[SQUEAKING]

[RUSTLING]

[CLICKING]

JOHN DOLHUN: Good afternoon, everyone. So I'm going to start off today with a small demonstration. And I wonder if somebody could tell me what are the states of matter? Yeah? Aisha?

AUDIENCE: Solid, liquid, gas, and then [INAUDIBLE].

JOHN DOLHUN: Solid, liquid, gas, and plasma. Good. Good. OK. So the plasma is one that we don't oftentimes talk about. And that's what we're going to be talking about in this lecture. So what we're going to do-- a plasma basically is a group of ionized gas molecules. The sun and the stars are plasma. This is a plasma globe, which on a small scale you're not actually going to be able to see the plasma inside because it's not hot enough. But we'll be able to see the colors from the emissions.

So ionization is when an electron hits a gas particle, kicks an electron off, and produces a gas ion. That's ionization. That's what's happening on the Sun and the stars. I mean, you've got this sea of ions that's molting hot. And then emission happens when the gas ion grabs its electron back. And what it does is then it gives off light. And that's what we're going to see here.

So I've got two plasmas actually. I've got the plasma globe. And I've also got a fluorescent light bulb, which is also a plasma. And I need a volunteer-- someone who wants to be a conductor between the two plasmas. Someone who's not-- Alex, come on down. All right. So Alex, you can stand right in the front actually, kind of over here. So we're going to start by just shining 120 volts through this globe. That's 120 volts going through.

And what I'm going to be doing is putting 70,000 volts through this. And then we're going to-- Alex is going to be the conductor. So we're going to put the 70,000 volts through Alex. They'll crawl along his skin-- the surface of his skin. And he's going to hold the fluorescent light bulb in his other hand.

And I don't know. Hopefully he'll be able to light it. I mean in that fluorescent light bulb, it's plasma. There's mercury. You have to ionize the mercury first. It gives off UV radiation, grabs its electron back, and then it shines that invisible UV on the phosphorescent coating of the bulb. And we see the white light given off.

So we'll try this out. Can someone shut the lights off there? Just turn those lights off? Yeah. I think so. Yeah. Just hold that in. That's perfect. So before we start Alex, I think we're going to have you-- let's see if we get this thing going here.

You want to just bring your hand up toward that? Yeah. OK. All right. Put this pair of goggles on just in case. OK. Mainly for the fluorescent bulb. OK. Now what's going to happen now is I'm going to have you hold your hand there. And don't take it off. You're not going to get shocked.

AUDIENCE: OK.

JOHN DOLHUN: And I'm going to have you hold this in your other hand. Now put your hand there. Good. Now here we go. Ready? Wow.

AUDIENCE: Really cool.

JOHN DOLHUN: All right. You feel a little warmth on your hand?

AUDIENCE: Yeah.

JOHN DOLHUN: Not too hot?

AUDIENCE: Not too hot. No.

JOHN DOLHUN: 70,000 volts going through him along the surface of his skin coming out the hand and ionizing the mercury in a fluorescent light bulb. So that's pretty good. Thank you very much, Alex. You're very brave. Yeah give him a hand.

[APPLAUSE]

All right. So you saw two plasmas there. And the plasma we're going to talk about today-- and here we'll bring the lights back up there. Oh, there we go. He's got it. We've got our own technician here. So excellent. So we've reached the final lecture in this series.

We're going to be talking about inductively coupled plasma mass spectrometry. And this is a lecture where you'll be able to impress yourself and your friends because there's only two of these machines at MIT. And it's a very rare opportunity. We're actually introducing this machine in 5.310. You're going to be the first ones that have an opportunity to use this machine.

So we're going to answer a series of questions here. What is ICP-MS? What can be detected with it? What are the main components? How it works. And some of the challenges we're going to face in using it. And then we'll talk a little bit about the MIT Experiment. And we'll spend the last 10 minutes or so talking about mercury analysis.

So inductively coupled plasma mass spectrometry. There are two things that separate this from all other forms of mass spec. And they are high temperature and high energy. And it's a combination of those two things that allows the sample to decompose.

It undergoes atomization and then ionization. So what you can actually detect with this is pretty much most of the elements in the periodic table at the part per trillion level. That's mind boggling-- at the part per trillion level.

