

Multi-Isotope Imaging Mass Spectrometry Workshop
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Note: Transcript has been edited for clarity, but has not yet been reviewed by the author. Accordingly, inaccuracies may be present. The author-edited version of the transcript will be posted at a later date.

George Slodzian: My point starting this workshop is to talk about general philosophy and to focus on some special features that are not often addressed; so I prepared a few slides. This is – we are talking about general philosophy – this is, in general, how the secondary ion unit is defined (Slide #1); of course, as soon as I see this light I imagine that you know where you are; we are in a workshop on NanoSIMS, on imaging. I imagine that you know that the basic phenomenon is to send the primary ion unit, for example, to trigger a collision cascade and to remove atoms from the sample and those atoms in the process – the ejection process – some of them are ionized and they make the part which is called secondary ion. So you send the primary ion beam and you get secondary ions and those ions convey some message about the composition, elemental composition, of the sample and isotopic composition. And in order to make the best use of those ions, to lose less information – because there is in that process, of course, loss of information about the composition – you have to be very careful within the way you collect those ions and you analyze them; so in any instruments you will have – with a magnetic sector – the spectrometer, mass spectrometer, you will have something which is an entrance diaphragm, an aperture stop, and an energy slit. And this, by their definition, just leaning them you know what really what it is – an energy slit – why? An energy slit because the ions emitted by the sample cover a fairly narrow energy bent but along with the mass they may have energies of to, say, 100 eV – the main part of the energy distribution to be between, say, 0 and 20, if we give or take – so putting in an energy slit you limit the energy spread of the ions. And as usual in mass spectrometry, you need an entrance diaphragm, which will limit the beam entering the mass spectrometer and an aperture diaphragm, which will limit the angle. And once the entrance diaphragm, the aperture stopping the energy slit, have been set, then you fix the mass resolving power; that means the ability to distinguish two ions with different mass. This mass spectrometer, it's a mass spectrometer, as any mass spectrometer, may be a little bit special, as you can see in the remaining of the workshop, but this mass spectrometer must be coupled with an optical system which will collect the secondary ions needed from the sample and this collection system is usually made, we are talking about general principle, is usually made by something which is called an immersion lens and a transfer lens. The immersion lens is really the objective lens that will collect secondary particles and the transfer lens is the lens that will match the beam coming out from the immersion lens to those two – if I could have a pointer – so this optical system must make the beam emitted from and collected to leaving the immersion lens fixed those two diaphragms so that you lose not the ions, you make the best transmission for the system (Slide #2). And, of course, not in all instruments, but for general principles, it's good to go in this scheme because it helps understand what are the coordinates, what may be the coordinates. The point is that usually mass spectrometry you do not care, you have just an entrance slit aperture diaphragm and that's all but now we have a special purpose, we want to make an analysis on small localized area so we will have a special beam coming out from the immersion lens and the transfer lens and we wish to control the beam. And controlling the beam means that we wish, for instance, to be sure that we collect always the secondary particles in the same collection angle. I don't know if you are familiar with the solid angle, the collection solid angle, it's a cone into which particles are collected. And so, what we want to do is to make those two diaphragms play an analytical role and the analytical role played by those two diaphragms is the first will be done in the collection angles and the second will be done in the analyzed head; so now you have, and this is a general principle, you have three diaphragm slits within three stops where you continue to do which give you mass resolving power, given mass resolving power, and then you see the functions of those diaphragms of course will limit

the collections of the angle; the second will limit the area over which analysis are perform; and the third here will limit the energy bent.

Unidentified Speaker: Excuse me, this aperture – is it fixed or malleable?

GS: They are, as with any instrument, they are malleable but being material apertures you cannot expect to have the ?? of what you have on ?? apertures – something which is adjustable continuously in size. So here it is you have a set of diaphragms that you put in, you can achieve what you put in an instrument – if you have the specific – . So I will go through rapidly what is an immersion lens and what it is for. An immersion lens is something – it's an optical system, the first part of which is made of a strong electrostatic field. Why do we need the strong electrostatic field? We need a strong electrostatic field because we want to catch the particles as soon as they leave the sample, as soon as they are ejected near the surface. We don't want those particles to move very far and then make a large beam and we cannot have high mass resolution if it be the end of the mass spectrometer with a large beam or if we handle the mass spectrometer with the large beam and we put a small aperture to have high mass resolution we would lose a lot of the ions. So the strong electrostatic field is here really to bend the trajectories and to make them so as you make a narrow beam coming from one point of the sample.

Unidentified Speaker: Question regarding that. Could you prepare the field straits for the NanoSIMS in the immersion lens area versus say the 3F ?? area?

GS: It's about double.

Unidentified Speaker: About double micro – is it meV's? What units would you – order of magnitude – what would you use?

GS: Then you go outside the area of philosophy. I would say it is 1 volt per micron in the 4F and here it will be 2 volts per micron.

Unidentified Speaker: Quite a high field.

GS: Oh, yes. Yes, but it has to be. It has to be. It is the purpose if you wish to collect a lot of ions. I think I am not even sure but I think that in the 4F, the 6F now, they have the ?? field which is twice that one and in the NanoSIMS it's a –

Unidentified Speaker: ??

GS: In three millimeters so it makes it – they are all ??

Unidentified Speaker: According to that study from the electrode sample it's –

GS: So if you compare it to a 6F, it's not so much big.

Unidentified Speaker: It's interesting because for some samples we've noticed you get field de-sorption without ion beam because of the strong field in the NanoSIMS so no primary beam could get signal and its quantitative isotope which is –

Unidentified Speaker: We see that sometimes.

GS: I said that I don't use those – I have no instrument. I told this many times – so you can have much more experience than I have. I point out the general philosophy but if you go into specific things and you tell me – well, I don't understand this funny shape of the beam, that I leave it to Frank, Claude, and all the users of the NanoSIMS. You know a lot more than I. As usual you take the man who knows less and you ask him to speak.

Unidentified Speaker: I don't think so. This is very good because the fundamentals are how you understand the little details.

GS: Yes, I didn't know that the field was strong enough to make this strong. Usually you need the needle to have a very high electrostatic field absorption; so, I'm surprised.

Unidentified Speaker: I was, too.

Unidentified Speaker: Just to explain maybe to Georges – when you express an ion beam, just a sample from some particle there is some –

GS: And you have no electron gun?

Unidentified Speaker: No, no. Nothing is on. I'm not sure that we're able to – there is some remains of secondary ions coming from the sample that show that we can ?? so Bill explained that some coalition of – I'm not sure – the fact that there is some signal somewhere else getting from the sample without –

GS: But if you don't heat your gun – shut it completely –

Unidentified Speaker: We have the valve shut.

Unidentified Speaker: Yes, we have the valve shut.

Unidentified Speaker: That's it. Maybe we have some electrons ??

GS: It's a negative voltage so they miss ions coming from the ion pump ?? and ions they move everywhere and you feel that it is vacuum and you are very concerned with ions everywhere. Because this (absorption) –

Unidentified Speaker: It comes from the sample.

GS: I would make a separate experiment in the vacuum – on the vacuum bench – and put a sample and see if really there is something coming out.

Unidentified Speaker: Actually, I've also started, I'm not an expert, but I started researching the field ion microscopy and they know that –

GS: Yes, that they have had a strong field. This is a weak field, a fairly weak field.

Unidentified Speaker: What kind of material do you experience that – a ?? or a specific material?

Unidentified Speaker: We've only seen it on one sample so far. We've only tried it. It's a very low signal; it's –

Unidentified Speaker: Compare this after you measured; the sample is excited a bit –

Unidentified Speaker: No, no.

Unidentified Speaker: I would make a suggestion – maybe we can move along because if we stop on such details not only you will have me this morning but tomorrow morning and this afternoon, too.

Unidentified Speaker: We have a full afternoon discussion tomorrow.

