

Historical development of ion sources for SIMS

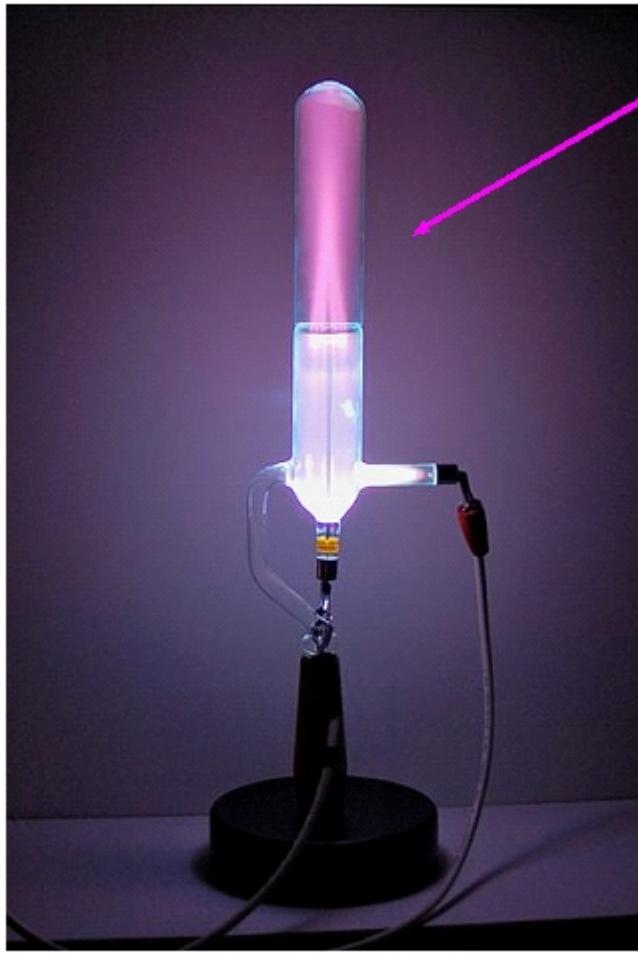
Peter Williams

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This is an invited talk presented at the 25th US SIMS Workshop in a session dedicated to historical aspects of SIMS. The organizers asked the speakers to make their slides available for the SIMS web site and I was delighted to do so. I have added a commentary that is fairly close to the content of my talk, and I have added back a few slides, dealing with massive cluster impact, that I omitted from the original talk in the interest of time. I have played with – i.e. built or modified, not just used – many of the ion source types discussed here so this talk is a mix of general history and personal reminiscences.

Gas ion sources

Let's begin at the beginning, with the 19th-century study of gas discharges.

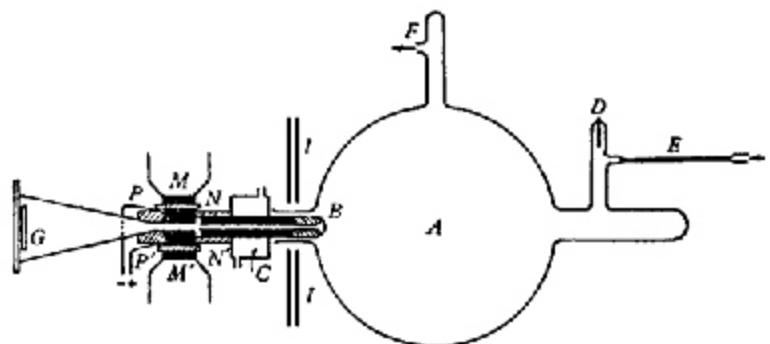
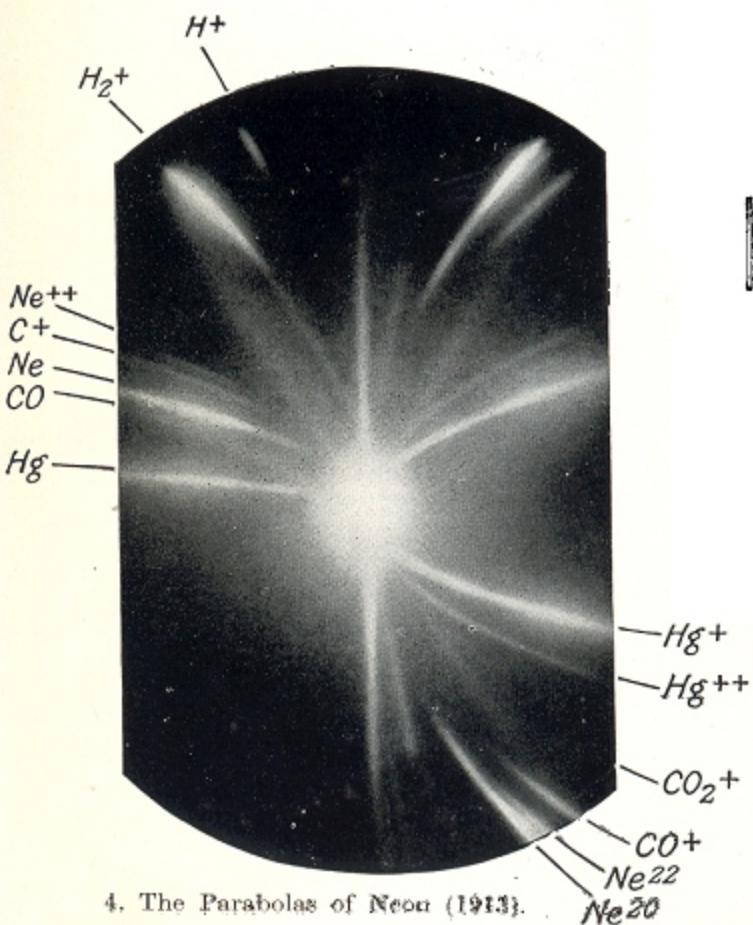


“Kanalstrahlen” penetrating through channels in the cathode of a glow discharge tube

Goldstein (1886)

Energy spread: roughly the full potential drop across the discharge

Slide 3: In 1886 Joseph Goldstein drilled channels in the cathode of a glow discharge tube and saw beautiful streamers from the discharge emanating through the channels. These were obviously positive ions that were accelerated towards the cathode. Wikipedia as usual has a great image. Goldstein’s “channel rays” (“Kanalstrahlen”) were the first source of ions for mass spectrometry. One feature to note is that the energy spread of these ions is high – roughly equal to the entire potential drop across the discharge.



J. J. Thomson
Parabola apparatus 1913
Discovery of isotopes



Slide 4. In the early 1900s, J.J. Thomson in Cambridge examined the composition of the channel rays using his parabola apparatus that he had used in 1897 to determine the mass/charge ratio of the electron and demonstrate that it was a new, subatomic, particle. In 1913 he ran the discharge on neon gas and discovered the two isotopes of neon (lower right on the parabola image). The effect of the discharge energy spread can be seen in this image: high energy ions go more-or-less straight while lower energy ions are spread out by the parallel electric and magnetic fields along parabolic images. This was the first demonstration that isotopes exist, an idea that had been floated to explain the fractional atomic weights of many elements by Sir Charles Crookes as early as 1896. This was just before the outbreak of World War I which shut down most basic research in Europe.

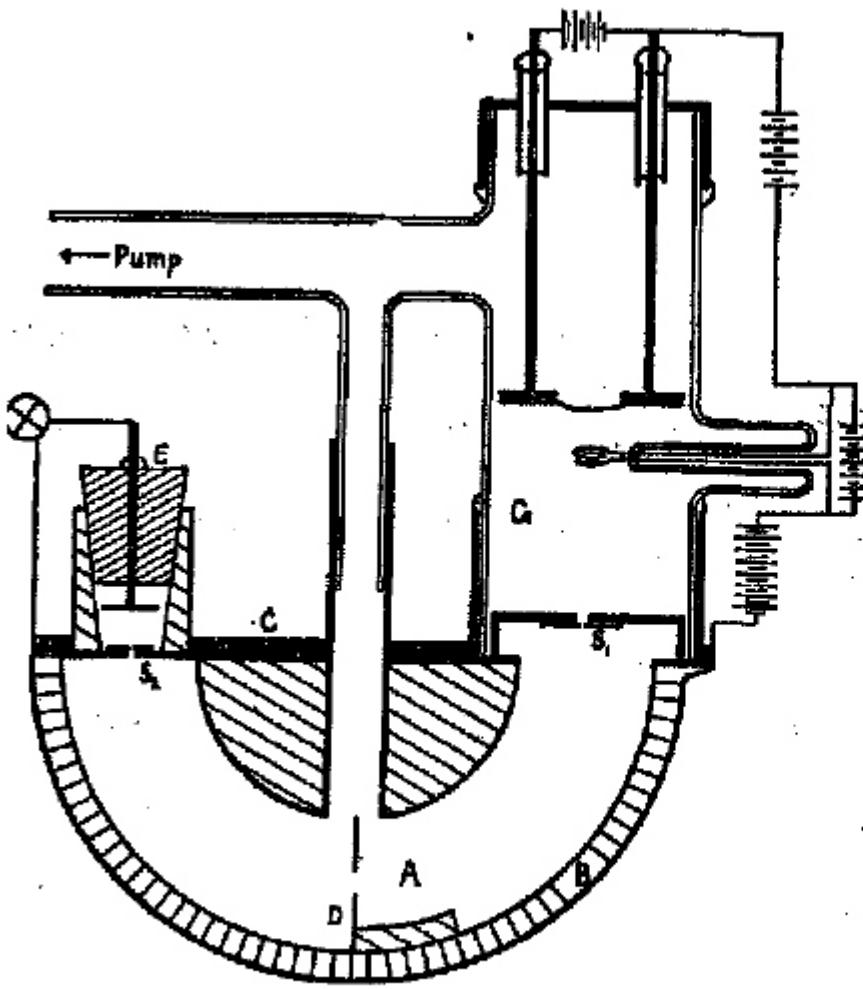


Fig. 1.

