can't be a hydrogen, or else you have a carboxylic acid. So that's the general structure of esters. And talking a little bit about background information about esters, they are found naturally in many plants, and you can synthesize them in the lab from carboxylic acids and alcohols, which we are going to be doing.

They are highly fragrant, as you guys will experience when you do this lab, and so as such, they are used extensively in flavorings, scent and polymer industries. And so some esters that you may have seen before in the world, this is a triglyceride. This is how your body stores fats, and it makes it from glycerol, which is an alcohol.. It has three OH groups and a bunch of fatty acids.

So that's one biological example of an ester that is very common in all of our bodies. And then this is ethyl cinnamate, which is an ester that is found in the essential oil of cinnamon, and it is what gives cinnamon its cinnamony flavor or scent. The most ubiquitous of esters is probably polyester. And so many of you are probably wearing polyester right now. It's in your fabrics.

It's what plastic bottles are made out of. You have water bottles or food containers, all of these things. If you see this symbol that is the symbol for this plastic, which is the most common one used in our fabrics and in the food packaging that we have, and it is polyethylene terephthalate, and this is the structure. And so you can see that there is the ethylene group. There's the terephthalate group, and then there is our ester bond in the middle.

And if so if you stack a lot of these together, you make a giant polymer, then you have all type of plastics that we use for many, many applications in our daily life. So a little bit of background about esters. And here's a chart of all of the different types of esters-- or not all of the esters. There's many, many, many types of esters that you can make, but here are some very common ones, especially ones that are found naturally in different food and natural products.

So you can see there's the part from the carboxylic acid and the part from the alcohol. So if you make any of these combinations of esters, then they'll have all these different scents. And so in the lab, you guys are going to be synthesizing a whole bunch of different esters, and one of the ways that you may be able to identify it is by what it smells like.

So if you look in the lab manual, there's a whole chart of the esters. It gives you their name. It gives you a bunch of physical information about it, and it also gives you the scent. So when you synthesize your ester, you will carefully smell it and see if it matches up to what it is supposed to smell like.

AUDIENCE: What are the boxes that say ethereal?

SARAH HEWETT: Ethereal? That is kind of-- I've never smelled something that smells ethereal. Does anyone have a good description of what that may smell like? I think it doesn't have like a concrete scent. That's how I kind of interpret that. But you can see there are some that smell like vanilla, pineapples, different fruits. Those are ones that smell like balsamicy, like vinegar, coconut, all kinds of different things.

So we're going to talk about the reaction that we're going to be doing. This is Emil Fischer. He is half of the team that is responsible for creating or inventing this reaction. I could not find a picture of the other guy. He won the Nobel Prize for chemistry in the early 1900s, and now it is typically just called a Fischer esterification reaction. So you take your carboxyl acid, your alcohol, some acid, and then you can synthesize an ester.

And so we'll walk through the mechanism really quickly so that we know what is happening. And you guys have probably-- have you guys seen this in your organic chemistry classes? Yes, so this hopefully isn't too new. So you start off with your carboxylic acid. We're going to add a strong acid in our case, sulfuric acid, which is very corrosive. Be careful when you're handling it in the lab.

That is our proton source. So the first thing that we're going to do is activate this carbonyl. We get our carbonyl. Now it has a proton and a positive charge on it, and we can draw a resonance structure where that positive charge gets put down on this carbon here. And when we do that, we have our alcohol. We can add our alcohol in, and these electrons can come up here and attack that positively charged carbon.

We can add our alcohol group to our original molecule. So now we have this guy here, and now the positive charge is on this oxygen. And so we can lose a proton to get rid of that positive charge. So then we end up with a proton over here. That's an unfortunate proton. And now we have this structure here with our extra proton.

We can protonate this oxygen up here and form this charged species. And now we have made positively charged water, and we know that water is a good leaving group. So we can leave and make water, and that is where the water comes from in our synthesis. And to kind of balance this whole thing out, you're also going to have these electrons come down and form a double bond to help drive that water out.

So now we have a double bond here. It has a positive charge and a proton still on it, so we can have this proton leave as a proton. And we have made an ester. Tada. And then we've regenerated our acids, so that's why the sulfuric acid is our catalyst. So I guess we can leave this here for now. So that is the mechanism of the reaction, and like I said, you guys have probably seen that before.

It's pretty straightforward, and so this is the reaction that we will be doing in the lab. Now we need to talk about naming esters, and there are a couple of conventions that are used when naming esters. There's a few ways to do it. So the first one is the IUPAC straightforward way to name esters, and you start with the part of the molecule that comes from the alcohol.

