

Fundamental Laboratory Techniques for Quantitative Chemistry

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[Beginning of Recorded Material]

[Music]

Dwight M. Smith: For the next few minutes, we're going to be discussing and illustrating a number of important techniques which you will find essential to do accurate and precise work in quantitative chemistry. We will also cover some of the reasons why we do things as we do. It's all designed, as I say, to make your work more accurate and more precise and safe.

On the subject of safety, before we get started, let me say a couple of words. First of all, you should not work in a chemical laboratory with short sleeves or shorts. It is necessary even in a laboratory of this sort -- a quantitative laboratory -- to protect your skin from spills of chemicals. And I think -- I would highly recommend that you not wear shorts or short sleeve shirts or tops to the chemical laboratory. Secondly, eye protection is a must. Especially if you wear contact lenses, you must wear a pair of eyeglasses of this sort. We recommend these because they have a little panel on the side that prevents splashes -- your neighbor undoubtedly being the one to do so -- but prevents splashes into your eye from the side. If you wear prescription eyeglasses in a course of this sort, that may be sufficient. But if you generally do not wear glasses or wear contact lenses, you must wear these at all times in the chemical laboratory. You should also be aware of where the first aid kit is, where the fire extinguisher is, and where the safety shower and the eye wash are. Your laboratory assistant will both demonstrate the use of those and remind you of where they are.

One final note before we get started concerns the record which you will keep. The laboratory notebook is an essential part of your work in experimental chemistry. That is especially so in quantitative chemistry where data are important -- numerical data. The notebook should be bound. The entries in it should be in ink. It should be possible for anyone with average competence to read your notebook after you're through the experiment and get the same result you did. If they cannot, then you have not kept an adequate book. This particular notebook is one in which we have a quadril type pagination. The page numbers can be put in here. The date and your initials -- when you finish your

initials – when you finish the day's experimentation. All the entries I said should be in ink. If you make a mistake, don't try to blot it out. Draw a line through it and then put the correct data in place of it. These are some of the principles that should guide your work and your use of a laboratory notebook. I try to organize a notebook in a chemistry laboratory so that I can look for the same thing every page after every page -- data and observations perhaps on one side; sample calculations, comments, procedures on another. If you do this – if you keep a careful notebook, it will not be possible for you to lose data by putting them on scraps of paper which can disappear. In fact, you will find some very hard-nosed laboratory instructors will appropriate scraps of paper on which you write data because you must be putting them directly into the laboratory notebook for posterity. The keeping of a laboratory notebook, in summary, is a very important, an essential part of accurate and precise and reliable work in the chemical laboratory.

[Text: Overview of Experiment]

Dwight M. Smith

Let us now begin, then, with a discussion -- an overview actually -- of the experiment that we're going to be carrying out. Discuss the discrete steps and then we will move in to a demonstration of the actual experimental techniques following that discussion.

The techniques to which I refer will be illustrated by a quantitative experiment in which we will determine accurately the concentration of a solution of sodium hydroxide. This process is called standardization. Standardization, therefore, of one-tenth molar -- that is one-tenth of a mole per liter -- of sodium hydroxide will be our goal. In order to do this, we have to have a reference material which we call a primary standard substance. Now that primary standard must have a number of characteristics. It must be pure. We must be able to weigh it and then know that we have an accurately measured amount of this. We then dissolve and dilute to volume this primary standard to use as a reference solution. Following that, we prepare our secondary standard which is the tenth molar sodium hydroxide – which is the solution we desire to prepare and determine the concentration of. In the course of this, we must take the

secondary standard and prepare it from reagent quality sodium hydroxide. We will then titrate that solution with a solution of the primary standard. That process of incremental measurement of solution is called titration – titration of secondary standard with the primary standard. We then will calculate from the data the concentration of the secondary standard – sodium hydroxide. It's about one-tenth molar, but we will know it accurately.

Let us now take a look at each one of these points briefly, individually. The primary standard, as I mentioned, has several desirable -- really essential -- characteristics. One of those is that it be obtainable in pure form, obviously. A second is that we need to have it dryable -- that is we must be able to remove, adsorb moisture from the atmosphere. It also should not pick up water very readily, so it should be nonhygroscopic. It surely should be stable in air, cause that's where we're going to be manipulating it. And it should have a high formula weight. A high formula weight because any manipulative error or any error in weighing will mean a whole lot less if we have a high formula weight because the number of individual ions and the species in solution will be less if it's a high formula weight. So a primary standard substance needs to be pure, dryable and nonhygroscopic, stable while we are measuring it, and have a high formula weight.

Now, such a substance is potassium acid phthalate. That's a mouthful, so we will abbreviate it KHP. KHP is a strong electrolyte which dissociates into K^+ and HP^- . The HP^- is this molecule -- this ion, really. One negative charge. Which dissociates in aqueous solution to P^{2-} plus H^+ . It has an ionization constant -- which is the second ionization constant -- of about 3.9×10^{-6} . It's therefore a weak acid, but it is -- it reacts with strong base -- which is sodium hydroxide -- rapidly and completely.

Now, the question always arises, how much of this do we need. If we're to weigh out or measure the primary standard accurately, we need to know how much. This has a formula weight of about 204.1 gram per mole. Thus, if I wish to prepare a solution which is 0.05 -- let us say 5.000×10^{-2} molar -- and I wish to have, let's say, 250 milliliters of this solution, the product of volume times the

concentration is 12.50 millimoles. Because this has a formula weight of 204 grams per mole or 204 milligrams per millimole, the substance that needs to be measured out is 12.50 millimoles times 204.1 milligrams per millimole – or about 2.55 gram.