A.J. Dempster

Univ. Chicago 1917

Direction-focusing in 180°
magnetic field

(Requires ion source with
small energy spread)

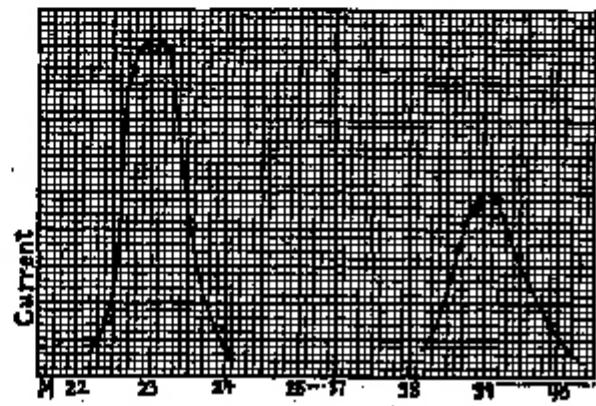
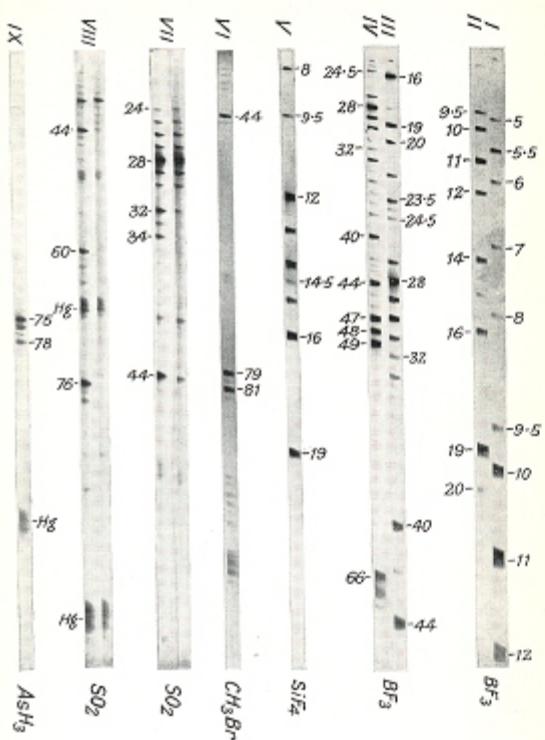


Fig. 5.

Slide 5: The first mass spectrometer that most of us would recognize today was built at the University of Chicago in 1917 by Arthur Dempster. He used the direction focusing properties of 180 deg. deflection in a magnetic field. This design has no energy focusing properties and so Dempster needed an ion source with a low energy spread, which drove him to develop a number of different sources with that property. In the instrument shown, ions were generated by electron bombardment of alkali metal salts coating the filament at top right, with the electrons generated by the filament poking in from the right. Note the use of electrical detection rather than a photoplate and the hand-plotted mass spectra. (The speaker built a Dempster-type mass spectrometer for his PhD research almost 50 years later – also with hand-plotted spectra.)

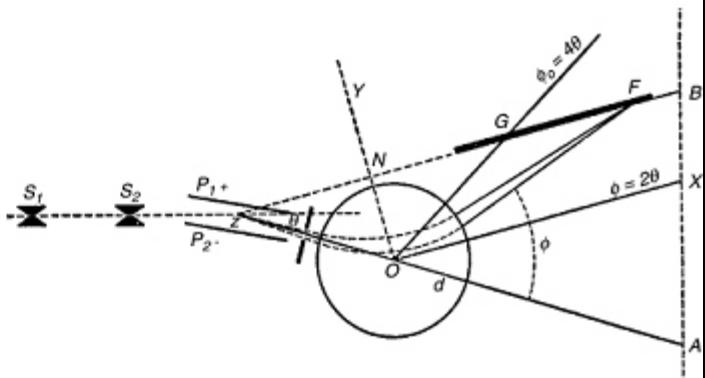
PLATE IV



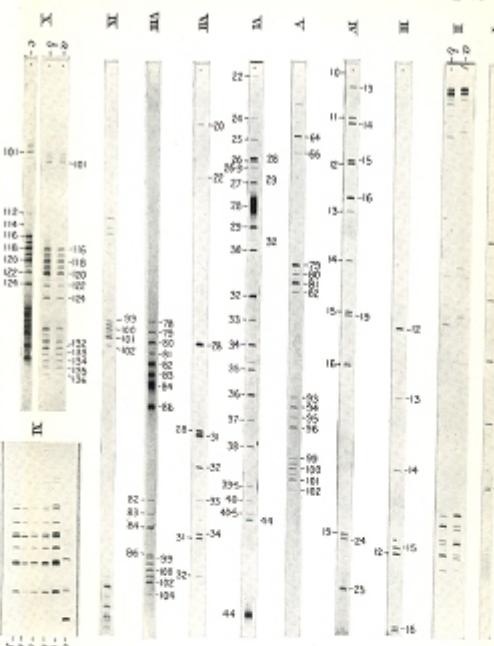
TYPICAL MASS SPECTRA OBTAINED WITH THE FIRST MASS SPECTROGRAPH, 1920.



F.W. Aston (1919): 1st mass spectrograph
(energy-focusing)
“Whole number rule” (Nobel prize 1922)



Slide 6. After the end of World War I (then known as “the war to end all wars” because no-one realized it was just the first of a series...), Thompson’s former assistant, Francis Aston, returned to Cambridge and continued Thompson’s pioneering study of isotopes. He decided to stick with the discharge ion source and designed a mass spectrometer that had an energy-focusing capability to deal with the large energy spread. Mass spectra were detected photographically along a focal plane, allowing a rapid survey of many ion species. Aston’s instrument had no direction focusing properties and instead the ion beam was tightly collimated by a pair of very fine slits (S_1 and S_2 in the figure). With this instrument Aston very rapidly looked at every element he could get in gaseous form. So boron trifluoride allowed him to discover the boron isotopes 10 and 11; silicon tetrafluoride shows the doubly-charged ion of ^{29}Si ; bromine isotopes are visible in the spectrum from methyl bromide, and so on. Aston summarized his findings in his “Whole Number Rule”, which stated that many elements are multi-isotopic and that the isotope masses are integer multiples of the atomic mass unit, which at the time was defined as 1/16 of the oxygen atomic weight. (Incidentally this verified a visionary suggestion in 1816 by the English physician William Prout, who proposed, only about 10 years after Dalton’s atomic theory, that all atoms were built up from hydrogen atoms, as indeed we now know happens in stars.) Aston was awarded the Nobel prize for his work in 1922, the only Nobel for mass spectrometry in the 20th century.



MASS SPECTRA TAKEN WITH THE SECOND MASS SPECTROMETER, 1925, 1926, 1927.

(Dempster discovered ^{235}U in the 1930s)

Mass spectra from Aston's 2nd mass spectrometer 1925-27

Note that the ions $^{12}\text{CH}_4$ and ^{16}O are resolved (CH_4 is $\sim 4\%$ heavier than ^{16}O). These data led to the packing fraction curve (1927) and ultimately nuclear energy.

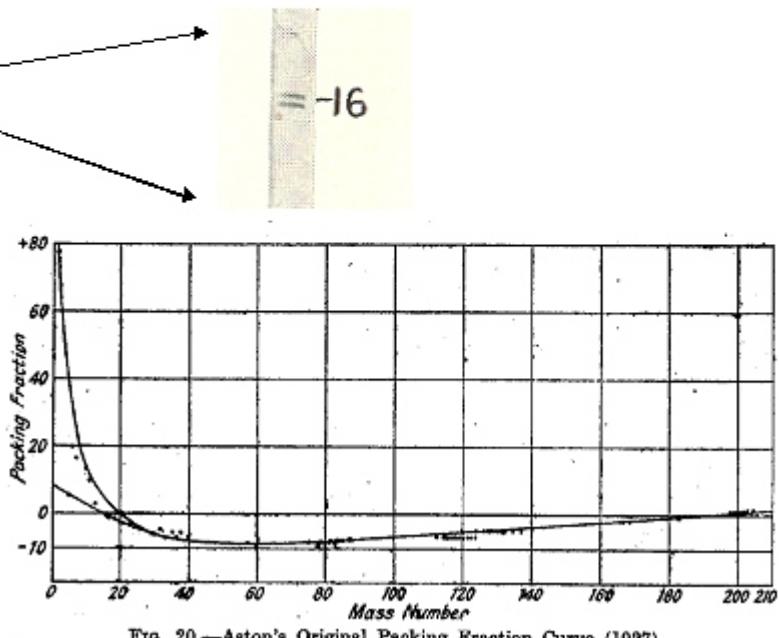
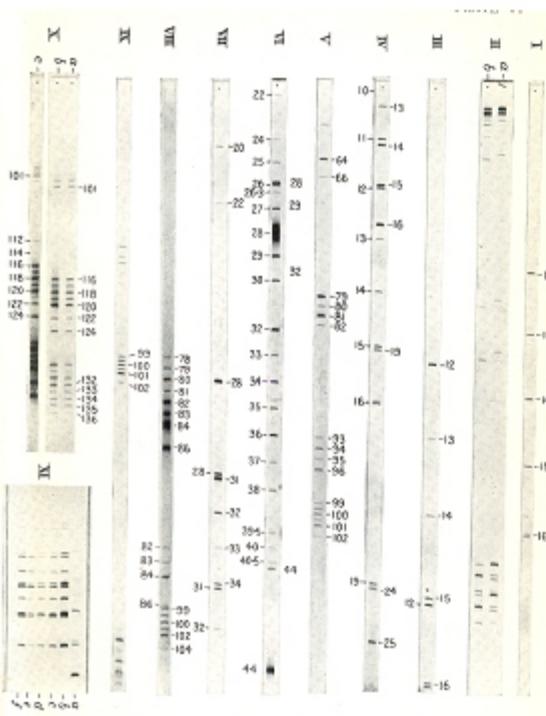


FIG. 20.—Aston's Original Packing Fraction Curve (1927).

Slide 7. In the 1920s Aston improved the resolution of his mass spectrometer and started to discover small deviations from the whole number rule. The image shows a blowup of the mass 16 doublet formed by ^{16}O and $^{12}\text{CH}_4$. Once again Aston moved with remarkable speed to make a broad survey of the range of atomic masses using anything he could get into the discharge as a gas and in 1927 published what he called his “packing fraction curve” (lower right). This is a plot of the deviation of atomic masses from the whole number rule: this deviation arises from the relativistic mass lost as nuclear binding energy during the synthesis of the nuclei and is essentially a nuclear binding energy curve. From this curve it is immediately apparent that fusion of light elements like H into heavier ones is highly exothermic, as is fission of the heavy elements to lighter fragments. Although the great physicist Ernest Rutherford dismissed the idea of obtaining energy from the nucleus as “moonshine”, it was only another 18 years to the explosion of the first fission bomb in New Mexico. Note that Aston was highly opportunistic – he made no effort at a systematic study of all the elements but grabbed anything he could get into the gas discharge to delineate the broad outline of his curve. So around mass 80 he had krypton isotopes, xenon around mass 130, mercury isotopes around 200, and so on – enough to define the curve. Dempster in the meantime had been working diligently to develop ion sources for solids, and indeed had discovered isotopes of many involatile metals, including the mass 235 isotope of uranium, but was far from seeing the big picture that Aston painted.