So if you notice over here, the blue stuff came from the alcohol, and it ends up as this group that's attached to the oxygen, not on the carbonyl side of the molecule. So you're going to start there. You'll name it as though it's an alkyl group, so something that is attached. So it'll have that -yl ending, like methyl, ethyl, that kind of thing. So this is a propyl group. It has three carbons.

The second step is to look at the other half of the molecule, and you want to name it as though it isn't just an alkane and count up all the carbons including this one attached to the carbonyl. So you have one, two, three carbons over here as well, so that would be propane. And then you want to drop the e off the end of the name and add -oate, So proponoate.

So the IUPAC way to name this thing is then to combine the names. So you'll get propyl, proponoate. So clear enough? It gets a little bit tricky because chemists don't always use the IUPAC or traditional names for everything. There are some common names that get used and thrown around when people are talking about different chemicals.

So does anybody know what this carboxylic acid is? Acetate or acetic acid. So acetic acid is what we typically call it. You'll hear it as an acetate group if you take off that proton. If you're going to name this according to the IUPAC convention that I just told you about, there's two carbons, so that's ethane, and you would call it ethanoic acid, but that's not commonly used.

This alcohol is ethanol. So if you combine these two, what would we call that ester? Ethyl ethanoate, or you can use the common name and call it ethyl acetate, which you guys may have heard of or remember from the ferrocene lab. Yes. So there are a couple of different ways to name the esters, and there's a whole list of esters. If you guys have looked in the manual, there's a whole list of possible unknowns that you can have and that you can make in this lab, and they come from all different combinations of carboxylic acids and alcohols.

And so in order for you guys to have some idea of what you may be making and the structures that you will be looking for when you are characterizing your esters that you make by different types of spectroscopy, we need to be able to name and draw the esters. So if you got this handout in the back, on one side, it has a sheet that has all of the common names for the structures that you may find in that list of esters that we'll be making in the lab.

And then on the back, there is a blank chart. Mine's already filled in, but there's a blank chart that has a bunch of different ester names. So if we want to take a moment and practice naming these esters using the information in the past two slides you should have on your PowerPoint handout and the structures on the back of here, you should be able to draw the structures of all of these different esters.

So take a moment do that and talk with your neighbors. Work it out. Ask your TAs if you're back there. And then I'm going to have people, when you are confident that you know the structure of one of these guys, come down here and draw it please. So I'll give you a couple of minutes to do that.

All right, can I get a few people to come help draw some of these on the board if you have drawn some of these on your paper? Go for it. Going to need a few other people, or else this is going to take forever. Excellent. Wonderful. Anyone from the back want to come down? Go for it. Thank you.

AUDIENCE: [INAUDIBLE].

SARAH HEWETT: Don't worry if it's wrong. If you want to draw more than one, go for it. If anyone else wants to come down here and be really brave and share their knowledge, that would be excellent. All right, we'll see how many of them these guys can do. Yeah, if more than one, go for it because it'll be faster.

AUDIENCE: [INAUDIBLE].

SARAH HEWETT: Yeah, sorry about that. One more. All right, how are we looking? Good, except this one, I think, these are the same molecule.

AUDIENCE: [INAUDIBLE].

SARAH HEWETT: So butyl acetate, it's just no double bond. Thank you. Well done. So there are the structures of some of the esters that you may or may not be making during this lab. It's good practice. So these aren't all of them, so you'll still have to draw out some of the possible structures when you are trying to figure out what your unknown might be, but this is a good start and good practice.

So it looks like you guys are good at drawing the esters. Well done. All right, so now that we have the idea of what the reaction looks like on paper and what our products could possibly be, we're going to talk about how we can actually do this in the lab. And so I brought some of the glassware that you're going to be using. And I'm going to put gloves on because I don't know how well whoever used this last semester cleaned it.

So the first technique that you're going to use is reflux, and so that's to do the first part of, or pretty much do the whole reaction here, where you're going to combine your carboxylic acid and your alcohol. You're going to heat it up, and to reflux means to boil without losing solvents. So it'll be boiling. You'll have a stir bar in there. So you can see you have your stir plate.

You're going to use a heating mantle again to heat your reaction. It'll be boiling in there, and then instead of using our Vigreux column like we did in the distillation, you're just going to put a condenser on there. So you'll have water going through your condenser. You'll want your water going in the bottom and out the top so that the whole thing fills up with cold water, and so that's when you're boiling.