Now, let us take a look at the preparation of the secondary standard. We know that the primary standard substance, potassium hydrogen phthalate, requires 2.55 grams in order to prepare 250 milliliters of this concentration solution. Let us now take a look at the preparation of secondary standards. This is the sodium hydroxide -- approximately a tenth molar, determined accurately -- that we've been talking about -- that we're going to measure versus the primary standard. It is a fact that one hydrogen ion in solution will react with one hydroxyl ion to produce water. You all know that. The sodium hydroxide is also a strong electrolyte totally dissociated into sodium ion and hydroxyl ion. Now that means that the number of reacting moles -- millimoles of H^+ is the same as the number of millimoles of base that will be required for reaction. That is the number of [milli]moles of potassium acid phthalate -- potassium hydrogen phthalate will be equal to the number of millimoles of hydroxyl ion required. You recall that 12.50 millimoles of HP^- or KHP were required. Therefore the volume of base that we need to react with the 12.50 millimoles of HP^- would be, ordinarily, the concentration of the hydroxyl ion containing solution -- which we want to be nominally one tenth molar -- and the volume of that that would be required is therefore given by V . Thus, we must have in order to react with 12.50 millimoles of HP^- 125 milliliters of the sodium hydroxide. Now 125 milliliters of the sodium hydroxide will be required to react with the entire volume of solution that we have prepared from the primary standard. However, it is not necessary, generally, to work with such large volumes of solution. So we will take what are called aliquot portions or measured portions of this solution -- of the potassium hydrogen phthalate to react with the sodium hydroxide. Now we are going to prepare a solution of sodium hydroxide that we want to retain for future analyses. So we actually will generally make a quantity larger than that required to react with the few samples of the potassium hydrogen phthalate standard. Let us say we will prepare 500 milliliters of the one-tenth molar sodium

hydroxide. That is, of course, 50 millimoles of sodium hydroxide. Because the formula weight of sodium hydroxide is 40 gram per mole, the amount required to prepare the solution will be 50 millimoles times 40 milligrams per millimole or 2000 milligrams or 2 grams. That is, it will be necessary to weigh out approximately 2 grams of the sodium hydroxide in order to prepare this solution -- this concentration, we're going to establish accurately.

[Text: Drying of the Sample]

Dwight M. Smith You will recall that one of the characteristics of the primary standard that we just discussed were that it be dryable. One of the fundamental operations in any analytical chemistry laboratory is to dry samples -- to remove, adsorb moisture, and the like. We have placed in this oven a couple of hours ago a sample of potassium hydrogen phthalate to dry. I want to discuss just briefly the use of the drying oven, the manipulation of the sample, and then how we allow it to cool before we carry out the weighing step.

Now, I said in my preliminary remarks that we always need to provide eye protection during any manipulation whatever. So, I'm going to wear these glasses while opening this drying oven, showing you the interior and the sample of potassium hydrogen phthalate that has been drying at 120 degrees for a couple of hours. Now, one of the things that is very important for me to point out in the use of a drying oven is that we never put vessels with labels or writing from these wax pencils that seem to be found around laboratories. Even at 120 degrees, these things evolve vapors that are particularly reducing vapors and any other samples that are subject to reduction that may be in this drying oven will be effected. So we use simple, glass vessels -- particularly light glass vessels - - like the weighing bottle that you see sitting there on the shelf. It's light because we want to weigh this sample by difference -- that is, transfer a sample of approximately correct size out of it and reweight it again to determine the amount of material that we have transferred. Now, to cool it, we generally will put it in a desiccator -- a drying vessel -- that is metal that conducts heat well. And we will then transfer the sample into this desiccator. As I do so, let me point out that because this is hot we will be very careful not to close this lid

because if I fully close this lid, of course, the heat inside will expand the air. Once it cools, you will create a partial vacuum in this and as you take the cover off, then possibly blow the sample out of your weighing bottle. So we must be careful about that.

Now, we have transferred the potassium hydrogen phthalate that's been dried at 120 degrees for a couple of hours into a cooling vessel in a dry atmosphere. We're now going to take this over to the balance – the analytical balance where we're going to weigh it. But first, we'll allow it to cool for a few minutes so that we do not have temperature gradients inside the balance and thereby induce errors in the weighing.

[Text: Weighing and the Analytical Balance]

Dwight M. Smith Now that we have removed the sample from the oven that's been dried and while it cools in the desiccator that we placed it in, we'll talk just a little bit about one of the most accurate and precise instruments in any analytical laboratory. There are many that are far more sophisticated, but this is probably the most accurate and precise measuring device you will ever use. It is called the analytical balance. This particular model is a so-called top loading balance -- single pan -- which will register in digital terms the mass on the front readout. You will note that even though it's sometimes considered a right-hander's world, the balance manufacturers have put doors on both the left and the right side of the balance so that you can manipulate from either side. There is a top door which enables one to carry out measurements of mass of objects that too large ordinarily to fit into the chamber. We keep these closed during the weighing process to avoid the effect of convection on the balance itself. The red button here, called tare, is used to set the balance to zero. I disturbed it by convection by opening the doors. We also want to make certain that temperature of the device – that's why we're cooling our sample. Anything that's being weighed must have the same temperature as ambient, so that we don't get, again, that convection setup and disturb the balance pan. This, then, now that the sample has probably cooled long enough, we will begin to demonstrate how to determine the mass accurately and transfer it to a solution.

Before and after weighing, actually, we want to make certain that the balance is clean, that the pan is clean. One of the ways of doing this is to use a camel's hair brush -- attached to this balance so it doesn't stray -- and clean off any particles, visible or invisible, that may be on the pan. Clean the base of the balance chamber and make certain that there are no foreign materials attached to the balance pan. Close the door. Allow convection to settle down. Reset the balance to zero. If it stays at zero, why it's a stable situation and we can then commence to weigh the material that we have -- in this case a sample of potassium hydrogen phthalate in the desiccator.

Now, we will transfer the sample from the cooling desiccator into the chamber. Because I'm right-handed, I'll open the right hand door. Slide the top from the desiccator. Take the sample out of the desiccator. Transfer it to the balance pan. And we note the total mass. The digital readout is -- it seems to have settled at 16.2870 gram. You will notice from the readout that this balance reads to the nearest one-tenth of a milligram. Again, a highly accurate device.