GS: It's okay, Claude, I don't mind, we can discuss it but if you wish I could go through. So, there is a high extraction voltage. Why? The first reason is to curb ion trajectories and to make a small beam; the second reason is that we use a fairly high-voltage power between 5 and 10 kilovolts because at the same time it has managed to reduce a relative energy dispersion; you have 10 volts over 1000 compared to 10 volts over 10,000. It makes the relative energy smaller and the spectrometer – the mass spectrometer – much better ?? We are also interested not in the NanoSIMS but we talk about general philosophy of those instruments in direct ion images of the sample surface so you will see, since you are asking me questions about the 4F compared to the NanoSIMS, so we can make this comparison more seriously. So the direct imaging means that 2 particles leaving a given point on the surface sample will have trajectories converging to image point and this repeated on many points of the surface gives you an image. So if you have – you can produce an ion image of the sample surface somewhere. Also, it is interesting that the third – so the third feature there is an exit pupil which is called the crossover in charged particle optics and that exit pupil is what is known in optical light – when you have a binocular or when you look in a microscope – if you know that if you put your eye not in the right place you won't see the whole field and you put your eye in the place where the exit pupil of the system fits the pupil which is in your eye. So each system, as always a couple – it's a terrible couple – it is a couple image pupil any optical system is imaging. It starts as the couple that existed everywhere and it exists here and here it has a specific role which is it also a rotation center which means that for all the beams coming out on the sample, and I will show you just an example, it means that if you take the surface points here which is on the axis, of course, the particle will go straight. If you are outside the axis, like this, the particle will be accelerated and then at the exit of the immersion lens it will go through the point which is the crossover because it crosses over the optical axis where is the exit pupil and you will see an application of that property which is very important in (planning) with the collection properties of those systems. Then the other point is that now if you put a diaphragm on the exit pupil of the system or on one of its images, given by the transfer lens also on, you will determine that given collection solid angle, which will be the same for all the points of the surface, which is something we know, and of course when you say that you have image of the surface any image has aberrations and aberrations depend on the angles of the trajectories which are converging at the image point and you control those aberrations by the size of the diaphragm – on the exit pupil of the system so you can improve,

you can reduce the aberration on the image point. If you were interested by images you would like to have a system which you do better images but of course if you put the diaphragm you eliminate opticals and lose (sensitivity). The next point here is a little bit missing but I will tell you. I put a one here because there –

Unidentified Speaker: Excuse me, how did you find the image point? At the footprint of the beam, the primary point?

GS: No, no. It's secondary particles, secondary particles, secondary ions mean the point of the surface, they diverge, they are extracted, collect, they curve, bend, and then they go and converge on another point. All the particles leaving a point converge —

Unidentified Speaker: ?? It's not a footprint of the primary beams?

GS: No, not at all. You can hold out with a probe – you can go a little bit you see – the point here, the point – maybe it's not appropriate my approach – I am sorry but I try to make, I don't want to give you just a design so you know that here it does this and that. I'm talking about general things; once you know those things, you can go to any instrument and understand and ask appropriate questions where – and you will know about what is a collection, what is a transmission. People talk about transmission principle – it's meaning this – when you wish to make a proper analysis. Except if you take the proper definition because you will understand how it works and you will see that the images exist always, even in the NanoSIMS. But it is put aside. My warning was here, I don't know if it's appropriate English for that, but the sample surface is the first electrode of your immersion lens. And you have really to have this in mind – if you change the geometry, if you have not a flat surface, if you have a bump, you will change the optical properties globally in your system. If you put a diaphragm on there because you want to select an area, you glue a diaphragm, you will change your geometry and your properties. Your sample is charging ??, the ?? lines will change and locally you will change optical properties of your sample and so on. And so you have to be aware of this part that sometimes, if you don't mind – and usually people say – oh, I didn't get it (works) – that is a magic word – sometimes it works but just as you – it dissolves – what can you say – it works; so this is an experimental fact you can't go against it. But if you go back to the first principles you know that something happens that change your collection efficiency somehow and the problem is to know to which extent it has changed your collection efficiency. If it is a small extent, you don't mind. It sometimes it's a very strong – if you have a big drain on the surface – it at least changes very drastically the properties and by the way, when I talk about ion images, how can get a contrast on the images? If you have a completely homogeneous sample, you have no contrast, if it is completely flat, you have no contrast, you will see a wide image. If you have a contrast, if you have a small bump, your local properties of optical course, it will be changed and then you will not collect, for instance, ions with ?? start with too big angles and then the diaphragm which limits the solid angle will introduce a contrast and it's why that diaphragm is often called – if you have used this ?? instrument – the contrast diaphragm because it refers to all the times where direct images were very important to people, they are still important, but they were very important and for them what was important, if you wish to adjust something, you need to have a contrast just to see a difference between two ?? . I will come back to that but just to have in mind that your sample is the first electrode. Now I move to the part NanoSIMS ?? – What is a transfer system? A transfer system is something very easy to understand. (Slide #3) Immersion

lens gives you an exit pupil and you will take the lens, you will transport the exit pupil, and the image of the surface somewhere. Where? On the diaphragms we find ET and FA; so that if you have a diaphragm here, the entrance diaphragm will limit your solid angle and the field aperture will limit any given area on your sample. So now let us look – and this is where it becomes interesting – let us look what it does when I refer back to the sample surface. I'm sorry for those who are only being educated in NanoSIMS – let us take a probe – and the probe beam covers all the sample surface and the field aperture will limit this area on your sample. So all the ions leaving this area will go to the mass spectrometer to be analyzed and the entrance diaphragm limits the solid angle like that, in fact it's a little bit more complicated, I made things as simple as possible. Because there is an aperture here, you have aberrations. I figured out aberrations like some blurring of the image – it's just an artist's view. If, for instance, you misalign or intentionally you move aside the entrance diaphragm, instead of collecting this angle, you will collect that one, which is ?? so you see that you play on the collection dynamics – that is an important thing to understand – you play on the collection dynamics. It may do nothing, it may not hurt, but in some occasions, it may be really a lot. Then when you use the transfer lens and you keep the entrance diaphragm in the field aperture fixed so you have a given mass resulting now because you enlarge your image to the field aperture, you reduce, at the same time, your magnification is lower on the exit pupil and then diaphragm, being the same, you collect in a larger solid angle. And this is something absolutely classical in optics – it is called the optical event – when if you take, when you reduce this, you will increase that. And you see now the point is that you will think that you just collect on a smaller area, which after all everyone is trying to do that point, collect on a small area, but you collect it much better, with a much larger angle. So you improve your collection efficiency for one point; your intrinsic collection efficiency. And now let's imagine, for instance, that you talk about transmission; you make the experiment – you go from situation A to situation B and what do you observe – the gun doesn't change. The gun doesn't change because what you collect on the smaller surface but on the larger angle and the gun is constant. So if you do the experiment you don't see any difference and you say it's useless. No, not exactly. You have now the ability to make the measurements on a smaller surface but it is at a price and the price is that you have much higher aberrations. So you reduce your field, you improve your collection efficiency and you increase aberrations. And let us push a little further. You reduce; you go to the situation now where you reduce the field being analyzed to something very small. You have a large collection solid angle and absolutely gigantic aberrations. You can't do imaging with that but you have very good collection at the foot. And this extreme case here is specifically the case of the NanoSIMS. In the NanoSIMS, even though the fields are not so different and things like that, the NanoSIMS pushed the principle of the transfer optics to its extreme limits where the aberrations are so big and you have the man who, the designer, must think the optics of the instrument no more in Gaussian optics but calculated trajectories because the Gaussian optics is no more appropriate for that situation. Nonetheless the crossover stayed – so I tried to summarize what I call intrinsic collection efficiency for a joke, in fact, because there was heat wave in France when I was preparing and I suddenly realized that intrinsic collection efficiency meant ICE and it was refreshing to prepare something on ICE. (Slide #4) This is a collection efficiency referred to a point and in summary when ICE increases, blurring increases, and field size reduces and you lose the ability to have direct imaging and now you have to go to ion probe; use an ion probe to regain the localization of the emission of the ion. So you see the first time it was the ions leaving the point to converge on the point image, now they converge to a point image but then they miss it so it's too big and if

you wish to be able to make an image, you must focus a fine beam; in the first case you could focus a large beam, and now you produce a fine beam.

Unidentified Speaker: A question – by analogy again so if somebody's used a 3F or a 6F I like what you just said about pushing essentially the transfer lens site is different for the NanoSIMS you now have –

GS: I oversimplified the point because if you can say essential – the story is a little bit more complicated but essentially I agree.

Unidentified Speaker: So the collection efficiency is better because we essentially have a very small image field.

GS: The ICE is better. The intrinsic collection efficiency is better.

Unidentified Speaker: So in practice for people who might have used the 3F or 6F you go from, say, 400 micron or 250 micron transfer lens to 25 or whatever.

GS: If you wish but I don't like those numbers because it is just for the users. But I am not a user.

Unidentified Speaker: Let me ask you this way – in terms of transfer lens field strength or focal length, then, what would be the order of magnitude difference between the smallest field –

GS: I cannot answer – I said it's roughly like that. I cannot answer your question because on the NanoSIMS all the optics have been recalculated in the non-Gaussian world. So you can talk about focal length but it depends how far the particles go in the lens and which aberrations they suffer. In principle, it is like I told you. But now the general philosophy, then invent the stuff, and once you have the general philosophy then you have to go to work. And to design the system, to make it work, you call on those general principles. So in the details may be – it's why Claude asked me to be the first speaker so that I can give the general framework and then you will have François and Frank to show you the detail around really how it works because all of what I say, it's good to have it behind you, but if you don't use – but if you know it, it helps.

Unidentified Speaker: If I could just add something. If we don't have, as you said before what you call the crossover and what you call –

GS: I said we would come back to this point.

Unidentified Speaker: ??

GS: But maybe it's not the best thing to do. I don't know.

Unidentified Speaker: I like the approach, though, because it gives somebody who is a user of an older instrument, like you say, a framework to understand.