And what this machine does is it scans from 5 lithium-- this is the mass scale up to 260, which is uranium. Now that's another big difference between this and the other forms of mass spectrometry. Because the other forms-- we have molecular weights that are in the hundreds of thousands for these nucleic acids, these carbohydrates, the proteins that we're trying to study. And from regular mass spec, which is a much lower energy, much lower ionization, we're looking for molecular weight information about these biomolecules and some fragmentation information.

So we're primarily concerned about carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur. Those are pretty much the six elements regular mass spec would be concerned with. With this machine we're rapidly scanning the whole range of all these elements and the mass range-- the top mass range is 260 for this machine. So that's the big difference.

Now, what are the main components? So what we've got is we've got our sample introduction. And the sample is going to be a liquid. So it's a liquid that enters the sample intro. And that liquid is converted to an aerosol. And the aerosol gets shot into a plasma ion source.

And in that ion source, that's where your ionization takes place. Sample is going to be dried out, decomposed, atomized, and the elements are going to be ionized. And then we've got an ion lens, which focuses that ion beam. So this focuses the ion beam. We also have a collision reaction cell, where we actually introduce helium. And the helium bombards our ions and gets rid of the interferences, like the polyatomic ions we're going to talk about. So this removes interferences.

And then the monatomic ions that are left to enter this quadrupole mass analyzer, which is four rods-- the ions travel down the center of those rods and they're sorted by their mass to charge ratios. The ions are then counted at the detector. And we've got-- the detector actually records the counts per second of every ion hitting it.

And these counts can be like hundreds of thousands of counts for each ion every second. So counts per second recorded. And interestingly, the detector takes those counts per second and then it goes and looks at our calibration standards. And it associates those counts per second with our concentrations in our calibration standards. And then you've got concentration for your samples.

So the counts per second then head into our data system and the software analyzes all this and produces us some data. Let's take a look and see how it works. So here's our sample-- a liquid sample. And we've got a little peristaltic pump that pumps the liquid up to this thing called the nebulizer.

The nebulizer is going to convert it into an aerosol. But coming in here, notice there's a dilution gas. The dilution gas is argon. And argon actually dilutes our sample right at that point before it enters this spray chamber. Once the aerosol gets in here, there's a make up gas-- also argon-- that pushes the droplets down to the bottom of the tube.

Once they're down here, they have to make two right turns to end up outside the ion source. And those two right hand turns cause the larger droplets to be pumped out and fall by the wayside. So the most sample that is actually going to enter this ion source is only about 2% of our original sample.

We've gotten rid of the rest. Now once it goes into this ion source, there are three concentric glass tubes. So the ions will go into the center tube here. And look at these gases coming in here. Plasma gas and auxiliary gas-- they're coming in at right angles. And both of those gases are argon.

So the gas comes in at right angles and it forms like a mini tornado inside of this tube. It's like a hurricane going on in there. And that cyclonic motion picks up the sample into a vortex. And what goes into a vortex stays in a vortex. Right?

So you've got your sample trapped up in this vortex moving through this tube. And then there's an electrode sending electrons out. And look at this. We've got this Rf coil wrapped around the glass tube. That's producing about 1,500 watts of power. It's like 27.1 megahertz.

And look at my hand. The old right hand rule goes into play. Remember this. What are my fingers doing? What are we making in that tub? Roberto?

AUDIENCE: [INAUDIBLE]

JOHN DOLHUN: Yeah, an electromagnetic field. And that electromagnetic field is thrashing around in there. And it's so powerful that it can rip an electron off argon. So we've got our argon hitting that energy. There's your high energy. And you've got argon ions plus electrons. And those argon ions and electrons are just smashing around, twirling around in there. And the collisions from that, the kinetic energy that's given off-- that's your plasma. So that's all happening inside of that tube.

Let's take a bigger view of it. This is a blown up view of what's happening here. So here is your aerosol sample going down the center tube. What happens to the sample is it's actually-- the liquid is dried out to a solid in that tube. And then that solid is vaporized. It's atomized, decomposed, and then ionized.