Now, one of the ways in which we can carry this out -- the way I will do this -- is to transfer a portion of the sample to the flask in which I'm going to make the solution, reweigh the bottle, and then by difference determine the mass of the sample. Earlier, I mentioned the importance of keeping all of the data in a laboratory notebook -- an accurate laboratory notebook -- and therefore we will need to record this value: the sum of the weighing device -- weighing bottle and the sample. 16.2873 gram.

We will then transfer the sample to the flask, weigh the weighing bottle and remaining sample, and measure by difference, accurately, the amount of material -- potassium acid phthalate -- transferred to the flask.

[Text: Volumetric Glassware -- The Volumetric Flask -- Sample Transfer]

Dwight M. Smith I know from my earlier calculation that about 2.5 gram in 250 milliliter flask will be necessary to prepare a solution of .05 molar potassium hydrogen phthalate. When I placed this sample in the oven, I put into this weighing bottle approximately 4 grams of sample. Accordingly, I should transfer a little more

than half to get 2.5 grams of sample into the flask. Let me say a little bit about this volumetric device, an important piece of volumetric glassware. It is calibrated. If you will notice on the flask TC at 20 degrees Celsius is inscribed near the volume – the nominal volume. That means it's calibrated to contain. You cannot deliver 250 milliliters from this flask. It is calibrated, with a calibration mark on the stem, to contain 250 milliliters. We will come back to this calibration mark as we dilute the sample. But one of the ways that it is proper to use a device like this is to remove the stopper. One of the things we don't want to do, however, is to lay the stopper down on the desk top. All too common for beginners. We rather hold the stopper between the fore and middle finger and keep it there during the course of this manipulation, so that then when we dilute the sample we can just replace the stopper without any fear of contamination of this stopper from laying on the desk top or on the book or something of that sort.

To transfer this solid, I have elected in this demonstration to use a small funnel to transfer the solid into the flask. Now, experienced analysts won't do this because it introduces another surface, or another possible source of contamination of the solid. But we have rigorously cleaned these and I think for people just beginning this work it's safer and better to use a funnel for the transfer of the solid. So we will place in the top of the flask this small funnel in order to effect the transfer of the sample into the flask quantitatively.

Now, there are a number of ways of doing this. I could use the forceps that I had shown you earlier. The problem is that I'm not left handed and I've extracted the stopper from the flask with my right hand and I think it's a lot easier to use an alternative manipulator which we can fashion very readily out of a piece of paper. I just simply take perhaps a third of an 8.5 by 11 sheet like this, fold it once, perhaps fold it again, giving me a little manipulator which will enable me to extract the flask – or the weighing bottle from the balance like so. Transfer roughly a half or a little more than half of the solid from the weighing bottle. We will weigh what's remaining and we'll see if we've obtained about 2.5 grams. That's 13.89, roughly. And if we subtract 13.8890, we see that the amount of

sample transferred is 2.3983 grams or roughly 2.4 grams. That's not bad, especially for a beginner. And we will settle for that. The important part of this is that we do not need to transfer exactly 2.5 grams as calculated. Because we know exactly what has been transferred we can calculate exactly what the concentration is. In this case, it will be slightly less than .05 but that doesn't matter because we will know exactly what the amount of material in 250 milliliters is.

Now, having transferred that – having recorded the mass of the weighing bottle and the residual sample, now we need to make certain that all of the material is washed down into the flask. Quantitative transfer is absolutely essential. We've determined by weighing exactly what the mass of sample is. We need to make certain that it's all in solution and some doesn't get removed by when I remove this small funnel from the flask. Now, I replace momentarily the stopper and we will discuss then the dilution to volume of this sample and the preparation thereupon of the standard solution. It's good practice to dissolve in the minimal amount of solvent that we can the sample. The reason for that is that there is a heat transfer always involved in effecting a solution in this sort. In the case of salt, like potassium hydrogen phthalate, the energy is absorbed from the surroundings and the solution gets slightly cooler in the process of dissolution. In order to minimize that effect, because the flask is calibrated to contain at 20 degrees, we should dissolve this in the minimum amount of solvent and then use the water – which is at ambient or laboratory temperature – to dilute to volume so that we don't dilute to the calibration mark, have the temperature change, and thereby have a different or inaccurate volume.

Now, the preparation of the secondary standard, sodium hydroxide, where we saw we needed in the neighborhood of 2 grams does not need to be done as accurately as the measurement of the primary standard. That is because we are going to determine exactly the concentration of this solution with the primary standard. So we would weigh out approximately 2 grams. Sodium hydroxide is not a primary standard. It fulfills almost none of the criteria for primary standard. It has a low molecular weight. It picks up water – that is hygroscopic.

It's not available in particularly pure form. So, we must take the approach of weighing approximate amount in solution, giving about the concentration we want, then determining it accurately with the solution of the primary standard.

Now, in transferring any reagent from a bottle of this sort, we never immerse a spatula or other device into a bottle of standard reagent. We might contaminate it with a dirty spatula. Therefore, we usually use the cap, for example, of this bottle to transfer a little bit of the reagent into the bottle cap. Then place on the balance pan, so that we can avoid contamination of the pan itself, a weighing paper – a very light paper which, as you can see from the digital readout, weighs only about a fourth of a gram. We then press the tare button again and the balance is reset to zero accommodating the weighing paper. That is the balance is set at zero including the weighing paper. So, the next digital readout I get after transferring this reagent will be the net mass of the reagent. What we need, you will recall, is about 2 grams. So, we will put a few of these pellets onto the weighing paper. That's 1.2 roughly. Let's see if we can transfer just about the right amount to make this 2 grams. Not quite. There we are. We will not return reagent that we have taken out of a reagent bottle to the reagent bottle. So, I will put that back on a weighing paper for disposal. Close the reagent bottle. Write again in my laboratory notebook the mass of the sodium hydroxide that was transferred. 2.0287 gram.