GS: So the point now is that because of this optical invariant, you see that if you put your probe here on the point of axis, the image, the main beam will be somewhere here, and if this, this image plane – you put the field aperture, you cannot (cheat) the mass spectrometer (the mass spectrometer won't see) but what we know is that we have a rotation point here and if we use plates we could take a fixed probe here, it could have this trajectory then I can bend this trajectory once, twice, and make it go along the optical axis (Slide #4). And now with a little bit of ?? it's not so difficult to do it, each time you change the position of the probe you will put the right voltages on those plates and the beam will appear to be fixed. That's why we call it the dynamic transfer. It means that now I can move my beam over large areas and get the best intrinsic collection efficiency. This is also made on the 3F or 6F instrument. It is made and sometimes used or not. But a person can use this very often but it is not absolutely necessary. With the NanoSIMS it's absolutely necessary because the aberration here filled completely the apertures; so here you want to have a piece of field of view free of those aberrations. Now what ?? mentioned, we'll talk about that now, is that the scheme of entrance diaphragm coincident with the exit pupil and field aperture creates an image is not the scheme which is usually taken with the NanoSIMS and the reason is the following. Many users, what they want to do, is to have the intrinsic collection the highest possible because the things are small, the objects to analyze are small, the densities are low and they want to have to high intensities and sometimes, very often, I should say, in imaging it's absolutely essential. To have a few counts per pixel you must have the highest possible collection efficiency. And in order to get that if you look at the structure of the beam you see that the analysis I have made exit pupil surface ?? that image of course you cannot recognize it very much because it has so many aberrations on it but what you have to think is to see where is the smallest stretch you wanted to waist – where is the waist of the beam. And it turns out that the waist of the beam it is the smallest stretch of the beam is not at the crossover, it's somewhere in between the crossover and the surface image so that very often the instrument is adjusted to get the highest current possible so it is adjusted on the waste of the beam. And the problem is that for most of the work – because you don't mind about that – but maybe in some conditions – for instance, if you wish to move to very precise as a topic measurements and things like that – it might have an influence. If, for instance, the isotopes are not emitted exactly with the same angular distribution, you don't know where you cut your beam. When you cut the waist you cut the ions emitted in one direction, maybe, and you leave all the ions emitted in the other direction, because just they go through the diaphragm entrance images on the waist. That is a matter of experience – maybe someday I will come back to the NanoSIMS and look at problems of that kind but generally nobody knows better than I do what is done by people but usually you are on the waist of the beam because you need to have a high intensities between neutrons. If you wish to make high precision measurements – maybe – I'm not sure – maybe there is a possibility that this might introduce artifacts in your emissions; that is the problem. I felt obliged to make a drawing. So, yes, there is something that I missed to say here. You see this a structure of 4F essentially – 4F, 6F, 3F. The ion probe, if you shoot with the ion probe like this you enter ?? and the point here is if you wish to make ion probe you must have somewhere the condenser, you put your condenser here which will focus a probe, but you see that the distance between the center and the condenser will be large. And so with ordinary sources, when you wish to make a small probe, you will have to have small apertures to reduce the aberrations here and you will have high aberration coefficients ?? chromatic aberration and so on and finally the gain that you will be able to put in your probe will be very low; so this is not good for making probe analysis so we will like to switch to another scheme so this is what

beam shaping optics is transfer lens and so on for me it's a box – this is the entrance slit and over there, there is the aperture stop. It is on the ???. We have an objective lens which can focus the primary beam on the sample with the shortest possible front distance between lens and sample and this objective lens will at the same time be used to collect secondary particles so the ??? is forming; (Slide #5) you send the beam like this – I tried to decompose the things – secondary particles go that way – this is ??? that make the beam go like that so you have the primary beam, secondary ions, and the last shows you the very new – François will probably say much more about that – this is the point of axis and we go through the crossover here and it will be deflected again and so you have the dynamic transfer which is made with those. So you see the features I have described. They look different because we are on the NanoSIMS and we wish to have a normal incident show the distance here and so on but in principle you have the crossover is featured with this deep valley NanoSIMS and so we can do exactly what I have described in different circumstances and so we can look now at fields.

Unidentified Speaker: Well, this is a general statement which is each time the diaphragm cuts a second beam there is a risk for ???

GS: All of this maybe it is based in factor of 5×10^{-4} or more, I don't know, because you change collection diameters and this is true for the 4F, the 3F. The other point is that if I focus on the isotopic problem, Claude is less sensitive to that because he is working with not so high precision, he doesn't need high precision on the isotopes, but for people who think that in the future they will need high precision of isotopes what exists always on instruments is there are ??? in the weak and wanted magnetic fields coming from, I don't know, from many places in the instrument. I think that originally at the beginning people thought that, and I was probably one of them, that weak magnetic fields doesn't hurt very much ion beams, it hurts electron beams, but ion beams they are less sensitive. In fact they are sensitive enough when you make isotopic ??? to make ???. (Slide #6) Those ways have to be found not canceling would be I guess probably difficult to put points around the sample. But at least to suppress the effect on the secondary beam at given points and to have the beam being the same suppressed – oh, yes, maybe I'm going too fast here. You have a beam and there is a weak magnetic field, the beam will move slightly. Well it's not important you have so many plates that you readjust your beam. But because it is a magnetic field, all the elements, and in the NanoSIMS it's important for elements, but for people working with isotopes, all the isotopes are going to deflect exactly the same way. So the beam does not select exactly the same beam and this makes fractionation, it is this fractionation that is needed to be suppressed, that you need to suppress, if you wish to make or if you're on the NanoSIMS, if you do at the same time carbon 12 and silicon 28, the collection efficiency will be different for those two ions so you also have to care for this type. And I want to introduce you to another effect which is I think is a little bit funny. So we have seen that an increase of ICE will be useful for local analysis, so obviously it's not necessary to make a long speech to accept such an idea. You need to have high collection efficiency. But there is at the same time, the effect always existed but now it becomes strong enough to be not a (symbol,) it's what I call QSE – quasi simultaneous emission and I will comment a little bit on that (Slide #7). If I define first the direct ion beam, which is the number of collected ions per primary ion effect, and let us take $K = 1$ and let us say that I imagine that Poisson statistics so you see that ??? Poisson statistics is that one impact on average gives you 1 ion but some impacts will give you 0 ions, others 1, others 2, 3, and you see that in proportion you have as many particles giving 0 as many primary ions giving 0 than primary ions giving 1 and you have nearly 20% of those

particles will give 2. (Slide #7). So you will see later on what it does on the detection side if you use an electron multiplier. So then of course you can play and why I talk about simultaneous is because those ions are emitted from the same primary impact. One primary ion can give 2 ions and the distance between the ejection time is within picoseconds.

Unidentified Speaker: That's only a problem if they make it to the detector at the same time.

GS: Pardon me?

Unidentified Speaker: If they make it to the detector at the same time you have a problem but they don't necessarily do that –

GS: Oh, yes they do, unfortunately, because their energy is very – the difference in energy is very low, is low enough for the path beam to arrive within the width of the pulse.

Unidentified Speaker: That's a general problem.

GS: Pardon me?

Unidentified Speaker: That would be a problem for any ion probe.

GS: Oh, yes. I just said that it may be a problem here if you have a very good collection efficiency and you look at one of the major elements you will be in trouble if you make measurements. It depends – if you want to make measurements in 1, 2, 3, 10% – okay, no problem; but the valid point is that you will prove the collection efficiency and then one event, which is made either the 1, 2, 3 event, something happens when the primary beam arrives, then you have a probability that the event to be produced by two ions is 29% – it is a high probability so if you wish to make measurements you better take care of that. And when we go back – and I think that normally people show you results where the effect is there; it's not just in the imagination, it is real. Maybe it doesn't follow Poisson statistics, that I don't know exactly, but it exists and since we've talked about that we forget about NanoSIMS in general and we turn to detection; detection is a problem. I don't know how many Nobel prizes will be given, on how many people will be given a Nobel prize because they intend to (make a new) detector – it's not the case here; we use very old detectors, we use electron multipliers. I suppose that no one really knows what is a electron multiplier. I just made a schematic diagram. You have one ion arriving on the metal surface which is made of ?? oxidizing ?? . This ion produces secondary electrons and ?? which is ?? average number of ?? is NP and then those electrons, secondary electrons, are cut by a second dynode where they produce more electrons with a yield which is higher than one and the third dynode does the same and so there is an amplification cascade and finally we end up with 1 pulse which is somewhere here and the pulse is a charged pulse which is, the time is depending on the multiplier, we say it's between 5 and 10 nanoseconds. It's nanoseconds and it's ?? to the flight path and the difference in initial energy. The ions may look like that. Well because it is a random process the emission of the first conversion of ions we collect is random, the electron emission is a random process also, all the pulses have not the same kind and what I have forgot to say, of course, is that those charged pulses are converted by appropriate electronics include voltage pulses and voltage pulses are detected ?? and you can also measure their height. So because we deal with random processes all the pulses have not the same height

and there is a pulse height distribution which means a PHD. We have got PHD here on this point (Slide #8), though the round open circles represent experimental points, I would say a word about some kind of modeling of those pulse ?? what is important maybe to notice is that well if you wish to see the shape here, you notice that here you have on the low pulse ??.