The temperatures in here-- they can get up to 8,000 kelvin. I mean, you're talking like the temperature of the sun is what? 6,000-- a little under 6,000 Kelvin? So the temperatures are very hot. And you can see this plasma when the machine is on. You'll see the glow of this white hot plasma that's actually formed in there.

So what you've got is your ions coming out. Your plus charged ions will come out here. And what's going to happen is they will then enter the ion lens, which I'll show you. So what I've done here is I've actually opened up our machine. And this is the ion source. That's where the plasma is generated. It's a glass tube. And you can see the Rf coil there. And right behind it, you can't see, is this sample cone. So what I did is push a button here and moved this back to reveal the sample cone.

Now think about this. Inside of this box you've got like 6,000 Kelvin going on in there. Outside is room temperature. It's like putting the Earth a couple of miles away from the sun. That's what you're doing here. And what this cone is, it's made of copper. And it's got a nickel center with the little hole in it. And what happens is there's a grounding system here. So the electrons coming out of this torch box, coming out at the speed of light, go to ground. The positive charges-- the ions-- cannot go to ground. So they build up on this cone.

And here you've got a cone with all these positive ions building up with a tiny hole in it. It's a no brainer. They get pushed through. And so on the other side of this box is the high vacuum low pressure area of the mass spectrometer. So we've got here-- we've got this high temperature, high pressure.

We've got room temperature and then we've got low pressure. Three areas of this mass spectrometer. So the ions going through this, that's the best definition of an ion lens you can have. And I unscrewed this so you could see inside. There's a skimmer cone-- another cone-- before you get into the high vacuum area.

So now let's talk a moment about the challenges with this system. There are some challenges. Nothing is easy. Right? In this world everything can be challenging. So it turns out that there are a lot of isotopes of different elements that have the same mass. They overlap.

These are isobaric overlap-- calcium 40 and argon 40, iron 58, nickel 58, indium 115, and tin 115. Isobaric overlaps are pretty easy to take care of because we can choose an interference free isotope of the element. That means that every one of these elements has at least one isotope that doesn't overlap. So with the ICP-MS we can key in on that isotope and measure just that isotope and we're good.

The only problem is indium 115 doesn't have any isotopes. They all overlap with something. So what we have to do is type an equation into the mass spectrometer to take care of that. And the main interference is tin 115.

So the equation is pretty simple. We take the counts per second of indium that we want to find. And we take the counts per second of everything, which is the indium 115 plus the tin 115. That's the total counts we're seeing. And then we subtract the counts per second of the interferent.

And the way we get that is we multiply this by an isotope ratio. We multiply it by the abundance of the interferent divided by the abundance of an isotope of tin that does not interfere, which would be tin 118. So we can take those two abundances, get a ratio there. Multiply that times the total counts and end up getting our counts for indium 115. And all this is done by the software.

There's one other equation I have to put in this mass spectrometer. It's for lead because lead 206, 207, and 208-- any time you dig up lead anywhere on the Earth basically, the isotope ratios will always be different because of all the radioactive decay that's going on from when the Earth was formed. And so we put this in. And we add all the isotopes of lead up to the 208 and we get a total and that that's good. That's how we do it.

Then we have these polyatomic ions. In the plasma you've got argon and oxygen. So they can combine with each other to form these polyatomics, which interfere with other elements. They overlap directly. Argon, argon, which would be argon 40 and argon 38 overlaps with selenium. And then if we add our matrix like our acids-- hydrochloric acid you're putting chlorine in. Sulfuric you're putting sulfur. Nitric you're putting nitrogen.

So you can have a whole slew of these. The two most challenging ones are selenium 78 and arsenic 75 because those two elements give the weakest signal of all the elements for ICP-MS. The only ionize about 30%. So we've got to get rid of these polyatomics.

Another thing that can happen is you can have doubly charged ions form. Cerium is an element in our tuning solution. Cerium has a molecular weight of 140. If it's doubly charged, you divide that by 2 and you get 70. So a doubly charged cerium would interfere with gallium.

So somehow, we've got to take these into account. And there's a whole table of them. Look at this. I'm giving you this so you don't have to search for these in the dark. This is everything right here. Everything that I wrote up there is included here. And typically, most of these interferences come below mass 82.