MASS SPECTRA TAKEN WITH THE SECOND MASS SPECTROGRAPH, 1925, 1926, 1927.

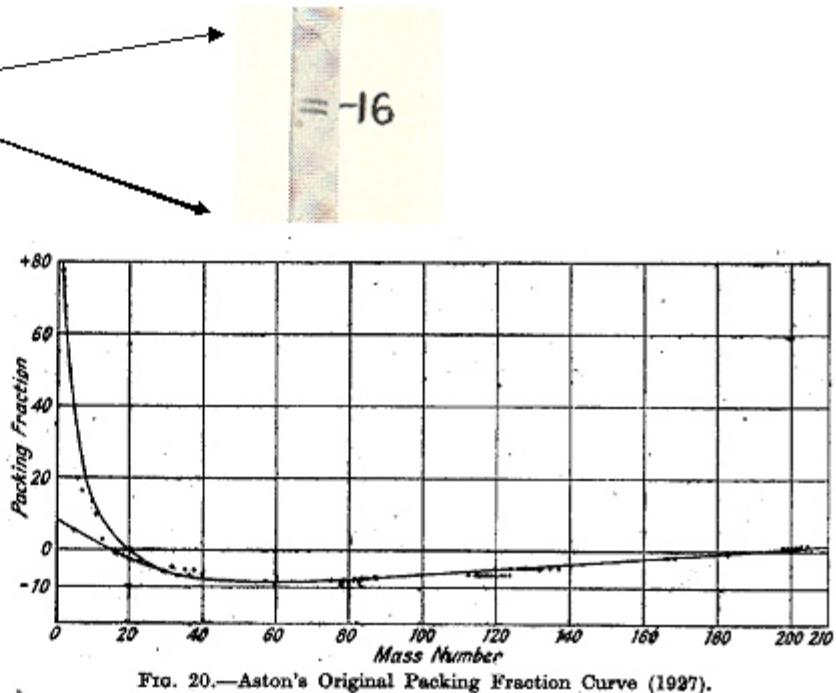
Mass spectra from Aston's 2nd mass spectrometer 1925-27

Note that the ions $^{12}\text{CH}_4$ and ^{16}O are resolved (CH_4 is $\sim 4\%$ heavier than ^{16}O). These data led to the packing fraction curve (1927) and ultimately nuclear energy.

(Dempster discovered ^{235}U in the 1930s)

H.E. Duckworth,
Univ. Manitoba

P. Williams



Slide 8: Since this is a historical talk, I'd like to point out that Dempster is in some sense my scientific "grandfather". My postdoctoral mentor at the University of Manitoba about 40 years ago was the distinguished Canadian mass spectroscopist Harry Duckworth, who had been a graduate student of Dempster in Chicago in the 1930s. Aston, on the other hand, had no students and after the packing fraction work he famously announced that mass spectrometry was finished and that the field would die with him. So I guess we're all zombies...

The earliest SIMS papers studied negative ions:

Woodcock, U. Chicago

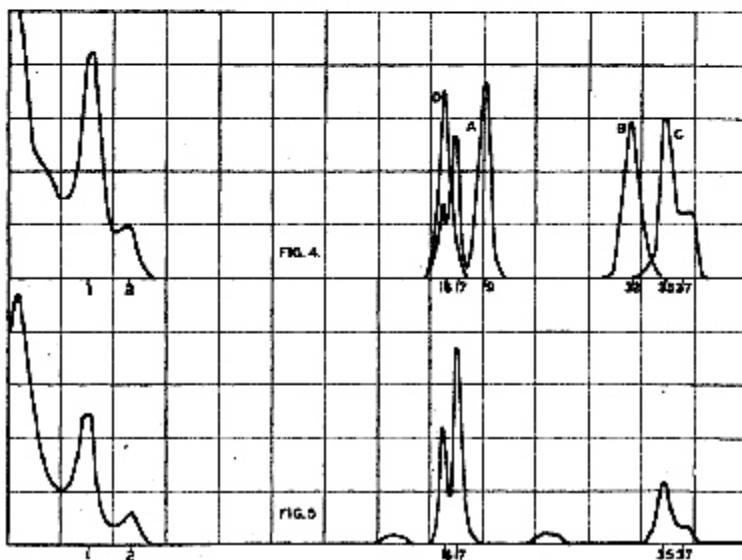
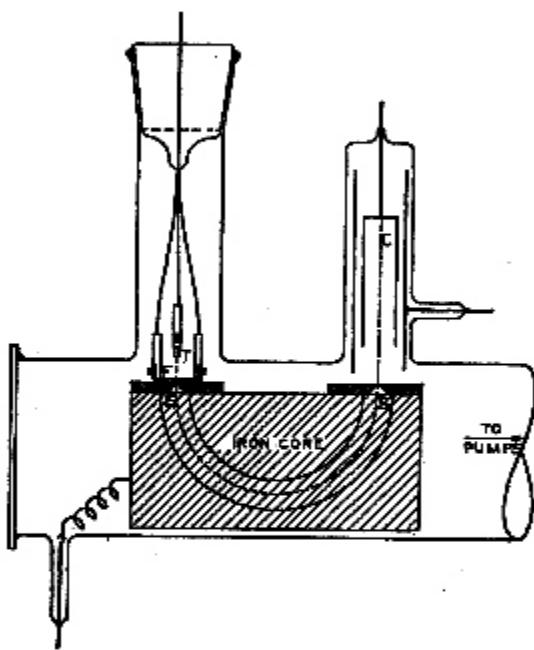
Phys. Rev. 38 (1931) 1696

Li^+ bombardment of:

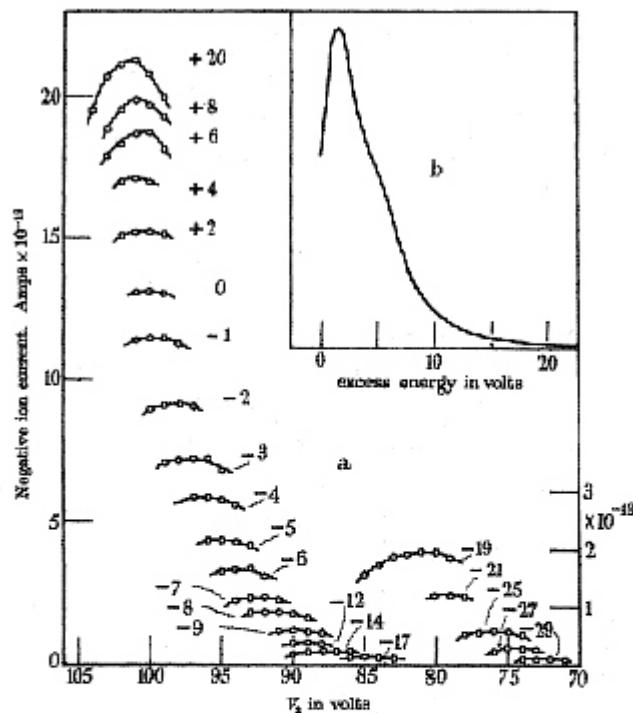
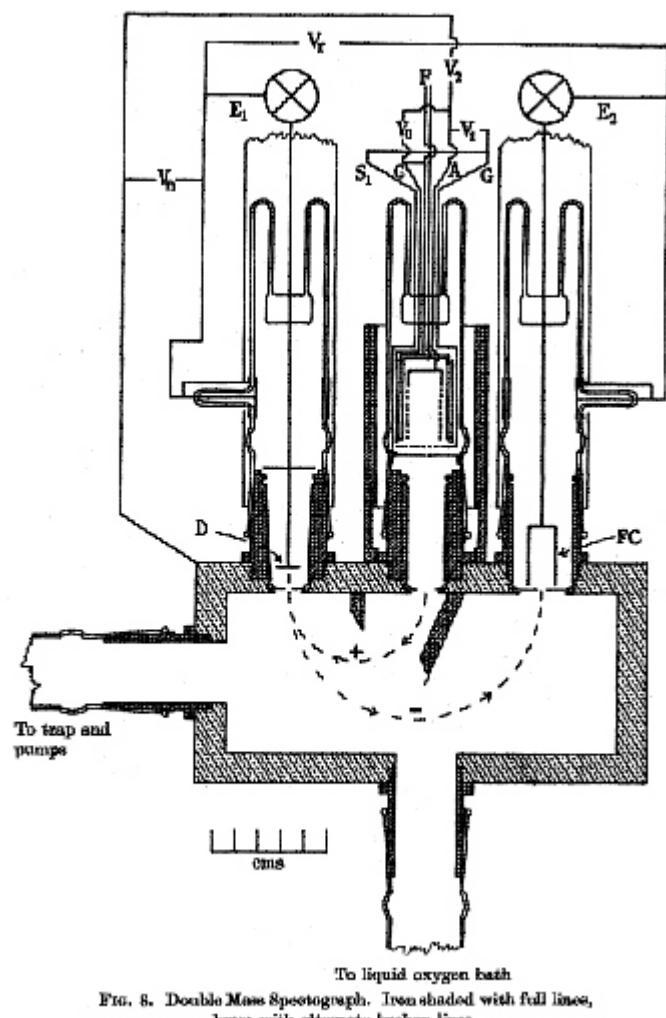
Fig. 4: a) Fluoride salts b) Sulphide

c) Chloride d) Oxide

Fig. 5: "Clean" metals



Slide 9. The earliest SIMS reference I've been able to find is a paper by Woodcock at the University of Chicago in 1931. He generated Li^+ ions from a heated filament to bombard metal salts coating a second filament and analyzed the resulting negative ions in a Dempster-type mass spectrometer. He saw F^- from a fluoride, Cl^- from a chloride, and so on. He also discovered the difficulty of keeping metal surfaces clean, as evidenced by the O^- , OH^- and Cl^- peaks from a "clean" metal target in the lower figure.