(Inaudible group discussion.)

GS: The point I want to make is that you have to put the thresholds, that means to count which is above, you have to get rid of all the low counts because they are counts and you don't want to count counts. It might not be the damage – I don't know – but it's better to remove these counts. So you have to put the threshold and you have just to say a few words on noise – I don't if it's absolutely interesting but you have two types of noise (Slide #9). You have this noise they call it without any signal, just like in your experiment, you have no signal at all and it is what we call a static noise; and then this is the simulation, the pulse side distribution should go up to here with some contribution of zero concludes that you have a chance – when you (shoot) the ion drives give no signal at all. And here – this is another (recording), which was made by removing the static noise; and you see that there is another kind of noise, which is directly linked to the fact that we are counting. There are many origins, incidentally, ?? or so secondary emissions of the sputtering of the ?? conversion time, I don't know. So you have this type of noise which also exists so that is a very annoying problem but you put a threshold here and you get ?? . And so it brings us to the fine detection quantum efficiency which is the number of pulses above the threshold in ratio to the number of incoming ions and so that the detection quantum efficiency depends of course on a given threshold, depends on the threshold, but it depends also on the yield on the first ion and the yield depends on the isotopic mass; when mass rises or changes, there is a small change in the yield (Slide #10). It depends on the impact position conversion factor because changing, you have two effects – you change the collection efficiency by the second dynode and you change also because the first dynode is not necessarily made on a homogeneous material and it may change from one place to another and I will show you an example. And also it depends on how old is your multiplier because there is a slow wearing out– with the first dynode it receives ions, it bombards sample surface changes, and so it changes, and also, of course, there is a global gain which means all the other – you may think that electrons don't hurt the other dynodes in the multiplier but there is contamination by ion carbons, there is desorption, electron desorption surface state continuously changing and electrons – and there are many dynodes, there are 16, 15, you remove the first dynode and must make a lot of surfaces and it's difficult to control what at least the manufacturers don't control all those surfaces ?? so the gain is changing. And when the gain is changing the old PHD pulse and distribution shrinks and so the position of the pressure in the distribution changes and so the detection quantum efficiency also changes and this is annoying when you use the single detector; but when you have not only detection, you have to control all your detectors, and that is one of the problems which is possible. If you are not too tired I may say a few words on modeling those things (Slide #11). It's not tremendous theory; it's just taking Poisson statistics for the first, the second, and so on for all the following dynodes and to see what is the distribution of the number of electrons coming out and it could be too difficult involving the ?? all the dynodes ?? when after a given (prank) the shape of the distribution is set and it doesn't change and then using empirical algorithm we can make a comparison between experimental and calculate the PHD. And I wanted to show you just something because it might be interesting to know it even if you won't use your instrument in this mode. It is isotopic fractionation produced by the model. The

isotopic fractionation on the multiplier because on the same multiplier receiving three different types of ions occurs because there is the same gain, everything is the same but conversion yield is not the same. If we take increasing masses, for instance, it's higher for light isotopes than for heavy isotopes. So because isotopes are close the yield variation is small. We can approximate this by a relative variation, which is proportional to the relative mass variation. If we put efficient here which is around .5 and you can define here a kind of relative change of the detection quantum efficiency. You see this is a detection quantum efficiency for isotope 2 divided by detection quantum efficiency for isotope 1, - 1 and multiplied by 1000 because the numbers are small and the ratio count is traditionally is to make those measurements per mille. Because there is a simulation it is possible to have magnitudes of the numbers, it's not immediately the exact number because it's model dependent slightly, and it gives you, for instance – I like to put this here because usually people are very much afraid, they say it's terrible we are losing a lot of ions – this is a realistic case, and sometimes multipliers work better than that, but it's not an exceptionally good multiplier, but look if I put a (full page) threshold here 60 volt, I have only 2% loss, so it means that I am able to count 80, 98% of the ions. And you see that when it shrinks you go from 2%, if it shrinks so that apparently it makes the threshold move by 10 mV, you will go from 2 to 3. So it has an effect but if you are not looking to high precision, maybe you can live with this for one day; for instance, it will not age too rapidly. So it's good to have this in mind, not to be afraid of something that is not so terrible after all except when you wish to make precise measurements. And now if I compare, for instance, for Si 30 and 29, it is the dream line which is here and now you see at 60 mV, you have 2 per ml so at 60 mV you have a loss of 2% but the difference between, because it's differential effect, the difference is 2 per ml if you don't make measurements at 2 per ml, well you can very well live with that and it is good to have for high precision needs, absolutely important, and it is the kind of linear fractionation because you see if you look at numbers you see that here it will be about, it's a little less than 2 per mV, and here it's a little less than 4 per mV and this is 30 over 28, so there is 2 mass differences and the effect is 2 masses higher and remember we had delta which was roughly speaking first approximation because there's M over M and here the M is twice for difference between 30 and 28, is twice difference between, of course, 29 and 30 (Slide #12). So this modeling gives an idea of what you may expect, a fact due to the limited quantum efficiency and I'm sure that François will tell you a lot more. Just this is to point out one aspect that may interest people who wish to get rid of this, this is a diagram where the measurements were put on a scale where 30 over 28 difference was – relative difference between the isotopic ratios were measured – here 29, 28 – and what you see is measurements made at different thresholds; you have seen that there is a fractionation and you can see the fractionations, the first threshold, which was 44 mV, second 68 mV, the third, 94 and you see that if you make a precise measurement, according to the place where you are, you set your threshold, you get the different isotopic measurement (Slide #13). But, and I did not stress this point which was obvious from the previous slide, but just to say that if you are a little bit confident in your algorithm when you have an algorithm what you can always do if you make a given number of measurements you can use the algorithm to know from where you are coming, to reconstruct the information, it's just like you have a bad image and you use an algorithm to improve your image – it may be realistic or not, it depends on the quality of your image and the quality of the algorithm – but if it is consistent with your calculations and the instrument making the image and the object itself. And this is what I have reconstructed here. This is reconstructed information. And so, in this information the strange thing is that is included those ions that have

not given any pulse accounts so this would be true of course if you do it with a given certainty because of the algorithm in itself and the measurements and so on. But it's funny to see that you can reconstruct the information and get rid of the aging multiplier, I don't know if can be useful but it's a kind of thing that if you know it exists you will find a way to ?? . Well there are sources of known, what I call the other one because they are with bigger mass difference, the other sources of discrimination I call them nonlinear (Slide #14). There is the problem with the (dead) time that commence with the quasi simultaneous arrivals, we have already a little bit discussed with the fact that different impact areas will be different for different isotopes but you have not that problem in the NanoSIMS because you use different multipliers. There is a problem you should be concerned about the conversion dynode agility and we give an example and there are many others that are not listed because some of them I have not identified. Multiplier is really an unpleasant problem because it is not easy to find a good solution. So I come back to the point rapidly that if ions are created within a second set in an energy band ?? pulse width and they will be recorded as a single (ion) so this is if you take again the Poisson equation to have the statistics to have an idea of what is going on and as we present the true number of ions by ?? and we remember the number of counted events 1, 2, 3, 4, 5 times then you have this relationship between an S and P and you can the ?? difference the use of K and find already showed you $K1$ which is exceptional of course, maybe someday ?? something else than the ?? . If it's not useful ?? it's a heat per primary ion, it is completely independent on the counting, even if you count 1 ion an hour you have the same thing as if you count 10,000 ions ?? so you see that the correction would be – or if you start something (that has) 1% of NanoSIMS is ?? perfect. So you have a collection of 5 per ml. You can forget about it, usually. If you have 10% you have a collection of 5% – how?

(Inaudible discussion.)