So how are we going to deal with these? We've got to figure out a way to deal with them. And in comes the collision reaction cell. So just to put this back in perspective-- here's our nebulizer and our tube-- our torch. And then this is the high vacuum low pressure area of the mass spectrometer. So we've got a collision reaction cell here that we put helium in.

And we fill it with helium and the helium starts colliding with the ions-- both the polyatomics and the monatomics. And those collisions give off the same kinetic energy, whether it's a plus 1 ion or polyatomic. However, think about this. Polyatomics are bigger so they start colliding more frequently with the helium so they give off more kinetic energy. So there's a positive discrimination voltage-- a kinetic energy of discrimination that prevents the polyatomics from going out of that octupole, that collision reaction cell.

This is amazing. I mean, 15 years ago or something they didn't have this. They had to put equations in for everything. Now at least there's a way to get rid of the polyatomics. So what goes through are the monatomic ions down this quadrupole mass filter toward the detector. This is the detector. It's a pretty fancy detector. It's got these dynodes, which are electrodes in vacuum that produce electrons. They multiply electrons.

This thing has 26 dynodes connected together. So when the ion hits, it produces a couple electrons. Those electrons hit the next dynode. They get multiplied exponentially and then it continues. And then finally, you get down here to the last dynode and that's called your pulse signal.

And that's where you could have a million counts or something. And once that signal becomes saturated then the machine says to itself well, wait a minute. I have to pull back. So it goes back a few dynodes, picks up the analog signal, and then the software multiplies that by some pulse analog ratio to make it look like a pulse.

It's quite complex. But you can actually-- when it's graphing your elements, if a point goes on the graph, you can tell whether it's a pulse or analog point and if it's been corrected. So this is pretty much the detector. Let's see what else we have here. So what are we going to detect in this lab? So we're actually going to be looking at these 29 elements. We picked 29 elements that we're going to be scanning and monitoring during our river lab.

What we did is we actually got standards that contained these 29 elements so we could make up calibration standards for you for this lab. We also have a set of internal standards, which are four elements that are not part of the 29 elements that we're looking at. And the internal standards are there to actually-- they're pumping through the machine constantly with every sample, with every calibration standard, with your blanks, and they're telling us about the drift of the machine.

We can look at this and see, oh, things look pretty good. They're hugging together very nicely. This run here is about a five hour run. And so if those internal standards are staying together, we know the machine is doing well. But if something happens to the internal standards, then we see we might have a problem. So we can actually go in and try to figure out what's going on.

Along with this, we also have quality control standards. Here's your 29 elements again. But we bought these from a different company than our calibration standards. And each one of the elements in this mix has a defined concentration.

So this mix comes from the National Institute of Standards in Gaithersburg, Maryland. And we'll be running one of these with your samples. So you'll be able to look at this and say, oh, these look pretty good. We're very close to the ranges we want. That means things are working well. Your results are really going to mean something when we have all these controls and all our calibration standards and quality control standards.

So a little bit of EPA terminology-- when you get your report, which will be a PDF file, you'll see various things like calibration blank. What this is just reagent water that's acidified the same way as our calibration standards. And we run that blank before we run the calibration standards. And then we'll run a series of maybe 10 calibration standards, do another blank, then we'll run our quality control standard.

And we'll also be running something called a laboratory reagent blank where one of the TAs will actually take water to the river Milli-Q water. And open it up and just let it breathe the air there. And then bring it back to the lab. And then they're going to filter that water the same way you're filtering your real river samples. And then they're going to acidify it exactly like you're acidifying your river samples.

And so we're going to have a blank called the laboratory reagent blank that will tell us, hey, there may have been something in the funnel we're using or something in one of those new filtering membrane disks that got into this sample and it's also going to be in your sample. So that's another quality control. And then we've got-- we're going to run 10 samples.

And then we run a CCB, which is a continuing calibration blank. It's another blank just to make sure everything's OK. And then we run a CCV, which is a continuing calibration verification, which ends up being one of our-- we pick one of our calibration standards. Usually the midpoint standard. And we stick it in there just to make sure things are still OK.