Mass-analyzed primary ions (e- impact)
Initial kinetic energy measurements
Proc. Roy. Soc. 168 (1938) 284

Slide 10: 1938 saw a beautiful SIMS paper from Sloane and Press at Queen's University in Belfast, Northern Ireland. These authors mass-analyzed both primary and secondary ion species; the primary ions were produced by electron impact in the ion source in the center. Primary and secondary ion masses could be selected, at a constant magnetic field, by varying the accelerating potentials. Sloane and Press had built their apparatus to investigate a report that Hg^+ ions striking a surface were reflected as Hg^- , a finding that, rightly, they didn't believe. Indeed they were unable to detect Hg^- but did show that there were sizeable quantities of cluster species from contaminating hydrocarbons. They also did the first measurement of the initial energy spread of sputtered ions using a retarding potential approach. It's interesting that the earliest work on SIMS studied sputtered ***negative*** ions, rather than positive.

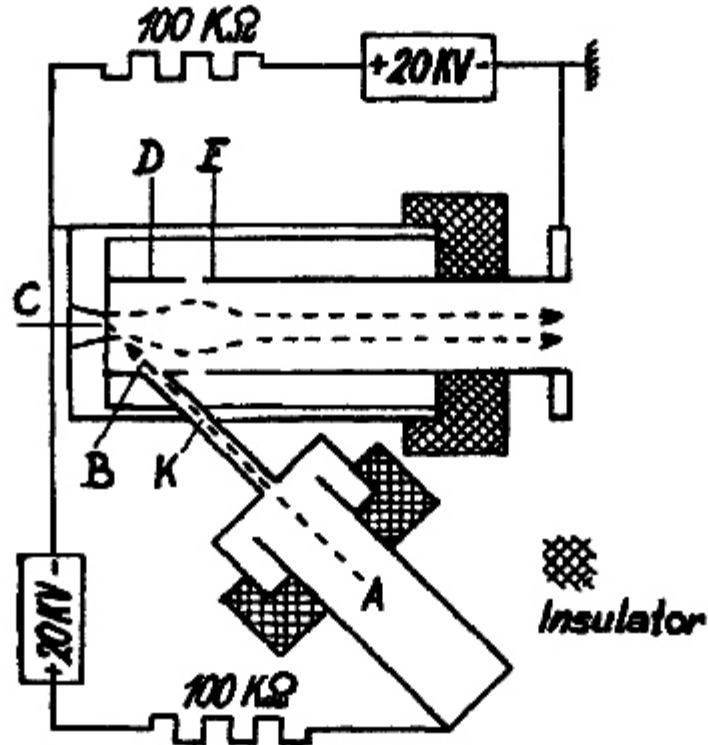


FIG.1. Schematic diagram of suggested ion sources.

Ion Source for Mass Spectrography

R. F. K. HERZOG AND F. P. VIEHBOCK

I. Physics Institute, University of Vienna, Vienna, Austria

August 1, 1949

Slide 11: After World War II (fortunately the organizers of the World War series have been less successful than the SIMS Workshop organizers, so we've only had two of the former...) Herzog and his student Viehbock, working in unimaginably difficult circumstances in Vienna, built an instrument that was designed for SIMS analysis. The ion source they used was a discharge/channel ray type. Richard Honig, in a SIMS history he wrote for the SIMS V meeting, pointed out that in post-war Vienna they could not obtain argon to run their discharge, so ran it on air and so became the first to generate secondary ions with an ion beam that was (at least partially) oxygen ions.

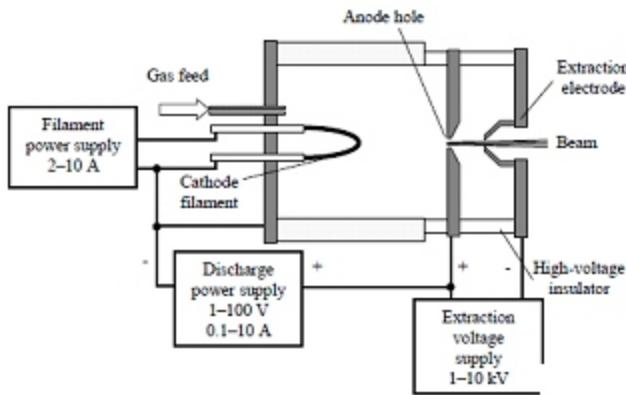
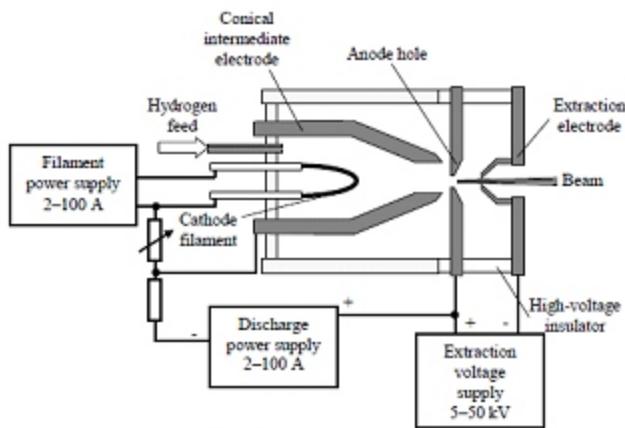


Fig. 7: Schematic of an electron bombardment source

A.J. Dempster 1916



Manfred von Ardenne 1950s
Fig. 8: A schematic of a plasmatron source

Slide 12: Returning now to ion source development, this slide shows at top left a stylized image of the ion source based on a design that Dempster reported in a 1916 paper. An arc discharge is generated using electrons from a filament, which allows the arc to run at a relatively low voltage (a few hundred volts) and, crucially, ions are extracted through an aperture in the *anode*. This gives ions with a low energy spread of $\sim 5\text{-}10 \text{ eV}$. Bottom right is an improvement on this source by Manfred von Ardenne in the 1950s. He introduced the idea of putting a constricting electrode in the discharge path so that the discharge was squeezed down to a much smaller diameter and consequently greater ion current density. Von Ardenne called this source a “plasmatron”. (Von Ardenne is an interesting character. A wealthy German nobleman, in the 1930s he dropped out of the University of Berlin after a year, declaring that he could educate himself much more effectively, and used his family fortune to build his own physics lab. At one point he even had his own private cyclotron. Towards the end of World War II, von Ardenne and some colleagues made a pact that they would surrender as a group to the first of the Allied armies to reach Berlin. That turned out to be the Russians, and so von Ardenne and his colleagues went to Russia to work on the Russian atomic bomb project. {For a fascinating and authoritative account of the Russian bomb development, read “Dark Sun” by Richard Rhodes.} Von Ardenne with his interests in ion source technology worked on electromagnetic isotope separation. In the 1950s von Ardenne was allowed to return to (East) Berlin, and had sufficient clout to be allowed to take his experimental apparatus with him. Back in communist East Germany he was able to retain his private fortune and even the title “Baron”!)

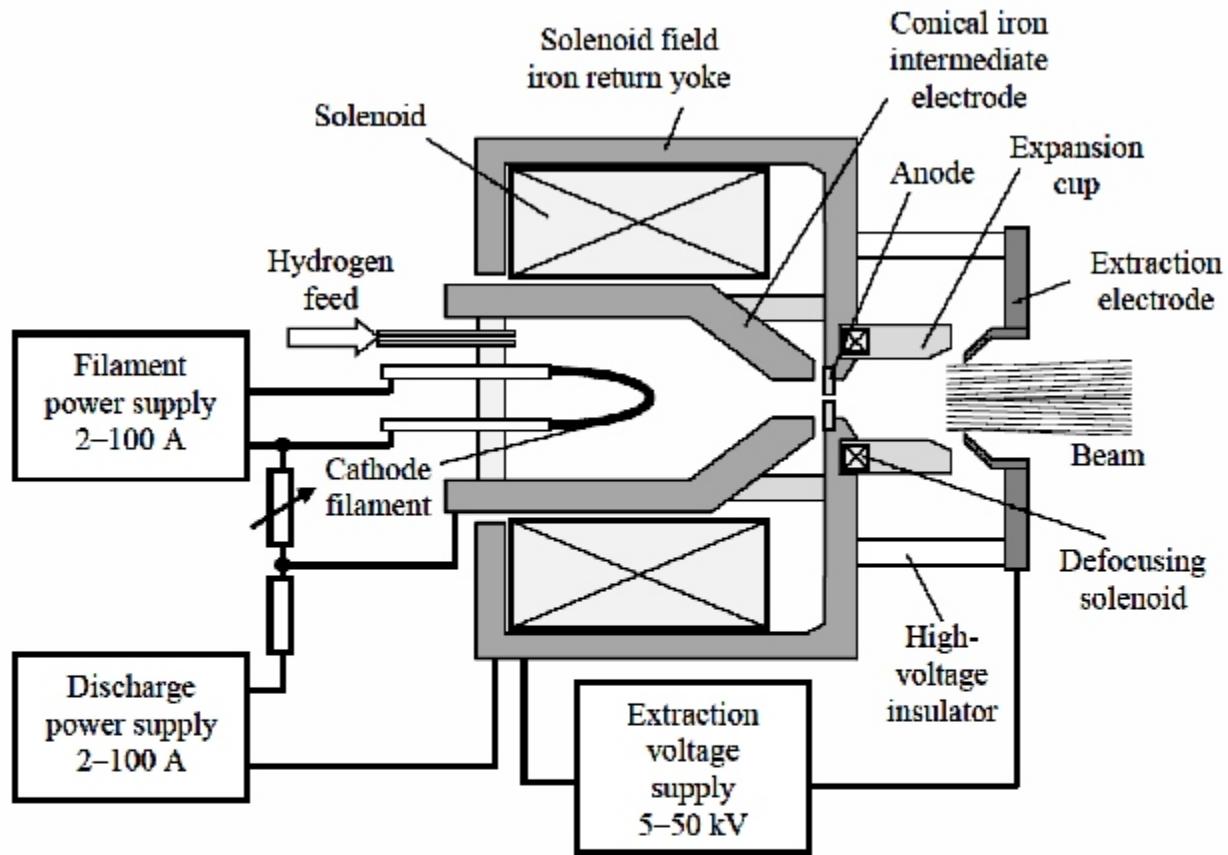


Fig. 9: A schematic of a duoplasmatron source

Manfred von Ardenne 1956

Slide 13: Von Ardenne's final source improvement came when he made the constricting intermediate electrode also part of a magnetic circuit. This electrode is called in German the *Zwischenerelektrode*, thus "Z-electrode" for short.