GS: And roughly speaking if you make a limited extension of this expression here you get something first images $1 + K$ over 2 and you see it's not exactly that but it's close enough. So it gives you a rough number of what the collection should be. You can do what you want with an image, you can contrast what you want, it's not that which is really important. The point is that how has this image been made. It has been made the following way. We in the instrument use ?? I made with Si 28. I made a small beam 30 (dynodes) ?? and I just scan the beam and recorded the number of pulses, it's not the number of electrons, it's the number of pulses and the unit threshold and I scanned and when you scan you have a table of (numbers) you can put the table in the form of an image this is easy to do and you see that this is 1 ml, 1 ml, roughly speaking, maybe it's 1 and 900 microns ?? but the point is that you see that you haven't really you may have for some multipliers some images really homogeneous and it means that if your beam is on this or on this side you won't get the same number of counts and this if you are in the NanoSIMS you are very sensitive to this because my point is not to criticize the NanoSIMS of course but it is just to make you more aware of the problems so now that you are aware and François will give you how he works to avoid those things but you will understand why he works that way. They exist and you have to take care, that is my general philosophy. And you see that it is not small. If for instance the mean value here is 460, 000 counts the beam here is 436 there is a big difference between the mean value and if you are under unlucky to put your beam which of course much older than that yes –

Unidentified Speaker: (inaudible)

GS: Yes, but when you take the mean here the mean will be different than the mean here and it will be different by several percent in the counting model. That is if you wish to make good measurements. So here for isotopes it is terrible for precise measurements for isotopes. Even if you use the same multiplier you have to take great care to address all your isotopes in the same place on your dynode which is very important if you move to another place you get (anomaly) counts and so on. On the NanoSIMS the problem is slightly different but it exists nonetheless. Now is another limitation on multipliers and the other limitations are the counting rates so this is a dispute about I say maximum counting rate $10^6 = ??$ but roughly speaking if you remember none of it, it is about ten 1 million counts (Slide #16). So if you look, for instance, on isotopes – I am focused, my mind is fixed on isotopes, I'm sorry – so here if you take O 16 and ?? 18, one million here will make roughly speaking 402 thousand here. If you wish to make precise measurements with 2000 (pixel), it could take you 500 seconds to reach 1 per ml statistics, statistical fluctuations on the O 18, so if you wish to go to better precision the point is that it is possible to have higher counts increase the ion (peak) for instance if you have ion counts. So if you go to such counts you get, you won't be able to use the electron multiplier but you will be able to use the electron multiplier on 17 and 18, so it makes part of the detection as it exists in EMS 70 and also on the NanoSIMS here you could make very rapidly excellent measurements ?? on Oxygen. So this is something that can be made with the instrument but then you must use (diaphragms) and this I could say nothing about that because I don't know much but for people who would like to use the NanoSIMS for precise isotopic measurements there's nothing wrong but it's a question of you see I put two question marks. When you use high counts in probe (it is not a problem with the primary beam) you take a risk of charged spaces and those charge space effect may affect the trajectories of ions differently for one isotope and another isotope, maybe from one end of the beam to another, I don't know. And this may induce some fractionation; the point, again, we don't know what will be the effect, what is the ?? to the effect. Is it in the percent ‰ or 1 ‰ change, I don't know. This brings me also to another point is that when you put a lot of primary points, a lot of ions on the surface on an insulator, you have to cancel that charge, why? Because if you have (gotten) positive ions and you collect negative ions you bring on the sample surface positive ions, positive charge you remove electrons so you leave a positive charge, so you have a positive charge which is going up on your sample and if you don't do something then you'll have a ?? unfortunately in this case we can do something and I'm talking about that. But it is not because you have no electron probe breakdown that you have no charge in your sample. And I will show you that the sequencing charging may change the collection efficiency of the particles so the problem is to know again if it changes the collection efficiency what is the effect on the measurement of ?? isotopes of ???. Here I just want to compare the Faraday cup and the EM (Slide #17). This is – here I put the number of ions per second even if they are measured for other peak emission times and here I put the relative error and those measurements were supposed – it is 4 s integration time, so the signals are given in counts per second because it's a lots easier for comparison purposes and I have take into account the electronic noise that was given to me as being 2250 c/s missing her for an integration time of 4 s, again, because with the inflation time. So I put these equations, they are very simple and this is only for measurements of 4 s it gives you the statistical, the relative yield of statistic fluctuations, which is typically ?? of time. Of course, if I use an ?? of time I won't get up to this point nor that point, so this is just multiplier would start from here. If you use a Faraday cup with this type of noise, the ability of error you make is higher than with the, for instance, the multiplier – it's higher but it's not that much higher. So you are in a kind of overlap where you

can make measurements if you take time, of course, if you take time to measure with the Faraday cup, you don't want it in counts per second, and with the multiplier, and once this is set you can't do anything about that. You can just reduce in general the magnitude of the error by going over and over again the measurements but the Faraday cup will always be worse than the multiplier and of course when you go to higher – and this is because mainly the noise – when you go to 10^7 , 10^8 , then the difference is greatly reduced. You see where it gives you an idea what should I use here, here it's much better to use a multiplier, of course. Here you have a kind of overlap, you won't be able to make ?? you can use overlap. It is useful if you make a decision and to know what error.

(Session break)

GS: (Slide #18) Well now I will talk about the subject that is not very frequently addressed in the presentation on general (SIMS) instruments and there is a good reason for that. It is because you are not very often aware that the sample is charging; only in exceptional cases there is electrical breakdown of – really all the signal is away and you start and something happens at the level of the sample. So I will make a general presentation and then switch to the specific case; I won't say even the NanoSIMS because on that part I am not very experienced to look at charging effects with the NanoSIMS. I made a few experiments with François but not very much. But my experience, if you are afraid that a non-experienced man is speaking, my experience comes from the 4F where the design is very close to what you use on the NanoSIMS usually. But I will again talk about general principles and not so much about the specific instrument. So the problem, as I mentioned, is that you send the positive primary beam, you bring in positive charges, you remove negative charges so there are positive charges left and you have an increase of the positive charge on your sample surface and of course the easiest thing to do is to cancel this positive charge with negative charges and what is easy to do is to use an electron beam because it's easy to produce electron beams and to send electron beams on the sample. But now what we want really to do is two things. We don't want this electron beam to arrive with high energies on the surface because there are two reasons. The first reason is that if you bombard with high-energy electron beam sample, the sample may emit secondary electrons and according to the energy you may emit more secondary electrons than what you bring if the yield is higher than one. So it won't cure the problem, it will aggravate it. The second reason is that it is better to work with – not when you work with (SIMS) you mentioned spontaneous emission but there is also when you charge a sample some elements, some ions, may be driven inside the sample or bring outside and you may change the composition of your sample. I don't know if you change it slightly or heavily, that is a matter of sample beam and so on, so it's better not to put too much energy in the sample with the high energy electron beam. For those reasons it seems that at least when you deal with negative secondary ions the best way to do it is to have an electron mirror configuration. An electron mirror configuration is simple to understand. You will make an electron beam arrive on your sample with the same energy initially from the filament. As the voltage of the sample it will arrive in decelerating field, touch the sample, and go back, so it will arrive with no energy and you will see a few other interesting features that I will describe. And this is what here is represented. Maybe it is about the same as what you have on the NanoSIMS. But you see those things are very general principle. You have the filament, the

filament is an electron emitter, it's heated, it has a potential $-V_F$ and electrons are accelerated to that voltage, they are deflected by some kind of magnetic field, and then they arrive here – let us just imagine that you have a diaphragm just to make the things more visual – and the electron beam. If they arrive of course they are open in direct with a given angle, they go like this, and arrive. The sample is at potential $-V_0$, we will in another view, we will see it, and they are reflected. The potential is the same as this one – they are reflected and they go back and then at the same time, of course, you have sent an ion beam somewhere, ions are produced on the surface. They move that way they are less sensitive to the magnetic field than electrons, reflected electrons, or electrons re-emitted, diffused, scattered, and so on – they got that way; they may be used to learn something about the sample eventually or in other circumstances what can be made is you bombard with a finely focused – when the sample is not charging up – finely focused ion beam and you take those electrons to make an image of the scanning ion electron image of the surface. So you can make use of those deflected electrons. I didn't want to complicate the set-up. Here there are other magnetic fields to cancel the effect of this magnetic field on the secondary ions. I have not represented that. Probably François will talk about that, though. Because I wanted, if you put too many things, you get distracted. And my main point I wanted to make was concerned with what happens here; how is the discharge working. It's not really discharging; it's a stabilization of the surface, the voltage surface of the sample, of the insulator. So usually how does it work? You take an insulator, you evaporate a thin conducting film – gold, carbon, whatever you want – you use the primary beam to open a window. In that conductor it is very thin, it doesn't last very long, and you have a conducting film and an open window open on what – on the insulator which is (the I) and you want to understand what happens there. Let me see if I can explain it. This here, if you forget all those things here, you have the conductor, the thin film, here you have the voltage $-V_0$ of the surface, this is the insulating sample, and here I have figured out, represented the incoming electron energy distribution (Slide #19). You cannot expect the electron leaving the filament will have only one energy. Probably in the instrument I have used we didn't make a good electron gun – this, just to give you a figure, this is about 3 to 4 electron volts; so it's not – we could probably make it a little bit shorter. But you will have an energy distribution. So you have zero, the lowest energy, at potential $-V_F$ and here you have higher energy so that the higher energy will arrive and touch the sample before. How many electrons will you use? You will use this integrated number of electrons. And those will be what will compensate Cs^+ if you use Cs^+ plus negative emission. And the electrons which are not used they will be reflected, so the part that will remain is here. So you see that you will use electrons between b and a, this distance here is a and b, you will lose on this bend, this energy bend with your ??, and the potential that will reach the surface will be the filament potential ($-a$), so $-(V_F + a)$. That will be the potential of the ?? surface if I imagine as I did here that I have wide ion beam covering all the insulator surface. And this is something that – well what about that voltage? – that voltage you can change it. Here this is fixed but it depends on the primary beam current, it depends on the selection of negative electrons, ions, and so on. Once you send, and it depends also on the intensity of your electron beam, so this is fixed, you can put this voltage and move it, of course – you shouldn't move it too, too differently because it may have other effects – but in principle it has no effect on this voltage. This voltage is fixed as long as the currents, the ion current, the electron current, and the secondary emissions are fixed. And then here I have just figured the situation where by adjusting where the $-V_0 = -(V_F + a)$ here and again here there is a conductor, the

electron beam arriving here because you cannot make now an electron beam could be broken, it's a conductor, but it will (attack low) energy first and then all those electrons here will be evacuated by conduction in the film. So this potential is stabilized because there is a power supply to accept the voltage at $-V_0$ and this voltage is stabilized because you have, of course, a power supply which sets the voltage at $-V_F$ at the very beginning and you have used a given amount of electrons here. And of course the electrons not used are reflected and they have (an effect). This is if you adjust, the easiest is usually to adjust this potential, if you adjust this potential carefully then you have the same potential on the conductor on the insulator and that is exactly what you would have done if you could put a conductor, a real conductor, on your sample surface. It's just like bringing the (Fermi) level; it's an image of the filament on the surface of the insulator. It makes the insulator, although it doesn't conduct charges, it makes the insulator like a perfect conductor as far as the surface potential is concerned. So I like very much this thing just for the pleasure to play with beams. Yes?