Next, we will transfer the weighing paper from the balance to a 500 milliliter volumetric flask, which is the volume of one-tenth molar sodium hydroxide that we were going to prepare, you recall from our previous calculation. Once again, taking the stopper from the bottle – either right or left hand, doesn't matter as long as you keep it there during the manipulation. In this case, because we do not have a particularly granular sample, I will transfer it directly from the weighing paper into the flask. The size of this flask is such that the mouth of the bottle is sufficiently large to transfer this without any fear of losing any, so we can avoid the additional surface that we found in the case of the potassium hydrogen phthalate was necessary. In this case, we'll again dissolve the sample

in the minimum amount of solvent -- distilled water in this case -- necessary to bring it into solution before we dilute it to volume.

Now, again, we know exactly how much was transferred, but that will not be used in determining, as it was in the case of the primary standard, the final concentration of solution. It gives us an approximate value for the concentration.

[Text: Volumetric Glassware – The Volumetric Flask – Dilution to Volume]

Dwight M. Smith

Now that we have dried, weighed, and partially dissolved our two samples, potassium acid phthalate and sodium hydroxide, we are going to discuss the proper technique for the dilution and adjustment to volume of these solutions. We use, as I mentioned earlier, the volumetric flask – the volumetric flask which is calibrated to contain at a specific temperature, 20 degrees, solution. We have dissolved the solid potassium hydrogen phthalate in a minimum amount of water to allow for the exchange of heat. These are now at laboratory temperature and we're going to proceed to dilute these solutions. Now, one thing that we need to remember is that we never extract the stopper from a piece of volumetric glassware which we're trying to use to do accurate quantitative work and lay it on a desk top. We hold it between the forefinger and the middle finger, thusly, and we take a source, as I have here, of distilled or deionized water and dilute the solution up to about the neck of the flask. Now, the reason we do that, of course, is to facilitate thorough mixing. It is very important that the mixing be thorough because we certainly don't want areas – regions within the solution that are of a different concentration than others. So, diluting it nearly to the neck of the flask, we can see the density gradients as I rotate this solution in the flask and now we have a pretty homogeneous solution.

Now, we can proceed to add further distilled water. I recommend at this point that we use a wash bottle, as we've used before, to bring the solution very near the calibration mark, which I want to talk about. As we bring this up near the calibration mark, we see that it enters a region of the flask which is very narrow.

All volumetric glassware is shaped this way, in order that any error that we make in the adjustment of the level to the calibration mark be – represent a minimum error in the total volume. If the dimension of the flask remained this, any uncertainty in the level would, of course, represent a much larger volume. So, we have this elongated neck and this calibration mark. Now, I recommend at this point that because there may be droplets in the neck, as we've seen here, that we bring the solution just below the calibration mark, we tightly secure the stopper, and we mix thoroughly and see where the level of solution ends. Well, it is still just slightly below the calibration mark, as you can see. Adjusting that calibra – adjusting the level of the solution to the calibration mark, then, should be done with a dropper, called these days a Pasteur pipet. We can just simply, then, once again remove the stopper, take our source of pure water -- distilled water or deionized water -- and add into this flask dropwise just enough solution to bring the bottom of the meniscus right level with the calibration mark. Once we have done that, then we carry out a final mixing – several inversions, allowing the air to rise to the bottom of the flask as I invert it, doing this perhaps a half dozen times in order to make certain that this solution is indeed homogeneous because if it's not homogeneous, our procedure for determining concentration with a representative sample solution will be meaningless. So we do this one more time and that should be thoroughly mixed.

Now, I'm am going to use the solution from this flask initially, but before we store this solution, we are going to put it in a reagent bottle, properly label it, and so on. We'll come back to that, because I want to proceed with this measurement directly from the flask because I want to make a point about measured fractions or aliquots.

Now, we're going to do the same thing with the sodium hydroxide solution. I've made, you will recall, twice the volume because we want to use this subsequently, then, to analyze acidic substances. So, we'll remove the stopper from the flask. Again, bring the level of the solution up around the neck of the flask before we finally mix it. While we're consuming a little time here, I think it's well worth to emphasize just how we go about doing this. We bring the level

of the solution up about to the neck. I'm a little above the neck, but that's ok. We'll now mix it well below the calibration mark – while the level of the liquid is well below the calibration mark, making certain that all the density gradients are eliminated as we do so and that we're fairly confident that the solution is indeed homogeneous. That looks to be fairly good because we're going to give it a final mixing. Then we bring just up below the level of the calibration mark the solution with our dropping bottle. Just a little below, again, to make certain that if there are droplets above the calibration mark on the neck that they're all mixed into the solution. Alright. Then, once again, we take our dropper -- our Pasteur pipet -- which contains a little distilled water or deionized water and let me hold this above the calibration mark so that you can see it. Bring it right exactly to the – so the bottom of the meniscus is level with the calibration mark.

Now, a word about the accuracy of these things. I made a great point of mentioning the importance of bringing this right to the level of the calibration mark. All of these flasks -- this volumetric ware -- is Type A glassware. Type A glassware has a tolerance of less than or equal to one tenth of one percent, so it is very accurate. It is a very accurately prepared solution, now. Again, reminding you that the volumetric flask is calibrated to contain at 20 degrees 500 milliliters of solution. Let us give this two or three more rotations of the flask to assure ourselves that we have a homogeneous solution. This is one of the very common errors that people just beginning quantitative work in chemistry make. They don't sufficiently, thoroughly mix the solution and wind up with a heterogeneous mixture.

Now, we've prepared these solutions, we are ready to carry out a process called titration for determining the concentration of the sodium hydroxide relative to that of our reference or our primary standard.

[Text: Preparation for Titration]

Dwight M. Smith Now that we have prepared our two solutions, accurately diluted the potassium hydrogen phthalate primary standard, and prepared a solution of exactly 500 milliliters of approximately .1 molar sodium hydroxide, we are going to

determine the concentration of the sodium hydroxide accurately against the potassium hydrogen phthalate solution through a process we call titration. Titration is the incremental addition of a standard reagent to a sample to a point of chemical equivalence which we can determine by a signal system of some sort -- I'll describe in a minute -- and at that point then, having measured the volume -- the accurate volume of the titrant, the solution that we're titrating with, into the sample, that's the solution titrated, we can calculate the concentration of the sodium hydroxide whose concentration we know now only approximately.