Your solvent will be evaporating, and then it'll condense and it'll go back down so that you don't boil to dryness and you don't lose all of your product as you're boiling it. And then on the top, you're going to put a drying tube, and your drying tube will look like this. And when you get it, it will be empty just like this one is, and then you will fill it. You'll put a little bit of cotton in here as a plug, and then you will take this stopper off and fill the rest of it with calcium chloride. Does anyone know why we're going to do that? And it goes right on top here.

So calcium chloride is CaCl2. It is among other things used as a road salt. So there are three ions in the structure, and if you remember your colligative properties, then it'll lower the freezing point of water when it has three ions in it. It's a very good electrolyte. It'll also lower the vapor pressure of a solution or increase the boiling point.

And the dissolution of calcium chloride is exothermic. It's very thermodynamically favorable and it's also entropically favorable, so it is a very spontaneous reaction, and it is a hygroscopic material, which means that it absorbs water. So it's a desiccant. You may see those like silica gel packets in things that you may buy to keep the water out. Calcium chloride is another material that's commonly used as a desiccant because it's hygroscopic, but it has a property even beyond being hygroscopic.

It is deliquescent, which means it'll absorb water until it becomes a solution. So this is what dry calcium chloride pellets look like. So it's just little white chunks of solid. And if you leave it out on the benchtop for long enough, it'll actually pull in the water from the air and turn itself into a calcium chloride brine solution. So if you spill some of this on the bench, you want to clean it up really quickly, or else it will start to look like that.

And so what we're going to use it for in our reaction is-- what are the products of our reaction? We're going to make an ester and? Water. So if we go back to our mechanism, we lose water here. And if you notice, most of these steps here are reversible steps. So if you remember Le Chatelier's principle, if this is our overall reaction and one of our products over here is water, and this is a reversible reaction, then how can we force the reaction to go towards the product side?

AUDIENCE: Take out the water.

SARAH HEWETT: Take out the water. You can either add more reactants or take out the products, and so we are going to be taking out the water with our drying tube. And so that will help ensure that our reaction goes to completion while we are refluxing. So once you've done all of your reflux and you have your product, you've heated it for a while-- it's kind of boring to watch, but reactions take time-- so then you will have your product in your round-bottom flask here.

And we will have our ester, hopefully, and what else? Potentially all of these things, right, and some sulfuric acid. So we don't know that our reaction went to completion. We hope that it got close, but we need to purify it from any impurities or remaining starting material that we may have. So we do that in a separatory funnel, and this is a separatory funnel.

And we do a liquid-liquid extraction, which means that we're going to have one liquid, and then we're going to add a different liquid to it. So we have two liquid phases, and we're going to partition the different compounds between those two liquid phases. And the only way this works is that we have to have two immiscible liquids that have different densities. So what does it mean for something to be immiscible?

AUDIENCE: They won't mix together.

SARAH HEWETT: They don't mix together. Good. So when you pour your two solvents in here, they need to not mix so that have two distinct layers and that you can separate your product between them. And it will separate them based on density. So when you have your separatory funnel, you will pour your two things into it, and you should get two layers. And so your more dense layer will be on the bottom and your less dense layer will be on the top.

So in our case, water has a density of about 1 and most organic liquids have a density of less than 1. So if you take your product, which is an ester, and you add water to it, what will be on the top and what will be on the bottom?

AUDIENCE: The water will be on the bottom.

SARAH HEWETT: Yep. So this will be our aqueous layer and this will be our product or our organic layer. And it's really important that you keep track of what is where when you're using the separatory funnel and that you know what you've drained out and what you have kept in there. And you want to save everything. Save all of the stuff that comes out of here. Save all the things that are in there until you know that you have your product.

So there are a couple of ways that we can use a separatory funnel or as a sep funnel, the abbreviated version. And the frequently used solutions for this type of extraction, the first type is an acid-base extraction or a chemically active extraction, and that's the first thing that you're going to be doing. So in our reaction mixture, we have hopefully a lot of product. We probably still have some carboxylic acid left over, and we know that we have some sulfuric acid in there. Yes?

Great. So the way to get all of that acidic byproduct away from our product is to use sodium bicarbonate, which is a base. And when we do that-- so if we have our carboxylic acid, if you add a base to it, then you can deprotonate it, and if we have sodium bicarbonate, it will form a sodium salt. And that is more polar than this, so it will be more soluble in our aqueous layer, and we will pull it away from our product.

So that's the idea behind the base extraction. And so hopefully, that first round of extraction will get rid of our acidic impurities, and then we're going to do another extraction using a sodium chloride solution. And that is sometimes referred to as salting out. So we will keep our product in there, and then we will add sodium chloride solution. And the sodium chloride makes our aqueous layer really polar, and so it makes our product less soluble in the aqueous layer, and it makes any water that's left over in our product layer more likely to come into the aqueous layer.