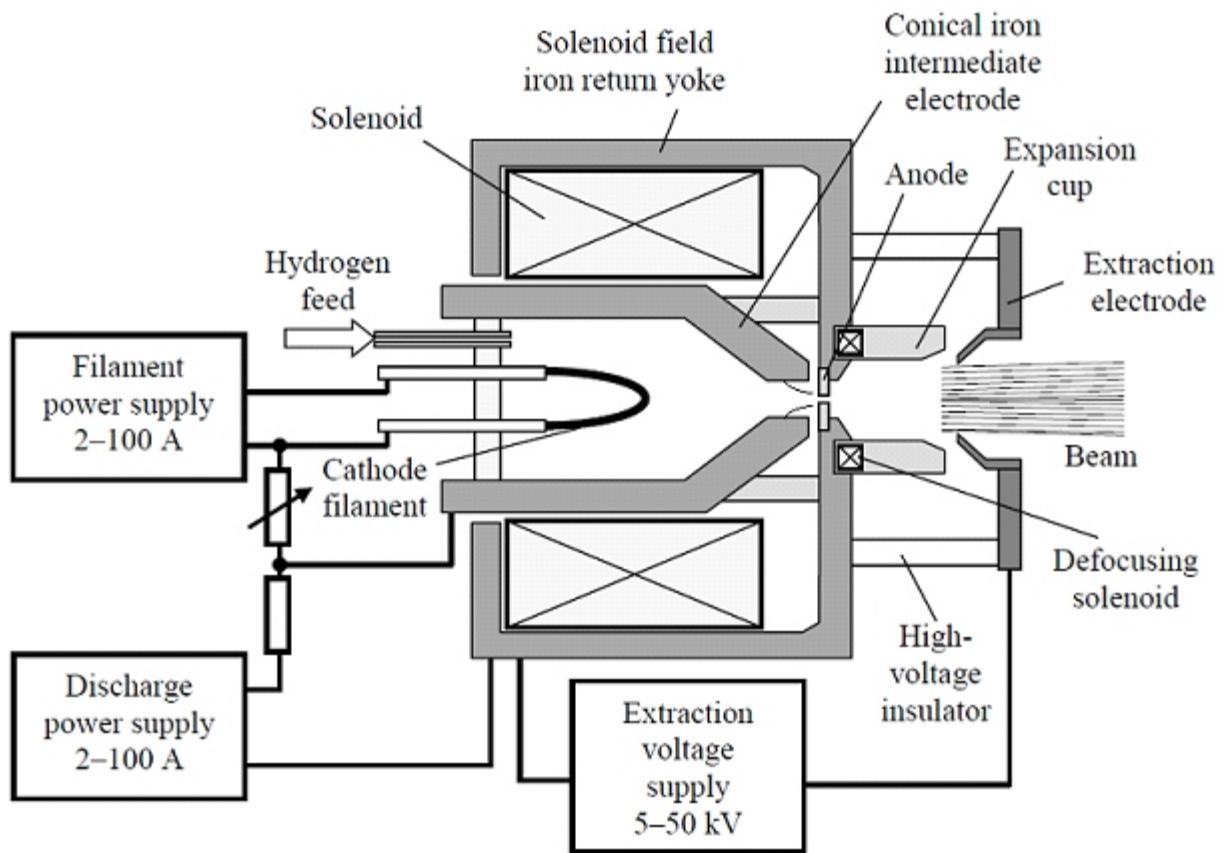
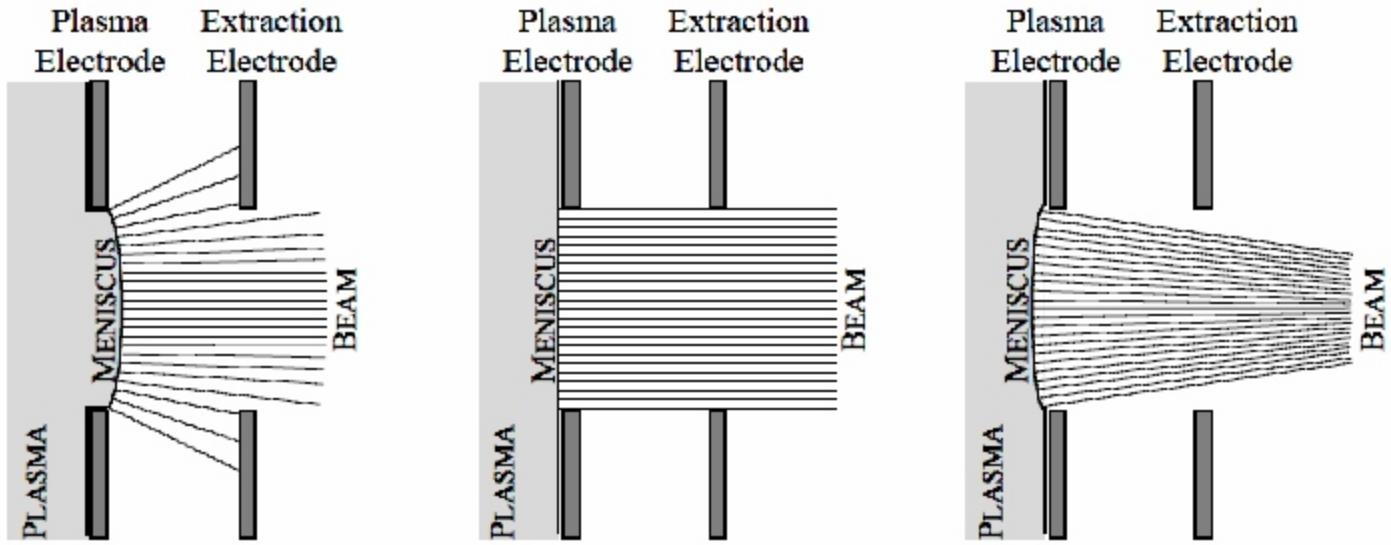


Fig. 9: A schematic of a duoplasmatron source

Manfred von Ardenne 1956

Slide 14. Shows how the magnetic lines of force from the field penetrating into the Z-electrode gap have a further focusing effect on the electrons (and thus the ions) in the discharge. The source parameters in the figure are for sources used in nuclear accelerators, which require huge currents. SIMS sources are much less aggressive – around 100 mA arc current for example.



Slide 15: This slide shows extraction parameters at the duoplasmatron exit aperture. The shape of the plasma meniscus results from a balance between the plasma charge density and the extraction field strength. High charge density or low field strength allows the plasma to balloon out and the convex meniscus leads to an initially diverging ion beam and poor ion optical performance. It's possible to achieve a balanced, flat meniscus, but this is not a stable situation. The desirable meniscus shape is concave.

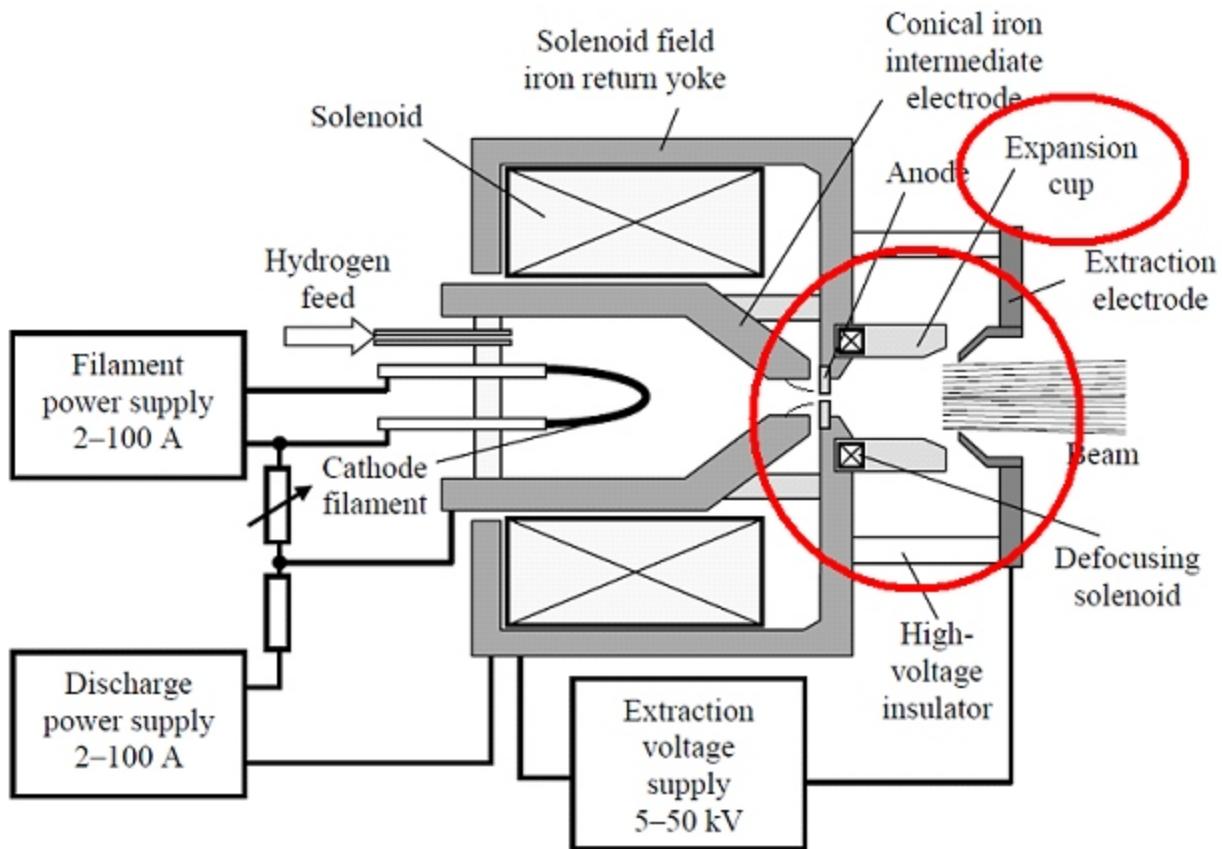


Fig. 9: A schematic of a duoplasmatron source

High-current sources allow plasma to expand into an expansion cup

Slide 16. How do we combine high charge density, for high current, with a concave meniscus? Accelerator source designers build in a plasma expansion cup: the plasma balloons out into this large volume which reduces the charge density and again allows a concave meniscus to develop. The Cameca duoplasmatron doesn't have such an expansion cup, and so when I bought my first ims 3f (#11 at the University of Illinois in 1980) I machined a small expansion cup into the anode aperture. The result was next to no current: apparently the charge density in this source operated at low arc current is too small to allow plasma expansion, and all I was doing was to shield the aperture from the extraction field.