Now, to do this we use the concept of taking an aliquot. An aliquot portion is an accurately measured fraction of the total sample. For example, in the 250 milliliters of potassium hydrogen phthalate, if I withdraw exactly one tenth of that solution or 25 milliliters, then I will have taken a one tenth aliquot of that solution. I know exactly how much therefore I have taken for titration and the calculation of concentration from that is straightforward. To do this -- to transfer an aliquot portion -- we use something known as a transfer pipet. The transfer pipet is shaped, as you may remember, with a bulb for the retention of the major portion of the liquid. It's calibrated TD -- to deliver -- 20 milliliters at 20 degrees Celsius, as opposed to the volumetric flask that is calibrated to contain. We cannot deliver exactly 250 milliliters from this and this one will not contain exactly 20 milliliters. It will deliver exactly 20 milliliters by the process that we're going to illustrate just now.

[Text: Volumetric Glassware – The Transfer Pipet - Aliquots]

Dwight M. Smith Now, we will use therefore this 20 milliliter transfer pipet to withdraw a fraction of the solution from this flask – a measured fraction. We will deliver it into the vessel in which we are actually going to carry out this process called titration. The manipulation of a pipet is one of those things that gives students who first encounter these perhaps the most difficulty. There are two methods of doing this, both employing pipet bulbs. There was a time when chemists used their mouths to pull solution up into the pipet, but in these days of safety consciousness we no longer do that. We use devices known as pipet bulbs,

simply depressing the bulb, drawing the solution up into the pipet, adjusting the level. Again, you notice the narrow diameter of this device so that any uncertainty in setting the level is minimized in terms of volume. Then, we will deliver the sample into the flask. Perhaps the easiest way is to use what is called the pipetter. It's a little bulb with 3 valves which enable us to regulate the level and release the solution into the flask.

Let me illustrate how that works. First of all, of course, we remove the stopper from the flask, holding it in our hand, and we immerse this clean pipet into the solution. Now, one bit of caution. This is a previously cleaned and dried pipet. You are going to be working with pipets that probably, because you don't have a lot of them at your desk, are going to have bits of water in them. So, it's necessary to take some of the solution into the pipet, rinse the pipet with the solution, so that you're sure that what is in there is all the solution of the now known concentration of potassium acid phthalate. It's very important that you don't dilute that solution with droplets of water in the pipet. To do this, then, we depress this top valve, depress the bulb, open the valve – just press it, depress the bulb, then fit it carefully to the top of this pipet while we immerse the tip just below the level of the liquid so that we don't spill the liquid by pushing it over the top. Depress this little valve on the side -- this release valve -- and you will see solution begin to come up into the pipet. Now, at this point, we will capture that level of the solution and rinse the pipet. I said this was a clean pipet, but we'll just illustrate how one goes about rinsing the pipet with the solution that we're going to use in that pipet. Very important that this step be done, because again we do not want to dilute the solution by droplets of water in the pipet. Do this a couple of times. Let it run above, or actually below in this orientation, the calibration mark and then let it drain back into this beaker that I have here that's appropriately called a slop beaker. Now we have a pipet in which there is solution in the tip, but it is the solution that I want to deliver into the flask.

Now that we're finished with the rinsing process, we'll proceed to withdraw the measured fraction -- the aliquot -- from this potassium hydrogen phthalate

solution, whose concentration we know accurately, by means of this bulb again. Depress the valve at the top, squeeze the bulb, and prepare it to withdraw solution into the pipet. Put the pipet into the flask well below the level of the liquid so that we don't draw air into the pipet and then depress this valve allowing solution to flow into the bulb and up above the calibration mark. Now, before we adjust the level, let me say that it's important usually not to keep your hands on the bulb of the pipet – just as it isn't on the body of a volumetric flask – because the heat from your hand will expand slightly that bulb, changing the nominal volume. Now we can press the side valve on this bulb and bring the level of the liquid down to the calibration mark. Once it's exactly there, we'll withdraw the pipet making sure that any drop clinging to the tip is transferred, put it into the titration vessel and deliver exactly 20 milliliters of potassium hydrogen phthalate solution whose concentration is accurately known into that flask.

Now, we can remove the bulb -- the manipulator, the pipetter -- and let me point out that one of the important features of a transfer pipet which is calibrated to deliver, remember, at 20 degrees is that we must touch off from the tip any drop adhering to that tip and there will remain in the tip a small amount of liquid which you see and that amount of liquid is intended to stay there. That is, the pipet is calibrated so that it retains this small amount of liquid in the tip. Then, we can set aside our pipet, stopper our flask, set it aside. We'll lay the pipet here somewhere where it won't put droplets of solution on the desk top. And we'll see that we have a small amount, 20 milliliters, of liquid in the flask. Now, because I touched the tip of the flask -- or the pipet, excuse me -- to the flask, I will rinse this conical flask just ever so slightly with water. That's perfectly allowable because I put a measured volume of a known concentration of solution into this flask. I therefore know the amount exactly. It doesn't matter if I add a little bit of distilled water in the process to dilute the solution. Now, we'll proceed to discuss the buret and the process of carrying out the reaction between the sodium hydroxide and the sample of potassium hydrogen phthalate that we have just delivered.

[Text: The Buret]

Dwight M. Smith

Now, that we have delivered the accurately measured volume of potassium hydrogen phthalate into our flask – our titration flask, we're going to demonstrate the process of titration using a volumetric glassware device known as a buret. The buret is graduated, as you can see, in divisions. This one happens to be 50 milliliters divided in major divisions of one milliliter each with subdivisions of one tenth milliliter. The process is to adjust to some level initially the level of liquid, read that level – it's common to adjust it to exactly zero, carry out the reaction with the incremental addition, flowing of liquid from the buret into the titration vessel, watching for our signal system that I'll discuss in a moment to tell us that the reaction is nearing completion or chemical equivalence. Then, we'll go more slowly until the signal system tells us to stop. We will read the volume and calculate thereby from the volume and concentration of the standard the concentration of the base.