So when this is polar, than all of the polar things, all of the water, get pulled into the aqueous layer, and any organic-y things, the product that we care about, gets forced out into the product layer. There's some terminology that you may hear when you are using a separatory funnel. So there's extraction, which is if your product is in a mixture and you to add another solvent to extract your product out of what's already there.

And then there's washing, which is we're going to be doing, which is where you're just going to pour your product in there and you are going to add other solvents to extract the impurities. You leave your product where it is and you pull out the impurities. A note on how to use a sep funnel, and I'm going to put goggles on just for safety here. This is just water, but the way that you're going to do this is you'll have a ring stand.

It'll hold itself up right here, and then you will first make sure that the stopcock is closed. So if you pour your product through here and this is open, then that's going to be a really sad time in the lab. So then you'll pour your product and whatever you are washing it with into the sep funnel. You will get two layers because you'll have two different liquids in there. This is just water. Then you will cap it.

And then you're going to shake it like so. Then you will point it away from any humans and into your hood and you will open the vent. When you are shaking things that have are really volatile like organic solvents, they'll build up pressure in here, and so you don't want anything to explode. You don't want this top to come flying off. You don't want the glassware to break. So you want to vent this. You're going to shake it a little bit, vent it.

When you first start, you want to vent it very frequently so that the pressure doesn't have a chance to build up. When you do this, you want to point it away because sometimes, liquid will come flying out. You'll hear it. It'll go pssh. So you want to be very careful when you are using this. Safety note. What happens when you add sodium bicarbonate to an acid?

You get a gas. You get carbon dioxide. Think baking soda and vinegar volcano. So when you are first adding your sodium bicarbonate to your product, you want to not do it right away in the separatory funnel, or else you're going to build up a whole lot of pressure, and it's going to create an unsafe situation. So you will add those to a beaker first. Wait for the bubbling to stop, and then you can pour it into your separatory funnel and you can do the extraction.

And what you're going to do is you will open the stopcock, and then you'll be able to watch the layers go down. And here's something. So if you open the stopcock and you say, oh my gosh, nothing's coming out, what's our problem? The top is on. So you want to close it first. Take the top off and then it will drain smoothly. And then you'll just pay attention, and you can stop it right when the interface between those two layers gets right to the bottom, and that's how you're going to use this to separate your solutions.

But yeah, inevitably, somebody always forgets to take the top off, and they're like, my sep funnel's broken. It's not. Just physics. So I guess we can still leave these on. So that's going to be all in day one. You will reflux your product. Then you will use your sep funnel. You will start to purify it, and then on day two, you're going to--

Oh, wait. Before, sorry. So after you have isolated your product, we have just added a whole bunch of water to it, right. We've shaken it up with sodium bicarbonate and sodium chloride solution. We don't want water in our product. That's not the point of this. We want to just have our ester, so we need to remove the water that gets left over from our separatory funnel situation using a drying agent, and a drying agent is similar to calcium chloride.

We typically use sodium sulfate or magnesium sulfate in the lab because they're easy to work with and they suck the water into their crystal lattice, and they necessarily dissolve very well, which is nice. And so these are fairly interchangeable. They're the most commonly ones used in lab situations. Magnesium sulfate sometimes can harm acid-sensitive compounds, so if you're doing something very sensitive in the lab, you may want to stick with sodium sulfate, but for our purposes, it will be fine.

So what you're going to do is it comes in powder form, and you will add some of it to your product and you will swirl it around. And you will look at it, and then you will run to your TA and say something like this, like, ah, is it dry yet. How much do I add? And your TA will look at you and say, I don't know. You should know this. So this is how you could tell if it is dry yet.

The first time that you add your drying agent, it will clump up and it'll all be in one big chunk, especially if you have a lot of water in there. Sometimes you can even see the water. If you hold up your flask, you'll be able to see a little bubble of water at the bottom. That's fine. You'll add your drying agent. It'll all clump up. You'll add a little bit more. It'll have some smaller clumps, and then you'll add a tiny scoop more.

And the rest of it that you add won't clump up. It'll look kind of like a snow globe. It'll swirl around and be free-flowing crystals, and that is how you know when you are done, when it doesn't clump up anymore. So you don't need to go over and weigh it. I think there's an approximate weight in your lab manual. Like usually, it's maybe around a gram. But don't bother weighing this out.

You can just kind of eyeball it, scooping a little bit at a time. Don't go too crazy with the first scoop, because the more of this that you have in your product, the harder it will be to isolate your product later. So let's say, if you think of it like at the beach, if you have a bunch of sand and then you put a bunch of water in it, your water kind of disappears.