Then we'll run another 10 samples, another CCB, and a CCV. So that's what those terms mean. When you see these you're not overwhelmed. You'll kind of understand what these terms are. This is from the EPA method that we're actually using.

The protocol is very detailed. And the TAs are going to go over this with you in the lab. They'll pull out the tubes, they'll pull out the filtration system. They'll show you how to connect it to the vacuum, show you what kind of bottles to take to the river and collect this from. So they'll be going through all of this.

Now we have to talk about mercury. There's a lot of mercury up there in the atmosphere. Who knows where all this mercury's coming from? Where does all the elemental mercury in the atmosphere come-- Brian?

AUDIENCE: Coal.

JOHN DOLHUN: Coal is a big one. Yeah. That's a man made source of some of the mercury. Yeah. What else? I mean, look at the mercury. Look at the elemental mercury floating around up there. Where else could it come from besides our energy source? Yes, Autumn?

AUDIENCE: Maybe if there's like a forest fire.

JOHN DOLHUN: Forest fires. That would definitely be a big source of mercury. Yeah. Anything else? Yeah, Ryan?

AUDIENCE: I mean, it's definitely in the water, but like for [INAUDIBLE]

JOHN DOLHUN: Yeah. Yeah. Oh, yeah. It's in the dirt and rocks and evaporating out. Yeah. I mean, another big source would be volcanoes-- natural source. Yeah. So probably about 2/3 of it comes from our fossil fuels and a third of it comes from natural sources.

But once it gets up there, once it's in the atmosphere, this elemental mercury-- there are plenty of things up there that can oxidize it. There's ozone up there. There's hydroxide radicals. There's chlorine and bromine in the troposphere. So this elemental mercury gets oxidized to mercury 2.

And then it rains outside. Right? Where do you think that mercury 2 goes when it rains? It's coming down on us. Right? It's going into the water. And once it gets in the water there are a couple of things that can happen. It can have it can be photoreduced here.

And you can form the elemental mercury back. And some of that can vaporize back up into the atmosphere. Or the mercury too can get down here into the depths of the water. And this is where the bad things happen. This is where the nasty methyl mercury is formed.

So once it gets down here we know that mercury loves sulfur. So it can attach itself to this-- there's plenty of hydrogen sulfide in the water. It can attach itself to the sulfur and form mercury sulfide. And this is a neutral molecule. Being a neutral molecule it can go right through a bacterial cell wall. And once it's inside of a bacteria-- there are some bacteria down there that produce methyl mercury.

Nobody knows how it's done. They know that the mercury sulfide goes in, but they don't know the exact mechanism. The other thing that's not known is that there are some fish out there that have millions of parts of mercury in their systems, much more than the surrounding water.

So there's got to be some other sources of this methyl mercury down there somewhere that they haven't really pinpointed. So once we get this methyl mercury-- I just told you it loves sulfur. Right? So you get this stuff in the body-- this organic form of mercury.

It's going to go for your cysteine amino acids. And it forms a covalent bond to the sulfur. So you've got this carboxy ethyl sulfonyl methyl mercury here. Now you think about the cysteine amino acids-- we've got them in our proteins. So this methyl mercury, once it's inside of ourself it can go for all the proteins and infiltrate covalently bond and hook up to all these cysteines.

Once we get methyl mercury inside of us from eating the fish, it's like bioaccumulation. It's down the biofood chain. It starts with the plankton, then the small fish, and the bigger fish. Then we get it. This stuff-- 90% of the methyl mercury can actually come out of our gut, get into our bloodstream, and it can pass through the blood brain barrier. So it gets into our central nervous system and can wreak havoc.

It can also go through the placenta. And the fetus is just in there. I mean, it's just developing. And once methyl mercury gets in there you can have total decontrol of the whole thing. Everything can fall apart for that. So this is really bad stuff. Now what we're going to be doing in this lab is actually we're going to be detecting this and we're going to be using our new DMA 80 atomic absorption spectrometer.

And this spectrometer operates under three things. There are three things happening here. So we've got thermal degradation. You've got amalgamation. And we've got atomic absorption. This spectrometer has two detectors and three cells. It's called a tri cell.