Now, the reason that we add the base to the buret is that sodium hydroxide is rapidly attacked or reacts with the carbon dioxide of the air. So, if I were to have this in the open vessel, it would pick up quite a bit of carbon dioxide from the air as compared with this narrow buret where the interface is just the small portion of the liquid at the top. So, I've chosen to add sodium hydroxide to our buret.

Now, to discuss the buret just a bit, let me point out beyond the calibrations the fact that the last calibration mark is some level above this valve which we call a stopcock. It is necessary to remember that you must stop in order that there be readability at some point above this final marking which is 50.00 milliliters. You see here in this stand two burets, one of which is filled with distilled water and covered with a small bit of material here that keeps the air and the dust and so forth from that. This is a material called parafilm, actually, and it's a useful material to cover the top of the buret if you're going to let it stand with distilled water in it. The other way to leave a buret is empty, dried in air and this one is inverted so the dust doesn't settle into the top. This, as empty, we can do this rather than have it upright and cover the top. You will notice that this valve, or this stopcock, is not in the same condition that this is. It's just wedged in here

with a piece of paper to keep the two portions of the ground glass – the barrel and the stopcock itself are both ground glass and we need to lubricate these in order that they behave properly. There are burets these days that have valves in them which are Teflon and we found that they tend to leak a bit from time to time. So, I'm using in this demonstration a stopcock that is lubricated with a stopcock grease and I want to illustrate how we do that. We will take this stopcock out, having cleaned the barrel and the stopcock itself, then streak on the surface of this small amounts of a stopcock lubricant. Reinsert it. Move it back and forth gently until the lubricant spread itself around the surface of this round, glass valve or stopcock.

So, with that in mind, let us then put our reagent, sodium hydroxide, into this buret and there are a couple of points I want to make about the proper filling of this buret. We will take our beaker – it's called a slop beaker. We will allow the distilled water to drain out. We'll need to remove our covering -- our parafilm -- from the top of this so that we can put the reagent into the buret. And we'll allow this to drain. This has presumably been cleaned and while this is draining let me say that detergent and a buret brush of this sort is the thing that you want to use to keep these scrupulously clean. Usually over the sink at the end or side of the laboratory. Then copious quantities of tap water, then distilled water are used to rinse the buret. Now, we'll let this drain and then, I want to make a couple points about transfer of the reagent sodium hydroxide into the buret. The first of these is that as I fill the buret with this solution, I need to run a little bit of solution through because, once again, we do not want the distilled water that inevitably clings to the side of this buret to dilute this reagent. So, we need to put in a couple of small portions of base and let them run through so that the solution is all the sodium hydroxide that we've prepared because we're going to determine the concentration of that.

Now that the distilled water has drained from this, let me caution you about trying to fill a buret above eye level. Even though we wear eye protection, spills are inevitable and we certainly don't want to spill reagent – certainly don't want to waste it, but mainly we don't want to create a mess and more particularly we

don't want it to splash on us. So, the proper way of filling a buret of this sort is to bring it over near the desk top. We'll remove this one from the clamp. We'll rotate this around in such a way that we can lower the buret below the level of the desk and avoid filling it above eye level. Now, while people whose profession is analytical chemistry would certainly transfer the liquid directly into the buret, for people who are just beginning to use these techniques I advise against that. Even though I will remind you that we try to avoid additional surfaces contacting our reagents, I think it's prudent in this case to insert a funnel and then pour into the buret a small quantity of the reagent sodium hydroxide. Now, you'll see as I move the tip of the funnel around, the liquid will drain down the barrel and rinse the distilled water down to the bottom of this buret from whence we can deliver it into our slop beaker. And we'll do that one additional time. Now, the rinsing of this probably twice will be sufficient for most reagents of low concentration, but the first one you must let run all the way through. You don't want any diluted solution in there. The second one we'll stop well above the bottom calibration mark and I'll show you how we can set up to commence this titration properly. Alright, once again, I'll lower the buret so I'm not filling it above eye level. I will take some of the sodium hydroxide which we prepared, diluted accurately to volume. Move the tip of the funnel so that it rinses the wall very thoroughly so we have no dilution of our reagent. And then, once again, we will deliver this full amount into the beaker that we've designated for waste.

This next time, then, we'll fill the buret up to a point where we can take the initial reading and then we'll talk about the adjustment of that initial point. Now, everything that we read as the liquid goes down the barrel of the buret must be -- everything delivered -- must wind up in the solution or we will have a faulty analysis. We're depending upon the fact that as we start here and finish, let's say, here with our titration process that all that liquid has gone to reaction with the potassium hydrogen phthalate. So, it's very important that when we finish this, we've transferred all drops from the end of the tip. We want to make certain that there are not bubbles remaining in the tip that could change volume as the solution pours through. Alright, once again, I'll lower the buret so

I'm not filling it above eye level. I will take some of the sodium hydroxide which we prepared, diluted accurately to volume. I can bring this up just somewhat above the zero mark. Now, we will remove the air from the tip. Remember, this can have no air in it because we don't want a bubble to be delivered into the reaction vessel simply because it would misrepresent the amount of liquid that's been delivered. There. All the bubbles must be eliminated from the tip.

Now, let's move this back to our place on the desk top so we can follow this process. Now, as we prepare to adjust the level of this liquid to the initial point, normally zero but not necessary as long as we know exactly what it is. We will prepare a little device called a buret reader. A white piece of paper with a black pen, just sufficient marking that we can see behind the buret to outline the bottom of the meniscus. We'll deliver this liquid into our waste beaker and holding the buret reader behind the buret, adjusting the height of the buret before we start to eye level. A phenomenon known as parallax where if we look at this below or above the level of the buret marking, we may introduce a small error, perhaps a tenth or two tenths of a milliliter error. So these are conveniently – the whole milliliter markings are conveniently scribed all the way around the barrel, so we can line those up and be sure that we are exactly at eye level. Now, we will lower, therefore, the level of the liquid until it reaches exactly zero, in this case a convenient place to start. I'll align the meniscus just behind right there. Bingo! Exactly 0.00. Now we touch off any drop that is still adhering to the tip because if we were to deliver that, since we're measuring our volume from here, that would be an extra drop added to the solution that we would not have measured. So be careful always to before and after these reactions to transfer any liquid remaining on the tip. Now, we're ready to carry out the titration itself, the reaction between the base that we're attempting to standardize and the standard potassium hydrogen phthalate solution.