And in this case, our product is the liquid, so in order to get our product back, we will gravity-filter this away from the drying agent. And so you want to have minimal amount of drying agent so that your product doesn't get stuck in it and it's easy to filter later. OK, so that's all day one. Then you'll have your semi-purified and dried product, and then on day two, we will purify it from anything that did not get taken out in your extraction process using distillation.

And what I didn't mention is that for this lab, you'll be checking out a kit from the stockroom, or your TAs will check this out, and you will get a kit that has all of the glassware that you need to do the entire lab in it. And there's a nice list on here of what goes in this kit. So on the first day, you will set up your reflux just like this, and then the second day, we're going to set up an atmospheric distillation, which is going to be very similar to the vacuum distillation that we talked about before.

But this time, instead of having all the glassware in one piece, you get to assemble it yourself. So you'll have your Vigreux column. Then you'll have a distilling head up here, and then you will put your thermometer in the top. And most of our thermometers have ground glass joints. And then you will use the same condenser that you used for your reflux on day one, and that will go across like this.

And you will clamp all of this glassware very well, and then you will add your spout to the end of it right here. And that is your distillation setup. You'll have keck clips in your lab, those yellow things that hold all of your joints together. So you want to make sure that everything is clamped and secure before you start distilling, because if you have gaps in your glassware and then you start heating and your product becomes a gas, you will lose it all.

So the distillation will purify your product from any remaining insoluble impurities or higher boiling impurities that we do not want in our final product. And when you do this, you're going to collect a few different fractions. And so the way that you're going collect your fractions in this case, we don't need to use a cow adapter because we're not going to be attaching anything to the vacuum line.

You can see that the spot over here, instead of attaching it, this is where you put your vacuum. It's just open to the air. And so you can collect your fractions in test tubes on ice, and then you will collect a few different fractions. So you usually collect the first few drops and then a few different fractions. If the temperature changes, you will switch your fractions, and your TAs will tell you how to do that.

And then you will monitor your purity by IR. So if we go back and think about the IR that we talked about last time, and if we think about our products and our reactants, what IR bands are we going to see in our carboxylic acid reactant? We have a C-O stretch, an O-H C double-bond O. And? You might see the CC, you may not. Those ones are kind of hard to do because they don't change dipole very much when that bond happens.

So sometimes, maybe a C-C bond. And what else? What's in this R group? Yeah, C-H stretches. What about our alcohol group? We'll have another OH stretch. Of we have a C single-bond O. Yep. Do we have one of these? No. None of those. We have some of this?

AUDIENCE: Yeah.

SARAH HEWETT: Yeah. And then again, maybe the C-C bonds, sometimes those are in the [INAUDIBLE] region. You probably won't. Don't spend too much time looking for these. These are kind of there but not easy to see. So now if we look at our product, what do we expect to be in our product, assuming we don't have any water because we've done our distillation and our extractions very well?

We have a C double-bond O. A C single-bond O. A C-H. Do we have an O-H? So what are we going to look for in our IR to tell if we still have starting material in there or not?

AUDIENCE: The O-H [INAUDIBLE].

SARAH HEWETT: The O-H. And so this will still have a C double-bond O, so that one might not be as easy to tell. But we definitely should not have an O-H peak. So if you take your Ir fractions and you take your fractions, you take the IR of them and then you start to see the O-H, the characteristic O-H peak up way by like 3,000 wave numbers, then you may want to test a different fraction because that one either has some water in it or it still has some of your starting material.

And then once you've determined which of your fractions is the most pure, then you will continue on with that to do the rest of our characterization techniques. And the first one of those is going to be boiling point determination. So we can determine the boiling point of the ester, and that is a characteristic of each ester. So you have a chart. That chart at the beginning of the lab, it has a list of all the boiling points.

So we will measure the boiling point of your ester, but before we do that, we're going to calibrate the thermometer just like we calibrated the melting point apparatus. So at this time, there are only two calibration points. So you'll measure the freezing point of water. So you'll get a beaker. You'll fill it up with ice, some water, let the temperature reach equilibrium.

And you want make sure there's still ice in it when you measure so that it's not water and it's not heating back up to room temperature. And then you will measure the temperature of the very cold water after it's sat for about 10 to 15 minutes. While you're doing that, you can also heat up a beaker of water on a hot plate, measure it and heat it up to boiling, and then you will measure the temperature of the boiling water.

And there's a correction factor in the lab manual that you will use to calculate the theoretical boiling point of water at whatever the atmospheric pressure is on that day. So you'll go get the barometer from the lab like we brought down to the river. You can measure the pressure in lab because we know that boiling point is related to the pressure in the atmosphere and the vapor pressure, so there is a correction factor for that.