Unidentified Speaker: (Inaudible.)

GS: The are also emitted because the primary ion beam produces all sorts – it produces negative ions but of course produces a lot of secondary electrons and the main effect – in fact there are much more secondary electron produced by the ion beam. Then they are negative ions so that the main effect is the emission of the – you have to feed back all – remove the electrons by the primary beam.

Unidentified Speaker: (Inaudible.)

GS: Oh, yes. Doing electron imaging with that, with the electron beam in place, would be difficult because it would require, if you remember the magnets, it will require here to make a special treatment on this beam; to make energy selection and that is a little bit involved. I don't think that right now or in all the days I planned to use that but I never – nobody was interested so I couldn't get the money for that. So there are questions about that? So I move to the next one. And just – this is to show you something curious also. The situation one is with a given electron intensity; situation two is the electron current has been multiplied by two but the primary beam stays the same. So what does it do? We need a given amount of electrons. Now the distribution is the same but there are just more intensity. So you move from a here to a' and this area should be equal to that area. And you see if originally you had, for instance you were in this part here, you are here, but this is just to show that even if you change the electron current you will get stabilization with a small change only on the surface voltage because (a one) won't change. Of course, it depends where it is the first. If the first if you reflect you were here if a was here, it would change much more than if it is in a position where a small change in the position of a allows to compensate more charges rapidly. Here the number of electrons – a small change in a will give you the extra electrons you need. Here I made a dramatic change just to say that if you have your electron beam you shouldn't be anxious about it must have exactly given intensity in order to get the stabilization of the surface – you don't need exactly an intensity; it's your choice. For instance, my choice would be to be here because here I put too much, too many electrons. I put charge space – useless – it may also create other effects – ionize the residue vacuum and make positive ions to bombard the sample and all sorts of things. So I would rather work with the lowest possible electron current in here (Slide #20). So that is one

important point to understand. Then I made a sketch of what happens – this is an artist's view – always remember it is a broad beam, so the broad beam, this is the analyzed field – we are more in a 4F structure but we will possibly to the a NanoSIMS situation – so this is the situation I have described (Slide #21). You have the voltage here, the same voltage on the insulator as on the – here a situation where ($V_F + a$) is smaller than – so the potential will start here; this potential here is always the same, and that. So I have drawn only one negative potential yet you can imagine the effect on other negative potentials so you have to pay very much attention to the place of the analyzed field. If it is too near here you will have effects on the collection efficiency. As I have said the sample is part of the immersion lens. You modify the potential at the surface, this is a good situation; that situation is less good, it's not horrible. And in the reverse here the visual would be like that and you will have distortion of the potentials, potential here and changes in collection efficiency. Yes, the question that often occurs is how can you be sure that you are in one situation or in another one. So there is a thing that can be done is to record the energy distribution of a given ion. For instance, oxygen; if this is quartz sample you have plenty of oxygen, if it is a gold layer, you have also oxygen on gold, that is wonderful – it comes from contamination and so on. So you make a record on here and here and you may decide how it should be made and then you this normalized to show the difference. And then you see that on quartz and on gold the energy distribution of negative ions are different and you have here how much different that are. So in this case we were $V_F + a$ greater than 0. If we go back we have to change the potential V_F and switch from this situation to that situation where it is (flat) and then you will have the two energy distribution exactly one over – and that I make many times and you can say within a little bit added between .1, .2 electron volts you can have exactly the same superimposed, the exact to energy distributions. So we can reach this state, it is possible. This I will skip (Slide #22-23) because maybe I can go back later, and I will switch to a situation where – I don't say it is a situation with the NanoSIMS but it is close to. Now imagine that instead of that you open your window and then you reduce – you have a probe, a new probe – you make an ion beam with a small diameter. The ion beam arriving with a small diameter – you see that here the ion density will be so high that what I have shown cannot work because there are not enough electrons because the sample will start charging up a little bit; charging up a little bit, it will become more positive, it will distort the potential lines. We have here an electron beam arriving with very low energy, it is very sensitive to the shape of the potential surfaces, so it will be attracted to (well) there so what happens is that you will attract electrons and since the probe is small but the surrounding is broad so you will bring electrons from the surrounding (Slide #24). You will gather them right at the place where you need them and then you can have charge compensation even with a probe. And even in a situation where it is a high ion density current and weak electron current density on the surface because of that defect and this, of course, the voltage here, when the probe is here, the voltage on the surrounding here will be $-b$ because electrons are high in here they will charge a little bit the surface and reflect so that the high energy electron will be reflected here so you can – just this is an artist view, didn't make any calculation on that – but what I know is that I will have something like that as a shape of this type of potential here. And this is interesting because you get to discharge your sample but at the same time secondary ions leaving they are focused by this film and so it is a case where you have a kind of – I don't know if you are familiar in American – you have a filament, you have what is called (venal) electrode which is an electrode which controls the intensity of the electron beam. And here you have a kind of (venal)

configuration. It means electrostatic fields focusing ions just as they leave, in a situation where they are very sensitive to fields of that type because they are slow, there are only a few electron volts imaging. And this gives a special, it changes the optics so you have to readjust, in fact, all the immersion lens, the other lens in principle at least on the instrument they have used, it had to be done. You have to readjust this and the strange point is that when the probe is moving the probe, when you scan your image, this configuration moves with the probe, and so you have a moving (venal) electrode which follows you all over the place and it's a strange thing – you feel very successful and it works and even if you don't understand it will take a while it works if you have no discharge but in fact I think that we should study this more carefully especially once precise isotopic measurements are to be made or in circumstances where it is important to control the collection parameters because this will act on the collection parameters. Again I don't know from the first principles what will be the amplitude of such an effect; it's probably much easier to do it by experience, by experiments, in an experimental way than to calculate those things because nobody knows exactly what are the angle of distribution, the energy distribution and so it would be difficult to put realistic numbers in that. Now maybe we can stop and discuss what we have seen here.

(pause in tape)

GS: I will remind you that there is only a limited number of atoms in a small volume and that you have to have this in mind when you think about an experiment not to try to find in the probe of 15 nm diameter more signal than there are atoms in the small volume being sputtered. So I have a few old viewgraphs that I can show you if you think it's necessary – if you have looked at these things many times in the past maybe I can skip.

Unidentified Speaker: (Inaudible.)

GS: You do. Okay. So now I switch to high technology.

(session break)

GS: So in the first time that goes back very far in the past we were wondering, asking people in your opinion is it interesting to do something like the NanoSIMS or not and the question which was coming very often was how many atoms would it be able to detect. So we tried to figure out what is the minimum that you can detect. I don't know if it is a very pertinent figure but it was the way we were thinking; so we came out with what we call detectability. There is a parameter which is extremely useful to consider; it's a number of ions which are detected of a given species compared to the number of atoms removed from the sample. This is a useful yield. So having that in mind you go back to Poisson statistics, the only statistics I know. As an example, let us imagine that you have a mean signal, given by the sample, that there be 3 ions mean – a mean signal. The probability from that region to –

Unidentified Speaker: (Inaudible.)

GS: The ionization yield is something which is, well, the point is the following; it will take me some time to explain. When you sputter a sample you remove monoatomic species and polyatomic species; for instance if you have a sample with two elements a and b, in the

sputtering phase, in what is ejected from the sample, you will have a, b, ab, a₂, b₂ – and so a lot of particles will be ejected during that process. I would call the ionization yield the ratio of the number of ions versus the number of monoatomic species ejected – the total number of monoatomic species ejected. For instance, you may have 100% but imagine that you are in a situation like you have an oxide. You have 100% of one element ionized but because you are on an oxide you have many polyatomic oxide particles. Those will go either in other channels or if they are ionized or not ionized at all – so what is important for you, of course for understanding the ionization process – it's important to know the ionization probability. But for practical purpose you remove a given amount of ions, how many I get and knowing that some of them will go in completely different channels. So ionization for me is ionization probability or ionization yield is the total number of monoatomic species being sputtered versus the number of ions I am considering if it is monoatomic; if it's polyatomic you change your (field) but –

Unidentified Speaker: (Inaudible.)