**DIRECT EXTRACTION OF NEGATIVE ION BEAMS OF GOOD INTENSITY
FROM A DUOPLASMATRON***

G. P. LAWRENCE, R. K. BEAUCHAMP and J. L. MCKIBBEN

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

Received 17 December 1964

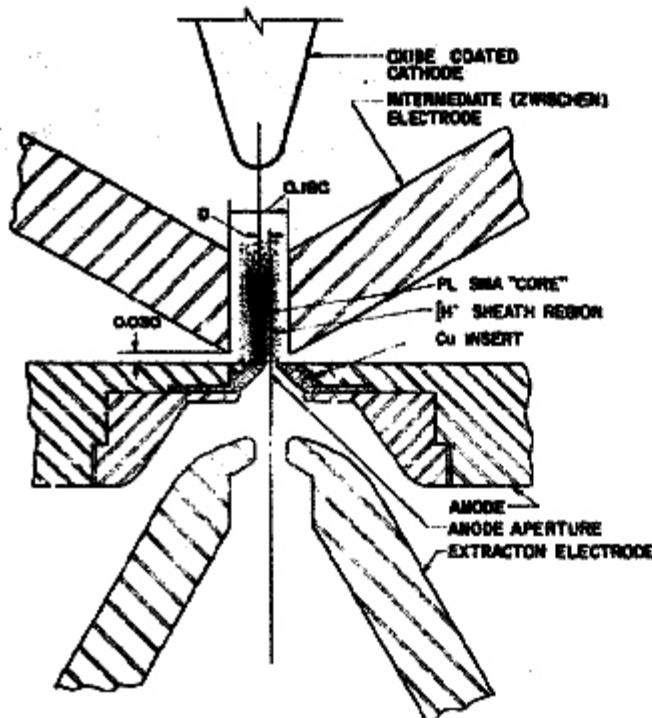


Fig. 1. Critical region of the duoplasmatron.

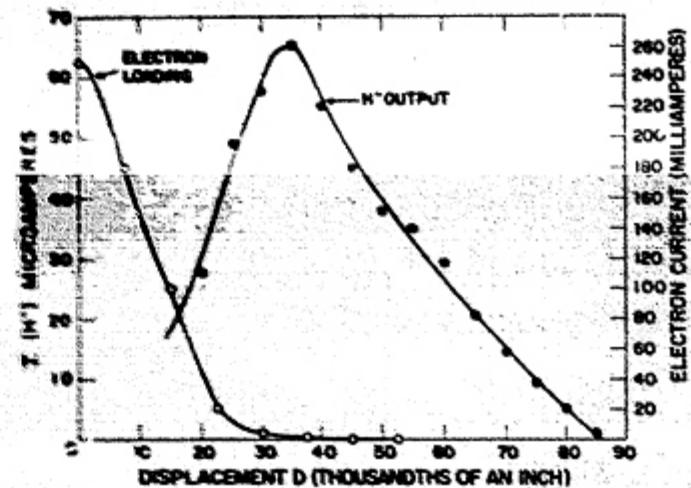
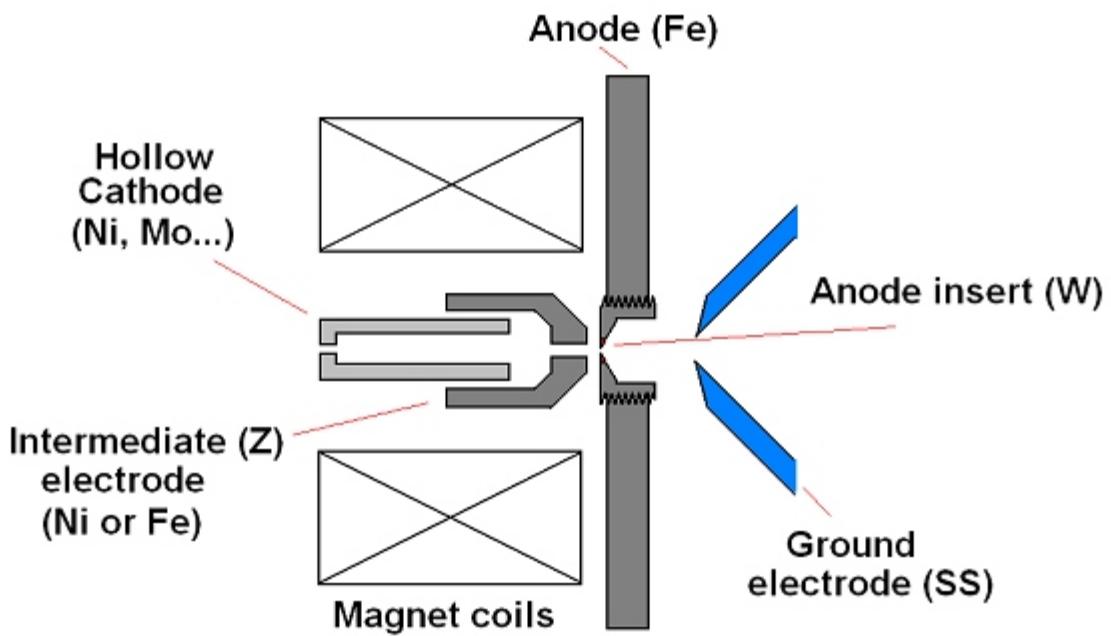


Fig. 2. H^- output and electron loading as a function of radial displacement.

Slide 17. There is a great need in SIMS to extract **negative** ions from the duo. This is also the case for tandem Van der Graaf accelerators. The problem is that simply reversing the source potential produces an intense **electron** beam that often can overload the accelerating power supply. (When I needed an electron beam to study electron-stimulated desorption on my first ims 3f, in the absence of an electron gun I ran the duo on argon so that the negative current extracted was just electrons; I could get these to the sample because there was no primary magnet.) Lawrence and colleagues from Los Alamos were the first to show that negative ions could be extracted if the Z electrode was displaced sideways with respect to the anode aperture. The plot at right shows the electron current (initially hundreds of millamps) dropping as the Z electrode shift increases, while the H- current (10s of microamps) increases.



Slide 18: Here is a simplified cross-section of a SIMS duoplasmatron. Because of the need to use oxygen the heated filament is replaced by a hollow cathode. (Although there are filament materials that are oxygen-resistant, such as rhenium, and I've often wondered if we would increase source brightness with a filament-driven arc.) There is still a lot of room in the source parameter space to play around and try to improve performance. One shouldn't assume that the manufacturer's parameters are necessarily optimum. In particular there can be many variations in the Z-electrode parameters.

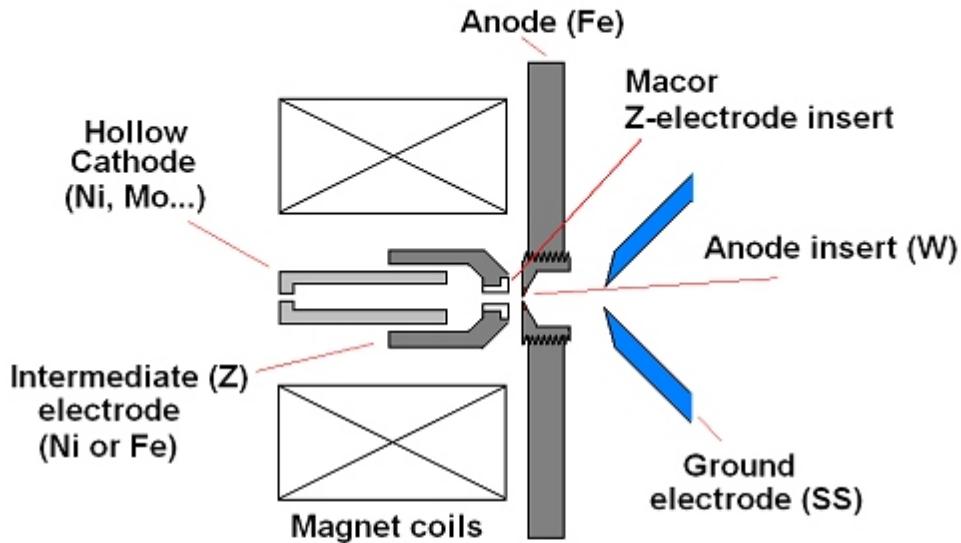
Z-electrode optimization:

a) AEI IM20 ion microprobe: Z-electrode aperture ~ 6 mm (1/4")
-- excellent +ve ion performance; poor for -ve ions (with 3 mm offset)

b) Early Cameca (ims3f #11): Z-electrode aperture ~ 3 mm
-- decent +ve ion performance; poor for -ve ions (~ 100 nA max)

Reduce aperture to 1/16 inch (x 1/8 in. long) to increase current density:
-ve ion current up to 1 μ A

Slide 19: The first SIMS instrument I played with was the AEI IM20 ion microprobe purchased by Drew Evans at the University of Illinois. As Drew noted in his talk, this was a fairly clever idea, to add an ion microprobe column to an existing high-resolution spark-source mass spectrometer, of which AEI had an installed base world-wide of around 50 instruments in the early 1970s, with users interested in solids analysis and thus potential SIMS customers. The attachment sold for \$100k versus \$250k for the competing Cameca IMS 300 and ARL IMMA, both of which were low mass resolution designs, so it had the potential to sweep the market. Unfortunately poor engineering and initially poor secondary ion optics design (which I was able to fix at Illinois) led to only a handful of such attachments being sold. However the duo design on this instrument was interesting. The Z-electrode opening was huge – 1/4 inch diameter. So there was essentially no mechanical constriction – all of the effect was due to the magnetic field shape in the opening. This source was the hottest duo I've ever worked with – for positive ions. With a spot beam I could drill into copper metal at a rate of a micron per second. But the negative ion performance, with a replacement Z-aperture offset 1/8 inch, was terrible. The Cameca ims 3f (#11) that I purchased in 1980 came with a Z-electrode opening of about 3 mm, and had decent positive ion performance (up to ~ 1 microamp) but maximum O⁻ current was no more than ~ 100 nA. I narrowed the aperture to 1/16 inch (~ 1.5 mm) and made the aperture length 1/8 inch, and was able to get the O-current up to 1 microamp, without sacrificing positive ion performance. Cameca adopted this modification and today delivers a Z-electrode that I think is 1.5 mm diameter by 3 mm long – roughly my dimensions in metric terms.