And then you will plot your theoretical boiling points and your theoretical freezing point versus the ones you actually measure, and that'll give you a two-point calibration curve for your thermometer that you're going to use to determine the boiling point of your ester. The apparatus that we will use to determine the boiling point of the ester is like so.

You will have your hot plate. Then you'll have a sand bath, and then you're going to use a very small test tube. And you will put a very tiny amount of your ester in, maybe a milliliter. And then you will suspend the thermometer. We're going to use digital thermometers. You'll suspend the thermometer a few centimeters above the surface of your liquid, and when you heat this up, your liquid will vaporize.

It'll hit the thermometer tip and it'll condense, so you'll see drips coming off of the tip of your thermometer. And the temperature will start to go up, and you want to wait. So the second thing that you'll need is a lot of patience. So the temperature will go up very, very slowly as the vapor reaches the boiling point. So if you've ever boiled water and you cooked something, you know that you'll start to see steam and water vapor before the liquid itself is boiling.

Same thing happens here. You'll start to see the drips, but then the temperature may still be going up. So this is one of those things that you don't want to sit there and watch because you will become very impatient and you'll say, oh, good, the temperature hasn't changed in 30 seconds. This must be it. But then if you come back in five minutes, the temperature has indeed gone up, and then you have the incorrect boiling point.

So this is one of those things you can set up and then check on it after a while. And once the temperature stops increasing, that will be your boiling point. The next thing that you will do is you will determine the density of your unknown, and this is our density instrument that is in the lab. So instead of having to measure the mass and the volume yourself to get grams over milliliters, which is our unit of density, you can inject your sample into the side of this instrument.

So there's the little lower-lock valve here, and there's a syringe, so you will inject your sample in and it'll fill up this tube. The instrument stays at 20 degrees Celsius so that we know for sure that it is the density at 20 degrees Celsius. And then you will press Go and it will measure the density for you, and it'll pop out the density number right there.

So very simple, and then you can use that as an identifying characteristic of your ester, and you can compare that again to the chart in the beginning of the lab manual to use as information to help you identify your unknown. Then we're going to measure refractive index. We talked about refractometry a little bit in the essential oil lab. In the essential oil lab, we used it to-- oh, that's a typo.

In the essential oil lab, we used the refractometer to determine the purity of our samples, but in this lab, we're going to use it as an identification technique for our esters. So every liquid has a characteristic refractive index, so we can measure the refractive index, compare it to the literature value, and that will also help you identify your unknown ester.

The second to last technique we're going to use is NMR spectroscopy. And how many of you guys have seen NMR before in your classes? A few people. All right, so in, I think about two weeks, Walt Massefski, who is the Director of the NMR Facility here in the chemistry department, is going to come and do a very, very thorough lecture on NMR and how it works and how to interpret it.

Unfortunately, that lecture will happen after some of you guys take these spectra in the actual lab, so I will do a quick briefing on NMR because we have some time. And then again, stay tuned. You will get a much, much better idea of this technique from Walt in a couple of weeks. So NMR spectroscopy, the idea behind it is that it uses a very strong magnetic field to align nuclear spin states.

And you don't have to know too much about that, at least for right now. I'm sure Walt will talk more about it. But the hydrogen nucleus has a spin associated with it, and if you apply a magnetic field in a certain direction, the spin can either align with the magnetic field, which is the lower energy state, or it can go against the magnetic field, which is a little bit higher in energy. And so this is a difference in energy here.

So once you have your protons in your field-- and you can do other nuclei too, but we're going to focus on protons for the moment-- there's a radio frequency pulse that is applied that causes some of these spins to flip. And then you remove the radio frequency pulse, reapply the magnetic field, and then you wait for the spin states to go back down to the ground state.

And because there's an energy difference associated with getting the spin to flip, there's also an energy difference associated with when it goes back to its ground state. So it will emit energy at a certain frequency depending on the environment of the proton. We can measure the energy that gets emitted and plotted, Fourier-transform it, and then you get an NMR spectrum.

This is the really quick, five-minute version. This will make a lot more sense when Walt talks about it later. So the important thing to note here is that the frequency of the energy that a proton emits as it changes spin state is related to the environment of the proton. So we can use this to get information about the different protons in our molecule, and we can determine connectivity, the number of protons that we have, and some information about how they're bonded together depending on the different NMR experiments that you do.