[Text: The Titration Process]

Dwight M. Smith We are now ready to carry out the process called titration. We've delivered into this flask our accurately measured amount of potassium hydrogen phthalate – 20 milliliters of approximately .05 molar solution. We know that value exactly

because we know the amount of potassium acid phthalate that we put into solution. We're going to then add sodium hydroxide solution to this to the point of a color change. I spoke about the signal system. We're going to add what is known as an acid base indicator. An acid base indicator is, itself, a weak acid or a weak base and in the acidic form they are one color, in the basic form another color so that as I put this initially into the acid solution, this is going to be colorless. As I reach a point where the solution becomes basic because I have added sodium hydroxide to it and perhaps in slight excess, the solution will contain then the basic form of the indicator and it will turn red and it will tell me to stop. I've reached the point of chemical equivalence.

Now, the measurement is typical of the measurement of reagents that are often used in titration. We're going to add a total of five drops – five drops of the phenolphthalein indicator. Normally three is enough, but I'm a little uncertain as to the concentration of this, so we'll add five drops of indicator to this flask. Then we will record the initial volume of base. It is exactly 0.00 milliliter. Now, you will notice that I've expressed the volume to the nearest hundredth of a milliliter. These divisions are to the nearest tenth, so you'll have to interpolate between the markings of a tenth milliliter spacing to the nearest tenth of a unit so that there is some approximation in that last figure. But if I move down the buret here, I see that I can achieve four significant figures in my resulting volume. So, I'm expressing the initial volume as 0.00 milliliters.

Now, we will replace our catch beaker, making certain that there's no drop at the tip, with the solution to be titrated which is in a conical flask – actually called an Erlenmeyer flask. Now, notice that this is in a white background to make it possible for us to more accurately pick up the change in color. Now, before we start I want to mention the fact that this little dropper, or Pasteur pipet, was used to add about five drops of indicator to the solution. It's very often the case that we want to add reagent in approximate amounts. We don't need to go to the trouble that we did of preparing the potassium hydrogen phthalate solution. There are several devices that are designed for this. The graduated cylinder is an important tool in the analytical laboratory. The

accuracy of this which is also noted as to contain, not deliver, but to contain at 20 degrees up to 100 milliliters. This has about one tenth the accuracy of the volumetric – of the 100 milliliter volumetric flask. The same with this pipet which is a graduated pipet – looks something like a buret. It's called a Mohr pipet and it is used to put in about a milliliter, about two milliliters, about three milliliters. Many reagents that are used to set the conditions of the solution during titration are added with such devices where we don't need a high level of accuracy.

Right. Now, back to our titration. We'll start at zero. Now, we can calculate very readily what we ought to need in this case, shouldn't we? We put in 20 milliliters of potassium hydrogen phthalate which is about .05 molar. We know it exactly. And we have prepared a solution of sodium hydroxide which is a tenth molar. What that means because the sodium hydroxide is twice the – almost twice the concentration of the potassium hydrogen phthalate that we should be using about half the volume of potassium hydrogen phthalate that we put in the flask. So, I ought to look for this color change somewhere around 10 milliliters. Now, in many cases we don't know those numbers – we don't know the relative concentrations and in those cases we use a technique that I guess we call the quick and dirty titration – that we just simply deliver into the flask at a fairly rapid rate, get right to the color change, mark where that is, then we go back and do the titration very carefully, splitting drops near the end to be certain that we have measured this volume very accurately. So, let me do this kind of quick and dirty titration and show you how it's done. First we start the buret dripping and we swirl the solution. You'll notice that where the local concentration was in excess that the color change commenced already. Now, that we would call a permanent color change. That's not done very accurately. It's done to tell me about what volume I ought to be expecting and if I put my reader back here, I see that's almost exactly 9.5 milliliters. Well, close to 10. As we said, about 10.

Now, we will do this more slowly and more accurately. In order to do so, we need to have a duplicate sample measured into our 250 milliliter conical flask

and we do that just as before. Now that we have done the rapid titration and discovered that the volume taken by 20 milliliters of the standard solution is about 9.5, we will commence with a more accurate titration beginning at this 9.50 milliliter mark. We'll record this in the book. 9.5 milliliter. 9.50 milliliter. Then, we will record at the end the final volume. Now, recall that this color change is colorless to red or pink, actually. Perhaps a better description. Move the buret tip down into the flask so that the inevitable splashing will not cause us to lose any drops out of the flask. Commence, then, with your titration knowing that right about 9.5 more milliliters we will observe the permanent color change. Let's check where we are now. Good practice. We're obviously fairly close to the end of this titration and the volume is 18 point – about 18.6. We assume that it'll be somewhere around 9.5 times 2 – or 19 milliliters. So, now we want to go very, very slowly in order to get the most accurate volume possible. So, now we literally want to squeeze drops out of this tip. So, open the stopcock or this little valve very slowly and allow a tip to grow – I mean allow a drop to grow at the tip. We're down at about – well, it's about 18.7 or so. Sometimes it's difficult to adjust these exactly.