CN-ion beam: Hervig & Williams, SIMS V

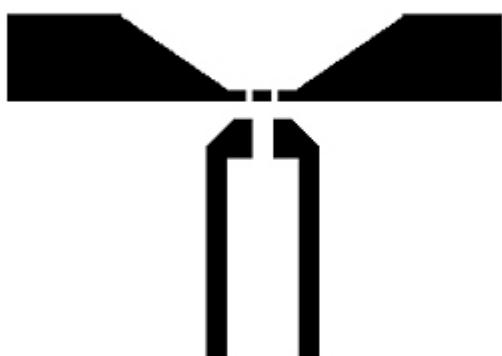
Corrosion-resistant Macor Z-electrode insert

Provides large magnetic aperture (+ve ions); small physical aperture (-ve ions)

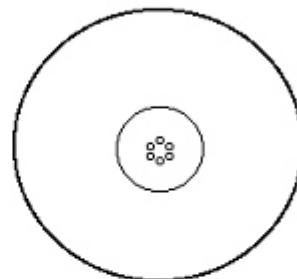
Slide 20: On the Cameca ims 3f (#64) that I bought in 1984 on moving to Arizona State University, my geochemistry colleague Rick Hervig wanted to measure oxygen isotopes on insulating samples. This was before there was an electron beam available for charge neutralization and we needed a negative primary ion beam that WAS NOT oxygen. We tried running the source on Freon and extracting F⁻ ions, which didn't work too well because the source wasn't stable. In addition to corroding the source components, halogenated gases tend to snuff out discharges and SF₆ for example is used to suppress discharges in the multi-MV terminals of Van der Graaf accelerators. So I had the idea to run the duo on a mixture of non-corroding CO₂ and N₂ to try to make CN⁻ (CN has one of the strongest bonds in chemistry and an electron affinity comparable to Cl, and so CN⁻ tends to form whenever carbon and nitrogen atoms are in the same county...). This worked quite well: we got about 75 nanoamps of CN⁻, but after running for 24 hours the current dropped significantly, and when we disassembled the source we found that the Z-electrode aperture had been eroded to twice its initial diameter. CN apparently is intensely corrosive for transition metals like Fe or Ni. Because the Z-electrode is normally floating, it occurred to me that we could use a protective insert machined out of Macor, and the insulating nature of the Macor shouldn't matter. The Macor would be corrosion-resistant and we would combine a small physical aperture (good for negative ions) with a large magnetic aperture as in the IMS 20, good for positive ions. This worked beautifully – in addition to ~ 75 nA of CN⁻ we could extract up to 10 µA of O₂⁺ -- and has been used by us since that time.

P. Hanley, K. Purser, General Ionex ~ 1975

Annular extraction of negative
ions from duoplasmatron



Cross-section

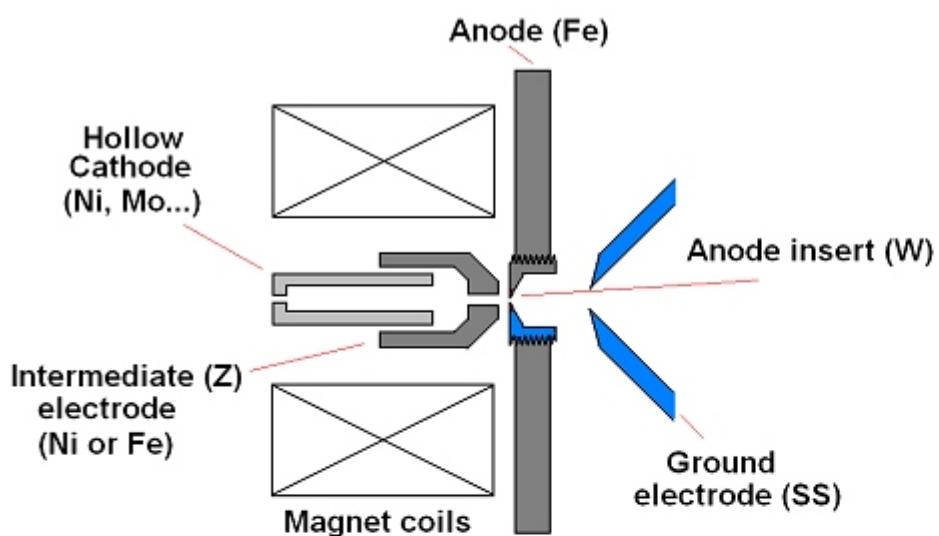


Top view

Do negative ions exist around the periphery of the plasma (requiring lateral offset of the Z-electrode)?

– NO!! Z-offset merely distorts the magnetic field and suppresses e^- extraction

Slide 21: Back to negative ion extraction. If you ask most people why the Z electrode must be offset to extract negative ions, the conventional answer is that the fragile negative ions hang out at the “cooler” edges of the plasma. This turns out to be wrong. In 1976, as I’ll recount later, Drew Evans and I were collaborating with General Ionex corporation to adapt their Cs ion source to our IMS 20 ion probe. Peter Hanley from GI told me of an experiment they did around 1975 that hasn’t been published to my knowledge. If the negative ions are formed around the edges of the plasma then the ideal extraction aperture, they reasoned, would not be a central hole but an annular slit. Obviously if you made an annular slit, the center would fall out, so instead they drilled a series of small holes around an annular path coincident with the edge of the Z electrode hole. The result was essentially ZERO current. They then realized that the effect of the Z offset was just to skew the magnetic field in order to suppress the electron extraction. This can be seen in the data of Slide 17.



DP with semi-magnetic anode insert holder
Hervig & Williams 1985

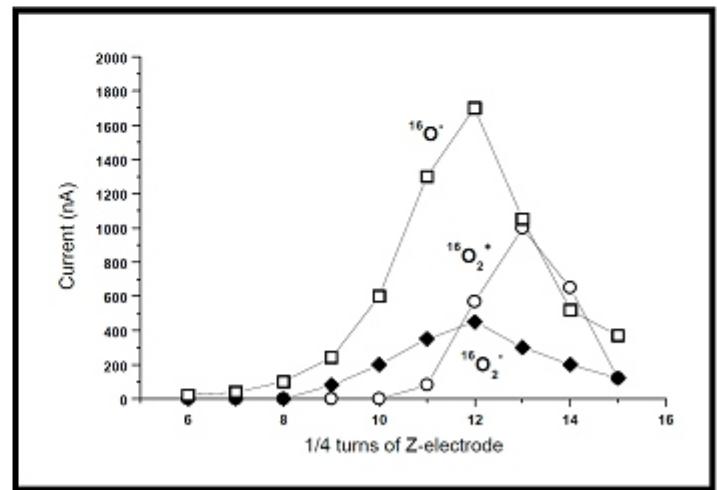
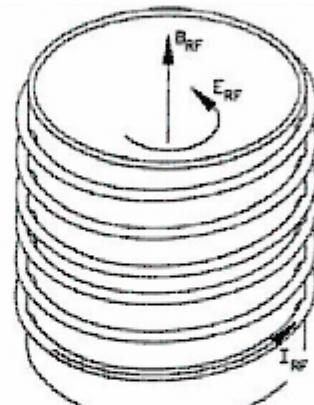
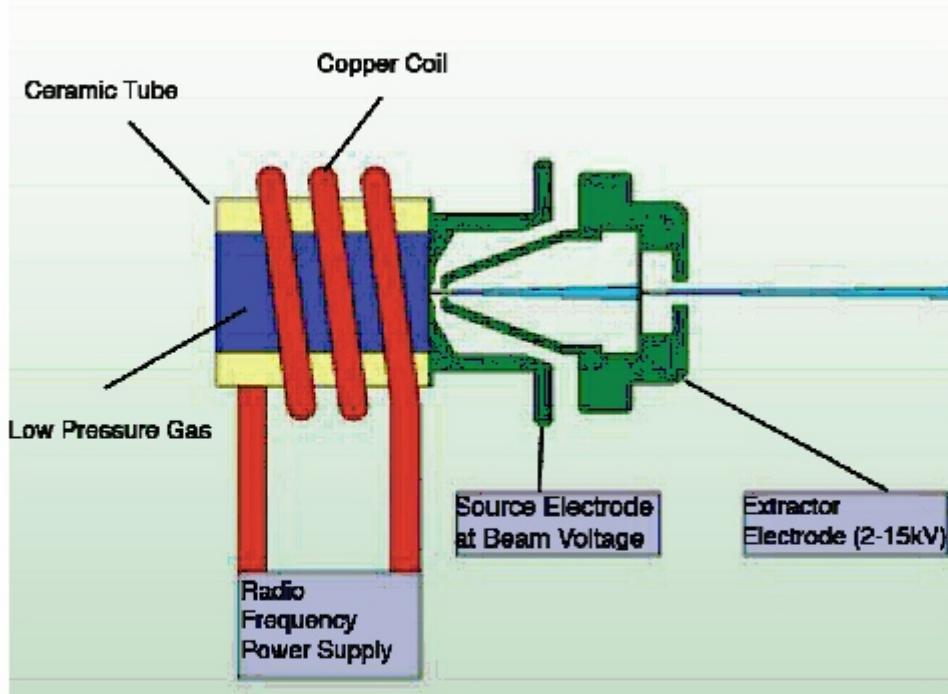


Fig. 1. Positive and negative ion current variation with Z-electrode position for semimagnetic anode source

Slide 22: Rick Hervig and I decided that instead of offsetting the Z-electrode, we would fabricate a magnetic asymmetry into the anode aperture holder to see if we could leave the Z electrode in place on axis. In the ims xf and other Cameca instruments the anode aperture (fabricated from a refractory metal such as Mo) is press-fit into a screw-in aperture holder made of soft iron. We had our mechanical shop braze together non-magnetic stainless steel (blue in the figure) and soft iron bars and then fabricate an anode aperture holder from this, so that in the figure the magnetic lines of force will flow upwards towards the gray soft iron half of the anode piece. The data bottom right show that the performance was almost perfect. If the O_2^+ signal peak delineates the on-axis position, the negative ion maximum is just $\frac{1}{4}$ turn of the displacement knob off this position, with pretty big current values. The hope was to get both positive and negative ion maxima to coincide exactly so that a simpler duo could be designed with no need for Z translation capability. I haven't taken the time to figure out why the two maxima are slightly displaced – it may be that we need the magnetic-nonmagnetic join somewhere a little off-axis, but for now we live with the situation shown in the slide. Let me note, however, that the anode works best with the join roughly parallel to the direction of movement rather than perpendicular as I had anticipated, so I'm not really sure exactly what's happening.