And the three major pieces of information that we will be using in our lab are the chemical shift of the proton-- so that's again related to the frequency of the energy-- the integration-- this tells you how many protons there are-- and then sometimes the coupling. So if there are protons next to each other, they will split each other's signals and you'll get multiple lines in your NMR spectrum.

So as a really, really quick example, we can look at our favorite ester here, ethyl acetate, and we can look at the different types of protons that it has. So how many types of protons are in this molecule? Three. So we have these methyl protons here, the ethyl protons here, and then these methyl protons over there. So these three are all in the same chemical environment. These are in the same chemical environment and these are in the same chemical environment.

So we should expect to see three signals in the NMR spectrum of ethyl acetate. So the way that an NMR spectrum is laid out, it's on a scale of 0 to 12, give or take.

It can go beyond that, but for the purposes of most organic molecules, all of the peaks will be found in this region. And the location that a peak appears or a proton peak appears is again related to its chemical environment. And the things that are very alkyl or have a lot of stages around them are going to be further upfield. We call this upfield with a lower PPM number.

And things that are closer to oxygens or electron-withdrawing groups are going to be-- they call it deshielded. So the electrons are withdrawn away from those protons. It doesn't shield= them from the magnetic field as much. So they come up more downfield, and the way that you can remember that is downfield or deshielded both start with D.

And so if we look at these protons, which of these do we think is going to be the most upfield or the furthest away from all of our oxygens? This stuff all the way on the right? Yeah. I just want to make sure that I am doing this right. So yes, these methyl protons will be the furthest to the right, and you'll get a signal here. And so this signal, the chemical shift value will be somewhere probably around 1 or 2.

And then the integration tells you how many protons it's for, and that shows up down here at the bottom. So how many protons will the signal equal? Three from our methyl group. All right, so if we look at the remaining two groups, which one do we think would be kind of the middle?

All the way on the left. So these protons here are right next to an oxygen, so they're going to be more deshielded, and these have a carbon in between, so these will be our next signal. So then we'll have another signal here. How many protons? From this group, three. And so that leaves our methylene group over here. That will have another signal that's further downfield, and this one will be two protons.

So already, you can see that there are different ways that you can use this to identify your molecules. So if you count up the number of different unique protons there are, then you can look at the number of signals you see, and that is one way to identify your product. You can also use the coupling, which is what is going to break these signals into not just one peak, but it'll be a few.

So coupling happens when there are protons that are next to each other. So this methyl group is next to two other protons, right. And so each of these protons, each of its neighbors, will split this signal one time. So if you have your signal and it gets split once, then you have two signals, and then if it gets split again in an equal magnitude, you end up with three signals. So this splitting kind of combines and this peak gets a little bit bigger.

So this is what is called a triplet. So if you have two neighbors, you get a triplet. So this peak, that methyl group will actually look something like this. It'll have three peaks to it with the middle one being the biggest, and that's the characteristic pattern of a triplet. What about our ethyl group here, or ethylene group, methylene group?

We have our two protons. How many neighbors does this group have, proton neighbors? So this has three neighbors. So that signal is going to get split three times. So you'll split it once. Split it again, so that would be our triplet. And then if we split it a third time, we get four lines. So this proton signal will actually look something like that. How many proton neighbors does this have? None, so will this get split?

No. So this will stay as a singlet, one single peak, because it does not have any proton neighbors. So anyone have any questions about where all of this came from? So again, that was the super quick version of NMR and the type of information that you can get from it. So when you are looking at the structures of the potential esters that you think you may have, you can probably narrow it down based on your boiling point in your refractive index, your density.

And you can narrow it down to a few, and then you will draw out the structures. And then you can, based on the structure, predict how many NMR signals you expect to see. And you can figure out what you expect the splitting to be, so if you expect them to all be single peaks or if you expect to see different types of multiplets. And then when you get your NMR spectrum, you can compare the number of peaks, the integration of the peaks.

So if you know that you have a methyl group, you should be looking for some signals that integrate to 3. And that is how you can use this as a technique to identify the structure of your unknown. And again, Walt will do a much better job explaining all of this in a bit. But just so you've seen it, before you get a chance to take your spectrum in lab, that is a quick introduction.

So once you have all of this information, you have your boiling point, your refractive index, your density, your NMR spectrum, your IR spectrum, you're going to attempt to identify your unknown, and this should all happen at the end of day three. You'll have all of this information, and then you'll be overwhelmed. You'll sit down, put it all together and try to figure out which of those unknowns in that table is the one that you made.

You'll fill out an identification form that your TAs will give you, and then you will bring it to your TA at the beginning of day four on the lab and you will say, this is my ester. And they will tell you if you are right or wrong, and you'll find out that day if you were correct or not. And then you will do one more technique for your final confirmation. So if you already know, then your mass spectrum should be super confirmation for you.