GS: So this is a useful yield, that is a practical number even if you don't understand anything about the ionization process, that number is important to you. It includes everything; it includes the ionization, the collection, the detection; everything you get, that is what you have. That is why it is called the useful yield. And the ionization yield then you wish to understand better what is going on and you sort out the particles and you see how many I have of that species and what is the process. So what I was saying is that if I just pick up a number I would have a mean signal of 3 ions; the probability to have zero is 5%, no signal at all, so that the confidence, if you wish to know the minimum number, the mean number, the minimum mean number should be 3 if you wish to have the confidence that at 95% that you have not missed the element present in the sample. Say, no, it is not here; it's not detectable. So with some degree of confidence – so if you take – and you will see why we went through this – if you take a yield, a 10^{-2} yield useful yield, then you need 300 atoms at least; it's a minimum number of atoms that you need if you imagine an experiment. And this is true whatever the size of your probe – you can have a very small probe, a very large probe – then it's you to figure out in the experiment I have in mind will I have 300 atoms if you make some calculation – you know your samples – you turn out that you have only 100 atoms so you won't be able to detect them with that degree of confidence. You will be able to detect them with a lesser degree of confidence that you can calculate. But this number you say – oh, 300; it's okay. But now if you have a yield of 10^{-4} then it is 30,000 atoms – that makes a lot more atoms that you will need; so it sets a limit of what you can detect with an instrument, with any instrument, but in particular the NanoSIMS. That was the first answer I tried to give. And the second part of that answer is the following. It is what is a relation with detectability and localization. So I take an example, an ion probe 100 nm erosion that – it shows this is just calculations so you can take anything. I have a detail, I put the probe here, I sputter volume which is given here, about ($8^{-5} \mu\text{m}^3$), and it gives you the number of sample of atoms that are inside that volume and then you see that knowing the number of samples, taking a useful yield of 10^{-2} , again you find this 300 atoms and you need 300 atoms over all those atoms so you have something like 65 ppm – the just detectable concentration. If you have in this concentration, which is higher, then you will be okay; if it is lower than this concentration, then pay attention. That was the message. And I hope that way to convince people that it was interesting. But you know very often people arrive with questions – I have

1 ppm here and you see if you have 1 ppm in the probe like that probe it won't be possible to detect it; it will be too – from time to time you will have an ion and it will be difficult maybe to find out if it is noise or something else. The point is that if the yield is very low you need much more atoms and then you will find out that the just detectable is 6.5% so depending on the yield it will be easy if you have 5% to detect. With that yield it won't be possible or to a lesser degree of confidence. So there is a limit. If you wish to make an experiment you should have minimum information in your sample in order to get something out. That is our second point. The other point which maybe you are less interested in but who knows is counting statistics and localization. I just took a yield 10^{-2} and I take mean atom of atoms being sputtered; so the mean signal is 10,000 ions and if you have 10,000 ions on the spot you have a relative standard deviation of which is 1% so don't imagine that you will get better precision on your point. And if you have an atomic concentration on 1% then you will be obliged to expel, to eject 10^8 100 million atoms to get that number of ions and this implies that you will be obliged, if you know that atomic density of your sample, something like $2 \times 10^{-3} \mu\text{m}^{-3}$ which is about a cube of an edge of 100 nm. So you see that this is a very limiting case – 1 nm^3 you could get with this yield with 1% precision, if you wish, a concentration of 1% but you need a given volume of matter to do it. And so it is always a discussion why don't you go to smaller probes. Well the problem if you go to smaller probes you have lesser atoms. So it depends essentially if you have a droplet of very high concentration put on 20 nm maybe you can do the experiment and go to small probes but if you have low concentration you won't find it because you will not have enough atoms. That's why I was hesitating to give those numbers because it seems so obvious that it was just because it came out so often in the conversation I had with people that I thought it was better to put numbers on.

Unidentified Speaker: (Inaudible.)

GS: I am talking in general terms. I would never make an experiment like that on a small probe because of course it would be all of 100 nm depth but the argument is I make an image – I will go like that – I make an image and each pixel of the image has a given amount of count and if I do it over and over I will have, in a given part, I will have to go to the statistics and now I think I don't want to use this more so the point is that the limit of detection and the statistical precision of measurement that can be made if someone is willing to give me a little help I will switch back to the computer.

GS: I would like to say just a few words about image registration and give an example (Slide #25-26). I will take a target with yield 5 target atoms per primary ion – this should be suppressed. The useful yield I take a high (useful yield) but I was told that in many instances it's possible to get an atomic concentration of 2×10^{-3} and atomic density of 6×10^{10} atoms/ μm^3 , the dwell time per pixel of 20 ms, François told me that it was reasonable; the number of pixel 256×256 which makes the total acquisition time of 22 mm, roughly.

(pause in tape)

GS: Also have this mind. Once you have fixed this and that you have that and this is

the registration and this is the data on the target. And then I take a primary beam in this (probe), François told me also that primary beam intensity of in .1 mml of 1.6 pA – it's reasonable, but I didn't pick that here – I wanted to simplify that number so I have 10^7 primary ions arriving per second in my probe. The number of primary ions per pixel, because I stay only 20 ms is this, the target atoms sputter per pixel is 10^6 , the yield is 5, the atoms in diameter still in is 2×10^{-3} – this number is 2000 and because I have a yield of 4×10^{-2} higher, 80 ions per pixel. What I have done is, for instance, here I have taken a field of 256 pixels and I made the probe overlap by 1 (radius) and so it makes a field of $12.5 \mu\text{m}$ per $12.5 \mu\text{m}$ and the eroded depth – maybe this answers your question – is 7 nanometers, roughly speaking, and the number of layers removed to make the image is 27 atomic layers. Always I have taken 6×10^{10} as an average atomic density. I don't know what it may change with the material. So it is just to give you a feeling of what is going on when you take an image (Slide #27). Here it's not a very high concentration – it's 2 per ml and this is a type of signal so you will have fluctuations on your signal and I don't know if I have put in – oh yes – this I also hesitated to put in because it is, in a way, fairly obvious but I was told that I shouldn't stop myself by obvious things. So the point I wanted to make here is here I take 3 adjacent pixel and I have a detail which is maybe this point which is slightly higher than the neighboring point here by a small factor ?? I put here. The point is that if you have, for instance, 80 counts you have a statistical fluctuation. So you have these wavy lines represent the statistical fluctuations and it will be difficult for you to say that, well, they are different because they are within the statistical fluctuations. You can use time or integration time as magnifying glass – you will multiply the integration time by K – a greater number – 9, 10 – and then what will happen is that this small – I put broken lines in because everything is multiplied, it's not at the same scale – you will increase this difference on the mean values by a factor of K, but here the fluctuations will be multiplied, compared to that case, only by a factor of square root of K. So the more you wait, if you have the patience to do it and also if your sample lasts that long to do it, then the small difference may be brought high enough so that you can see this difference – which is always when you have a background or something detailed in the background it is much more difficult to see, to visualize the differences if really it exists. Imagine on the contrary that you have a situation where this detail is very small, I didn't figure out, of the same type here, same height, but with no background at all and you will see it. And when you look at pictures, very often people show you – look at my beautiful pictures, and there are those statistics but on details that are alone no background because no composition and it's really beautiful and sometimes it's very helpful. If you have low concentration but on a very specific label, for instance, it will show you some detail in the sample very well so that all what I have said of – pay attention, I wish to have a good statistic – it's useless but if you wish to know something which is slightly above a given background, which is real, which exists in the sample, then it is a little bit more difficult. And you can, of course say, well, easy; I will cut this background here so I will see all the details. But you will see at the same time a lot of statistical fluctuations. So you cannot beat statistics when you are in this situation. So, in fact, when you look at images, especially with statistical fluctuations, you must be careful that the situation is not the same when you are – in this situation you have this figure and if you have an isolated detail ion, I mean by isolated it is chemically isolated, it's isolated by its emission; the surrounding does not emit particles, it's only the small spot that emits those particles – then even if you have a few number of counts, you will get the result. So I think I am through with what I wanted to tell you about those

general aspects. If I go back I wanted to make you aware of what are the constraints between collection optics shaping the secondary beam and the mass spectrometer, to stress the importance of high collection efficiency, which is obvious for local analysis purpose, with some small problems with the QSA and then, because I introduced this quasi simultaneous emission, I had to talk about detection, detection either with the multiplier or with the Faraday cup, and if you make a detection with a multiplier you have a few problems that you have to be aware and take care of. And the other point is that increasing the primary beam intensity to get more signal, it's okay, it's good, you should do it, but pay attention about (space) charge effects – I have no information about that. And sample discharging, which may, of course, in the picture I showed you, the more you put high intensity into your probe, the more the (venal) effect will become effective and oblige you to readjust the optics; and finally there is the detection limits or statistics that you have to be aware of, not to foresee, to plan experiments that cannot be done because there is not enough information in the small spot you wish to, or the small points, or the features you wish to analyze. I think I covered all these points.