So on the nanogram scale and the PPB scale-- one of the cells will detect from about 0.01 to 10 nanograms, which is like 0.1 to 100 PPB. The next cell will detect between 10 and 20 nanograms, which is 100 to 200 PPB. And the third cell will pick up the last range from 20 to 1,500 nanograms, which is 200 to 15,000 PPB.

The detection limit of this machine is to the thousandths of a nanogram. So detects text down to 0.001 nanogram. Can actually-- you're talking almost a part per trillion there with this machine. So it's really a fantastic machine. So let's actually see how this machine works.

So this is a little schematic of this machine. And I did this on ChemDraw. So ChemDraw is amazing. It is just-- you can do just about anything with ChemDraw. So we've got a tank of oxygen that you'll see it sitting in the lab. And then we have this autosampler, which is a 40 position autosampler.

And so we'll be massing out our fish, putting it into the autosampler. And then this little pneumatic arm comes out, grabs your sample out of the autosampler, and inserts it into this drying decomposition oven. And the drying decomposition oven will heat the sample up to about 650 degrees or so. And it combusts everything.

And all of the combustion products of your sample are carried by the stream of oxygen gas into this catalyst tube furnace. Everything goes in the catalyst tube. And that catalyst tube gets heated up to about 500 degrees. And it pulls everything out-- literally all the NOxes, SOxes, everything you can think of. Not only that, it converts every mercury species, including methyl mercury down to the elemental mercury.

The only thing that comes out of that catalyst tube is the elemental mercury. I know it's hard to believe that, but everything else stays in the catalyst tube. So the elemental mercury comes out and goes into a gold amalgamator. And all it is a glass tube filled with tiny gold beads.

And the mercury comes out, goes in there, and sticks to those beads. Then this gold amalgamator is flash heated up to 900 degrees. And bam! You release the mercury vapor. And the vapor goes into the atomic absorption part of the instrument that has our tri cells-- our three cells.

So we've got two mercury lamps. They're shining light on the samples-- like 254 nanometers. And the light goes in, shines on the sample, and then we record the height of the peak in the absorbance that's going on. And we figure out our concentrations of the mercury in our samples. So this is a great machine. Do you guys have any questions about this machine or the ICP-MS?

There's no sample prep for this machine, which is amazing. We can do solids, liquids, or gases. And you can actually follow your sample through. There's a system status that you can turn on and you can see your sample traveling through the various positions while it's going through.

It's pretty easy. Just three simple steps. You cut up your fishy. Right? And we'll have several native fish to the Charles River. So you'll be able to-- I know. It's not that bad. Maida. Don't pass out on me.

No, it really won't be that bad. But you'll take your fish, put a piece on the boat, and weigh it-- mass it-- and then you type your mass into the machine, put it in the autosampler, and that's pretty much goes. You're going to do this on Monday and Tuesday.

You'll do this at the beginning and then after that, you'll make up your standards for the phosphate lab. And you'll do the phosphate testing. You'll go to the river and get your bottle of water for the phosphate. Any questions? Yes, Autumn?

AUDIENCE: Is there any research on how to remove mercury from other animals or from us?

JOHN DOLHUN: They have-- there are certain chemicals that you could get prescribed that would actually chelate some of the mercury. Yeah. And chelate means to latch on to it and try to pull it out of your bloodstream. Yeah. I don't know anyone that's actually been mercury poisoned to that extent. But I know there are chemicals that you can take that will help mitigate some of that. Yeah. Other questions?

So when we're doing the ICP-MS next Wednesday and Thursday, we'll have you-- you can come in and take a peek at it. You can look at the plasma. You'll see it lit up. And you can see the signal on the screen-- how we're looking at the signal and we're getting it all ready for your samples.

I'll also have an associate here from Agilent-- a PhD chemist who is actually going to-- he wanted to come just for this lab. So I told him to come on. So he'll be a great source to talk to when you're coming in. Yeah.

Yeah. So I'm kind of excited that you're the first group to use this machine. And I think it'll be exciting for you. I mean, the Charles River is probably the cleanest river in America. Yes. Believe it or not. But you know, there's still-- it has to be monitored. We still find problems from time to time. So we will see you up in the lab. And next week, Dr. Sarah Hewett will start a new series of lectures.