And if you were a little bit off, then hopefully your mass spectrum will be that last piece that helps you to get your final identification. Mass spectrometry, you have already seen a little bit. We did the ICPMS in our last lab. But there are different, many different types of mass spectrometry, and a bunch of different ways that you can use that technique. So ICP uses plasma to break the compounds apart into their atoms and ionizes the compounds that way, if you remember, hopefully.

What we're going to be doing this lab is electronic impact mass spectrometry, which instead of using plasma just shoots a high-energy beam of electrons at your molecule. And it doesn't have enough energy to break your molecule apart into its atoms or anything, but what's going to happen is the electrons will hit the compound and it will eject an electron from the compound. So you'll make what is called a radical cation.

So it'll have one less electron, so it'll be a positive charge, but it only lost one electron, and since it's organic-y, it will be a radical. This also frequently causes the molecule to break apart, not always. Sometimes you will get the radical cation of your whole molecule that will make it through the mass detector, and you will get the mass of your actual compound.

And other times, it'll break apart and you will see a bunch of pieces of your compounds. You'll see the mass of different fragments of your molecule. So you can use either the mass of your molecular ion-- so I'll show you what this looks like in a second. So this is what the instrument looks like. It's right near the ICPMS. You may or may not have seen it, and it is slightly older and looks a lot like the GC that we talked about before in the essential oil lab.

And that is because this is actually a GC mass spectrometer. So you inject your compound. It actually goes through gas chromatography, so if you have more than one compound, it'll split it into the different compounds. And then it'll take a mass spectrum of each of those compounds. We hopefully are only going to be injecting one compound in, so you hopefully purified it sufficiently well at this point.

But then it'll still give us a mass spectrum, and the mass spectrum looks like this. So this is our mass-to-charge ratio or our mass units. So usually, the furthest thing, the heaviest thing, that is where you will look to see if that matches with the expected molecular weight of your compound. That's your molecular ion. So if it gets hit with the electron, forms a radical cation and doesn't break apart anymore, you will see a peak at your molecular weight.

And so that is a giveaway of yes, this is my molecule. Sometimes, that doesn't happen. If it's really unstable, it'll break into pieces, and you will see-- so each of these represents a piece of the molecule that has broken off. So frequently, you'll see losses of 15. So that's when a methyl group breaks off.

And Dr. Dolan will be talking a lot more about mass spectrometry and what you will do with this information and how it all works in another lecture coming up. Just to give you, again, an idea before you see it and have to do it in the lab. This is just a quick overview and you'll get a lot more detail about what all of this means coming up in a couple of lectures.

Last but not least, safety for this lab is very important. The carboxylic acids are corrosive and toxic. They smell terrible. You can ask Tristan. He was the one who made all of the unknowns. And Brydon did the alcohols, so he got it slightly better, but Tristan will tell you that the carboxylic acids are very nasty to work with.

Sulfuric acid is also highly corrosive, so you don't want to get that on your hands. And then you want to vent the sep funnel, like we said, away from people. So if you're working in a hood with someone, make sure that they're not around. Don't turn around to talk to somebody and point it in their face. The starting materials smell very bad. Your product will smell really nice, but it'll still smell a lot, so keep everything in the hood. This is a very, very smelly lab.

Even if you keep everything in the hood, if you're walking by, which everybody is doing this, you will know. So we want to limit the amount of fumes that get out in the lab. Keep everything in the hood. Do not put vials in the glass waste. If anything breaks, or if you like break a pipette or if you break a beaker or something that has contacted your solutions from the ester lab, there will be a separate waste container for those.

Your TAs will come around with a capped, plastic solid-waste container to collect all your vials so that they are not in the glass waste stinking up the entire lab. And this is key for everybody. Regardless of what lab you're doing-- so starting on Wednesday and Thursday, we're going to be doing three different labs at the same time, and we're going to try to keep the waste containers in the bays with the proper labs they're associated with.

But pay attention to the waste labels. Read the red tag. If you're holding something and you're going to put it in the waste container, take the extra second to make sure it is the right one for the lab that you are doing. There will be three different sets of waste containers out there, and we do not want to mix in between, especially not acetone with the catalase waste.

If you remember from before-- we may have talked about this. You will hear about it again. If you mix the acetone from any of these organic-y labs with the hydrogen peroxide from the catalse waste, you will generate explosives. So we are not going to do that because everybody is going to read the labels and dispose of their waste properly in this lab, and keep everything in the hood that should be. Good? Excellent.