Unidentified speakers: (Inaudible discussion.)

GS: You detect but you don't measure it. You know it's there. And there is – I just want to make a short comment on what you are saying – here, with mass spectrometry, it's not a true science that you are making because you destroy your sample and you can never prove to somebody else that it was really in the sample. You have to take a similar sample; here you destroy – all the atoms you remove, they are gone; with x-ray you have time. You ask an atom what's your name, what's your name, what's your name – as many times – maybe it will finally say, well – I quit. But you can ask it many, many, many times and then you can accumulate information. Here the other problem is if you go in that, you will, after a while, make erosion problems, and maybe you can do it. My role here is just to say – pay attention; be aware of the points. I don't say that you cannot do – people they earn their life in doing in-depth profiling in semiconductors for so many years that it must be working but a semiconductor is a very, very homogeneous system and even now, where they are looking at ultra-shallow profiles, they have a lot of problems – atoms migrating, quantification and so on. So it's not easy – on the biological sample I don't even imagine what it will do. I hope Claude will make studies and tell us; but probably the situation is less simple when you start to etch a lot of your sample – maybe not, I don't know.

Unidentified Speakers: (Inaudible discussion.)

GS: Yes, that is a very good question. If you have an insulated detail and a much larger probe, what you will get is just, in a way, you will record the ion density in the probe and in that respect if you knew the ion density in the probe, probably you could reconstruct and say, well, it is a small detail but that I have never tried. Well, maybe it should be possible, but I don't if it is possible to know the density distribution in the probe but we can model it, probably check, and do the things. I'm sure that people will work on such a problem. It should be possible. In principle I don't see why it shouldn't be done.

Unidentified Speaker: (Inaudible.)

GS: Well that what was some time ago the kind of thing that I would be delighted to look at but I have no direct experience on it. I can just figure out that if the charging is different, if the yield, for instance of electrons is very different you will have – and if it is an insulator – if it is a metal, the contact potential, they are not so huge. If you handle it carefully it might change slightly, the collection, but the main effect will be, for instance, channeling in the drains so you will not even think about the other problem because the problem I mentioned with the changing in the potential will be a small thing near something which has a much higher amplitude. On insulators I don't know how nature will do if you have two adjacent phases and the emission is very different. Somehow, and locally the electron beam, will have to adjust. It will not be exactly the same voltage. It will distort, it will change; it's likely the collection efficiency, maybe, to which extent you will be sensitive – if you have only 100 counts per pixel, for instance, maybe you won't see it because the statistics will not be good enough. You see the problem. I became aware of and I wanted to keep those problems in mind really for people like – maybe Frank one day will decide to make high precision isotopic measurements. Then it might hurt – I mean that if he has problems in reproducing and if he has gone through – oh, it's not the multiplier, it's not the magnetic field, it's not this and it's not that, then maybe it will be the collection efficiency which is not the same for all the isotopes. You see. And what is lacking right now is a reasonable evaluation of the amplitudes of those effects. But they exist. It's difficult to say something exists and you cannot show it. It's like God.

Unidentified Speaker: (Inaudible.)

GS: You have plenty of phenomena of those types but because the density is low at the surface for those atoms to recombine they must have some kind of probability to meet and this probability is low, it's not (vanishingly) small so you may have reconstruction particles will combine outside and give a polyatomic species that exists. Yes. So you will have it and if it is far from the surface, if it is a few microns from the surface, you will see it on the energy distribution because there will be a kind of deficit of acceleration voltage. So you will see it in the energy distribution but very often it's a small percentage on the main peak and you don't see it. But many people have studied in SIMS and secondary ion mass spectrometry they have studied phenomena of that kind.

Unidentified Speaker: (Inaudible.)

GS: No, not really, it is only a small fraction. Not really. You may have exceptional cases where no secondary emission exists and you have only those recombination or it's not always recombination, you have directly sputtered. People who are working with simulation, molecular dynamics, they show the surface which receives an ion – it's awful – it's waving in all directions, you have ions leaving, and so on. It's not the quiet, I don't know what is the truth of those simulations, but it's not the quiet situation that we imagined in the early days where you have an ion – it is just like in bowling – and you have the things forming the path and the surface remains quiet but you have a few particles leaving – all the surface is moving. So it exists – particles will leave with the same velocity about and they make a chemical bond –

Unidentified Speakers: (Inaudible discussion.)

GS: Yes, but your point, Claude, is that, for instance, imagine that you set your energy slits and you remove all the true secondary ions and you take the other one then you will have fractionation effect which may be very small but it will be on the limited portion of the beam and you will have to destroy a lot of sample before you become aware with reasonable precision that those phenomenon exist so it is – practically you can forget about it, in general, of course. You can find a situation where – just like ?? by the feet – you can find a case where –

Unidentified Speaker: (Inaudible.)

GS: Yes, ask ??, he has measured things even higher than that – 20%. (Speaking in French.) So you have probably 5% of useful yield.

Unidentified Speaker: Kind of a related thing – things like post-ionization, where does that stand? Generally successful?

GS: Oh, it was a great dream, I think. Yes, you can do a lot of things with post-ionization. I think basically it's a good idea. The point is that the ICE is very low temperature. I mean that you have not high collection efficiency from a point because you see the problem is always the following. In my opinion, when I was younger, I thought that I will work five, ten years on SIMS and quit because everything will be over. It's such a dirty phenomenon. Look, you bombard the sample, you sputter the sample, you have a lot of chemistry, it's complicated. If you take the electron probe, or the electron microscope, you have simple theories – that you have yields, you can calculate them, electron probe, you can calculate a lot of things; and here it's really the dirtiest phenomenon that you have for a physicist. But the point is that you catch the ions as soon as they leave. So you can get high collection efficiency, high sensitivity, and you can look – Claude, for instance, on isotopic ratio on really small surfaces – it's absolutely fantastic. What happens with post-ionization? How can you do it? You have a burst of particles, move in a large surface, and then you shoot a laser beam or electron beam over the laser which people think that it there is 100% ionization but then the problem is that you have to gather all those particles again. You can do it fairly well with time of flight, I was told that I should not talk about time of flight, well it was a little bit out of scope of the workshop; but now you have to repeat this point by point and it will take forever to have information on that image. So if you focused on images, on many adjacent points, the repetition rate has to be high. And so, for years I thought that the first work was made was direct imaging and direct imaging had virtue that the ion probe has not is that you get all your image points at the same time. The price to pay is that if you wish to have a good image you have to close an aperture to reduce aberrations and when you close the aperture you lose all the signals so you could very well have a 100 nanometers special resolution but with no intensity and it's your (specimen). But having worked with the ion microscope and having used an objective lens I knew about the possibility to collect in a large collection solid angle. And it is from that the NanoSIMS is (stemmed). It is weak in collecting a large solid angle and if we wish to regain special resolution, we use a probe. It's not a great idea – it's simple, it's common sense. NanoSIMS equals common sense.

Unidentified Speaker: (Inaudible.)

GS: I have no answer to that. I think the yields will be different. The only way to really maybe learn something would be to see if you can have some kind of specific ion emitted – probably atomic ion related – just like people in static SIMS do but now you are in dynamic SIMS where you make a lot of breaking of the molecules and I don't know if you will have enough molecules to retain the information at the level of, say, 100 nanometers. Now people claim – the great idea now – is that what is fashionable to do – in the last meeting in San Diego was people working with gold primary ions, gold 3 times, 4 times – polyatomic gold – or even different, people claim better – who knows – using C60 – splatters on the surface. They claim that they have a lot of nondestructive ejection of molecules. Why not? Maybe some day you will have a C60 gun on the NanoSIMS. The main problem then is to know if those sources will be bright enough to allow reasonable current in the probe and right now I don't know. Maybe it's better to use a gun which delivers gold AU₃, or 4; it's still a fight to know if it is more efficient, less efficient. You know, the NanoSIMS has been – the conception of the NanoSIMS was the following – we knew something very specific about collecting ions and making images in the most efficient way. We know less about ion sources so we looked for a cesium source, we couldn't find it on the shelf in the manufacturing company so we made our own source. And then once everything has been demonstrated, after that it's more development that has to be done. But of course the structure of the instrument is that you can – and it was at least at the beginning in my position that if someone comes up with a superb source I remove cesium cells and I pick another source. If somebody, for instance, would give me superb O- source – there is one duoplasmatron, it's not fantastic, you cannot make small probes and so on but we can use it. But if somebody arrives and says, look, I have this type of source with ?? of 4-, well I take it; it's the only way to do, to be open to all the progress that can be made by people who know better than we did at that time on sources.

Unidentified Speaker: (Inaudible.)

GS: Yes, I have finished. I am just answering questions. Usually I'm a lot longer, but this time I was allowed so much time.