Now swirl rapidly until it looks like the color is going to be permanent. We're getting there. Perhaps we ought to stop there. See what that brings us. Just goes away. Notice the drop at the buret tip. Let's just knock that off and see. As I suspected, we now have a permanent color change with the addition of less than a drop – a portion of a drop that was hanging on the tip. Now, it's very important because of inevitable splashing of liquid during the process that we rinse down the side of the flask. And we still see that there is a permanent, although somewhat lighter, a permanent pink color. If that lasts for 15 or 20 seconds, one can normally assume that -- because carbon dioxide is being absorbed by the solution making it gradually, slightly acidic and causing the indicator color to fade -- we can assume after 15 or 20 seconds that we have a permanent color change. And I would judge that to be a permanent color change. We'll add any fraction of a drop that's at the tip, rinse down one more time, and we still have a retention of a pink color in the solution.

So, now we will take the final reading using our buret reader and we will see that it is 18.92. Record that in our notebook. And there we have the result of the single analysis – a more careful analysis of the concentration of our sodium hydroxide with the potassium hydrogen phthalate used as a reference. Now, it's important when approaching the endpoint to go very, very carefully. Split drops as I did at the end. Inevitably, especially if the stopcock is not lubricated very, very well, you may find that you'll add, inadvertently, a couple of drops. I was lucky when that happened to me. Sometimes, you'll overstep it and at the end of this exercise we'll talk about the calculation of the exact value of the concentration.

[Text: Summary and Calculation of Results]

Dwight M. Smith

Now that we have completed this analysis, I should point out that we would ordinarily do replicate analyses – that is, we would do at least three titrations using the same procedure in order that we get a very good average value for this solution. There is uncertainty, of course, in every measurement and that uncertainty is something that we can assess by running replicate samples. So, if we were doing this analysis in order to prepare this solution of sodium hydroxide for future use, we should do at least three, perhaps as many as five, replicate analyses in order to get a good average value and therefore have the most probable value of the result, as well as some measure of its uncertainty. We would do that.

Now, having said that, let me point out that we do not store solutions, generally, in volumetric flasks. There is always some possible deterioration of the glass vessel and a slight change in volume – especially the larger vessels – when in contact with very caustic solutions, like for example sodium hydroxide. So, we need a vessel in which to store this solution whose concentration we now know exactly. In order to do that, we usually pick something like a polyethylene bottle because it's more resistant to attack by bases like sodium hydroxide. So we will use – let us say we will use this bottle as the final resting place, if you will, for our newly prepared solution. First, however, to make certain -- even though we may have rigorously cleaned this -- we will use a small

portion again of the solution to rinse the bottle and make certain that there is no impurity or no water that's undried in the vessel that would dilute that sample. Pour that out and then fill the bottle with the base that we have just standardized. Now, you'll notice that this kind of cap is perfectly acceptable to lay this kind of cap on the bench top. There is no way that the closure end can be in contact with the bench top. So, we will transfer this solution into the storage vessel – in this case a one liter polyethylene bottle. We will carefully clean and rinse with distilled water this vessel before returning it -- this volumetric flask, as we will all of our glassware -- before returning it to our desk. In the meantime, we now have a solution of a little less than 500 milliliters of standard base.

Now, it's very important to label this. The labeling of such a bottle can be done very neatly with scotch tape. I do not generally approve of using these wax pencils that seem generally to be available. And labels -- as you can see, this bottle has been used several times -- labels tend to adhere to it. Piece of scotch tape will work very nicely. You can take any pen, a ball point pen, and put on here the concentration of sodium hydroxide. We'll put the concentration in here. We'll not the date on which we did this. Today happens to be November 18th, 1998. And in addition to this, we will put our initials – my initials as the person who prepared this solution. That kind of record is necessary. If you ever come upon an unlabeled bottle in a stock room of chemicals, you should discard those chemicals. Or if it does not have those kinds of data that I have indicated should be on this label, you should discard it. This is the proper way to store for future use a standard solution of sodium hydroxide.

Let us now review our notebook entries from this experiment and perform the calculations that are required to determine the concentration of the sodium hydroxide at the end. In the first step, you recall, we weighed potassium hydrogen phthalate in the amount of 2.3983 gram. Because we diluted that to 250 milliliter and because the formula weight was 204.1, we see that the concentration of the potassium hydrogen phthalate solution -- our primary standard -- was .04700 molar. Now, the second step was the weighing of

sodium hydroxide that's not a primary standard for reasons I have cited -- lack of purity, hygroscopic, not a high formula weight -- and we weighed out 2.0827 gram of that, diluted that to 500 milliliters, thus preparing a solution -- as you can see from our calculation -- of .1014 molar. Now, if we assumed that the sodium hydroxide was a primary standard, as was the potassium hydrogen phthalate, that should be the concentration of the solution that we prepared. This is the solution, then, that we standardized against our primary standard.

You will recall that we diluted a 20 milliliter aliquot to 250 milliliter Erlenmeyer flask for titration -- that is an aliquot of the potassium acid phthalate. We found that the final volume for the preliminary titration was 9.5 milliliters. When we did it more carefully, the value more accurately established was 9.42 milliliters of the sodium hydroxide was required to titrate 20 milliliters of the primary standard, potassium hydrogen phthalate. What I have done here illustrates the point that I wanted to make earlier. Never try to obliterate or obscure a mistaken entry. I had intended originally to use 50 milliliters, changed my mind and used 20, so I have struck through the 50, put the correct value there. That is the proper way to keep a laboratory notebook. The same here. I mistakenly wrote zero for the final volume when I meant to write it in the line for the initial volume, so I struck a line through it, wrote 9.5.

Alright, the calculation of the concentration of sodium hydroxide, then, is the volume of the potassium hydrogen phthalate used times its concentration -- .047 molar -- divided by the volume of the sodium hydroxide required to titrate it. Gave us a value of about .09979 molar. You will recall that if we had treated sodium hydroxide as a primary standard, we would have obtained a value of .101 so that you can see the effect that purity, hygroscopicity, and so forth play in determining a proper reference for primary standard substance.

That brings us to the end of our demonstration. I think that if you follow rigorously these elements of technique that I've tried to demonstrate, your work will be accurate and precise as we intend it to be. This tape will be available for you to review in some form as you encounter each of these techniques as you go through the first course in quantitative chemistry.

[Music]

[End of Recorded Material]