Inductively Coupled Plasma Ion Sources

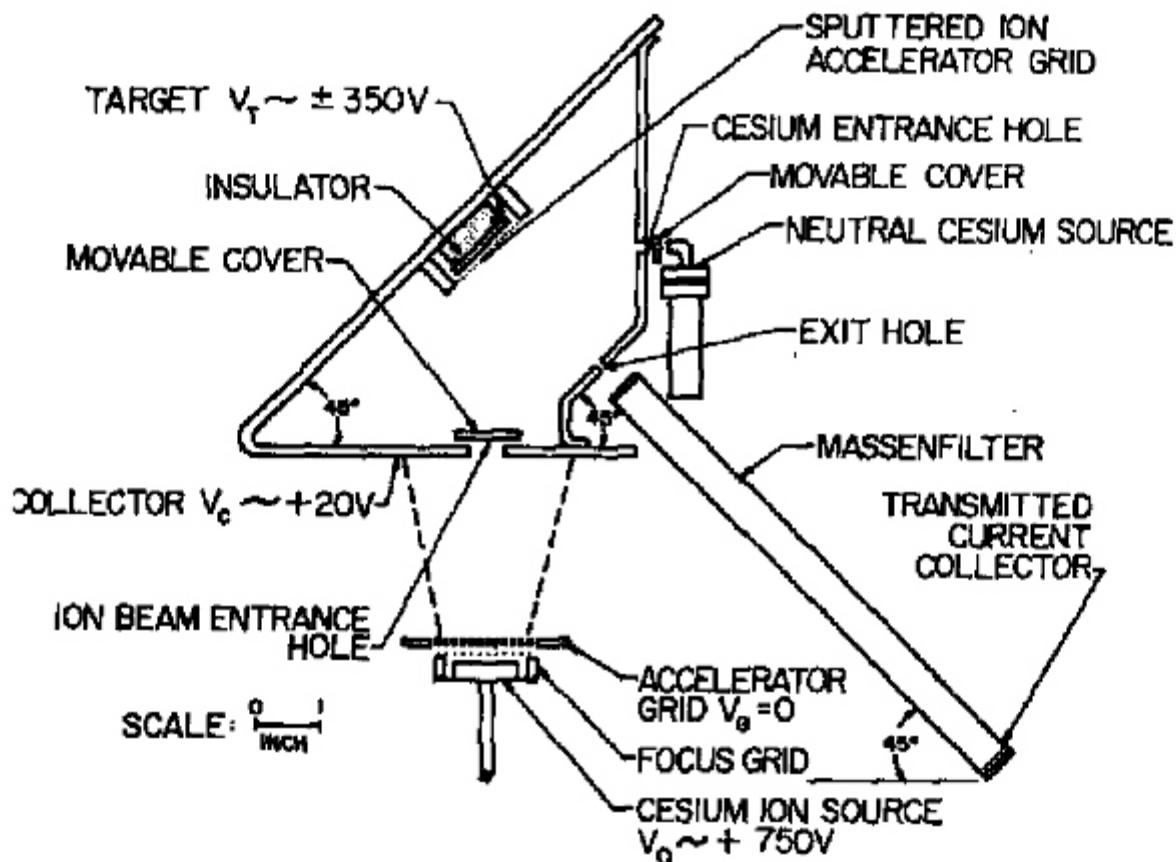


Oregon Physics (Noel Smith et al.): High brightness (low energy spread) RF source
~ 10x better than duoplasmatron for +ve ions; (-ve ion performance ????)

Slide 23: The future of SIMS gas ion sources, we hope, is with the RF ion source designs now coming from Oregon Physics. These generate a discharge using an external RF supply with no internal voltages in the discharge. The RF frequency is chosen so that electrons can be accelerated for ionization but the massive ions can't respond and so have very low energies. For a given plasma density, the ion energy spread is what determines the source brightness and thus the smallest attainable beam diameter. The RF source performance for positive ions is a factor of ~10 better than the duo and Oregon Physics is working with the NanoSIMS group at Livermore to try to optimize negative ion performance. The promise is an O^- beam for the NanoSIMS that will rival the Cs^+ beam size, i.e. ~ 50 nm or less.

Negative ions: Cs⁺ ion source

Slide 24: On to negative secondary ions and the Cs⁺ source



Cs+ SIMS Victor Krohn 1962
Space Technology Laboratories, CA

Slide 25: As noted, the earliest SIMS experiment used an alkali beam (Li^+) to generate negative ions, but this was mainly an experimental convenience – it was easy to generate alkali beams thermally. The first suggestion to use a Cs^+ ion source to deliberately enhance the production of negative ions came from Victor Krohn in 1962. There was intense interest around that time in ion sources for space propulsion (ion propulsion) purposes, out of which came technology for Cs^+ sources, liquid metal field ion sources and glycerol massive cluster electrospray sources. Krohn was working at one of the companies set up to pursue these technologies (and NASA money...). Krohn used a thermal Cs^+ source (with a very wide tungsten frit ionizer designed for space propulsion) to bombard a target and analyze sputtered negative ions in an early quadrupole mass filter. He even had a capability to spray Cs vapor onto the sample surface. This was a visionary effort years ahead of its time. Krohn later moved to Argonne National Laboratory where I met him when I postdoc'd there in the late 1960's. Bright, creative guy. We'll see him again a little later in this talk.

Evaluation of a Cesium Positive Ion Source for Secondary Ion Mass Spectrometry

H. A. Storms,* K. P. Brown, and J. D. Stein
General Electric Company, Vallecitos Nuclear Center, Pleasanton, California 94566

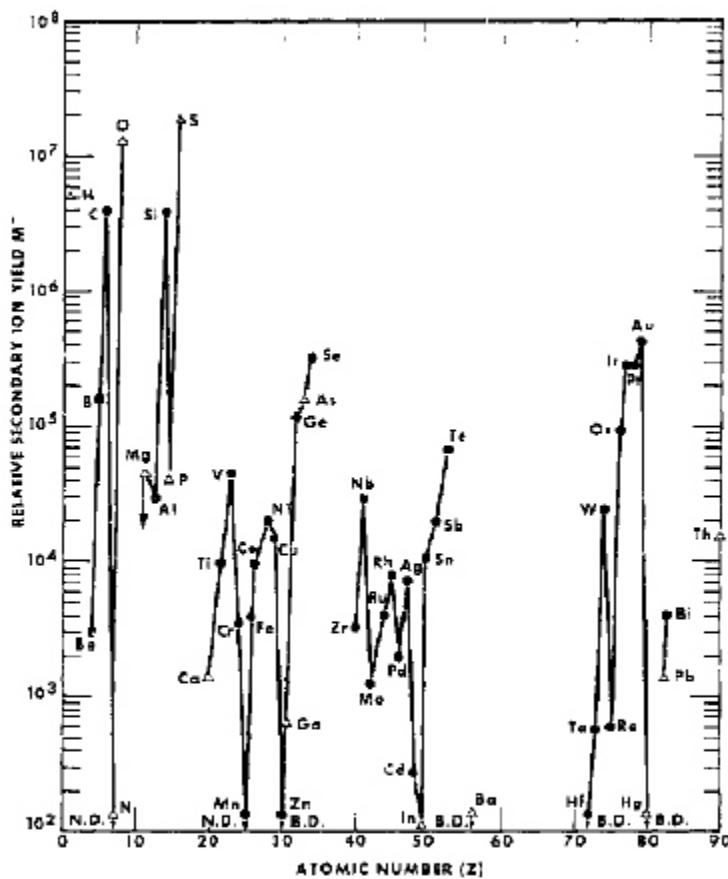


Figure 2. Relative secondary negative ion yield (M^-) from Cs^+ bombardment vs. atomic number of secondary ion. Relative Intensity is given in units counts/second/ 10^{-8} A. (●) Pure element. (△) Compound. B.D. = Barely Detectable. N.D. = Not Detected

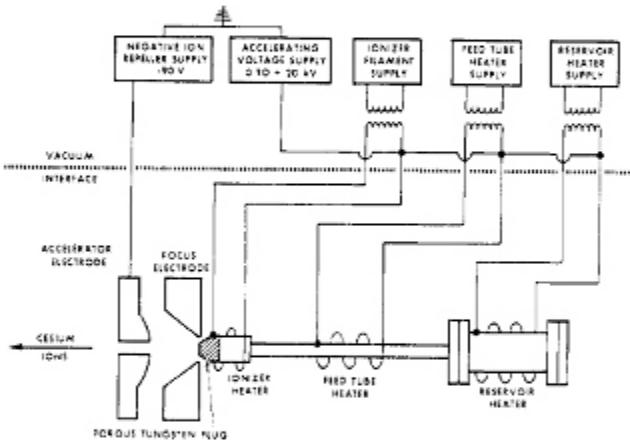


Figure 1. Experimental cesium positive ion source

ANALYTICAL CHEMISTRY, VOL. 49, NO. 19, NOVEMBER 1977 • 2023

Slide 26: Modern Cs source technology began with a joint US-Japan SIMS seminar organized in Hawaii in summer 1976 by Drew Evans and Japanese colleagues. I was able to attend and at the meeting Howard Storms from GE Vallecitos presented results from a Cs^+ source he had built for his ARL IMMA SIMS instrument. The source used a liquid Cs reservoir feeding a porous tungsten frit ionizer. Amongst other slides Howard showed the iconic slide reproduced here (and widely reproduced elsewhere) of negative ion signals from a range of mostly elemental targets sputtered with Cs^+ . Drew and I talked and agreed that we really had to get into this game and on returning to Illinois Drew hooked up with General Ionex, the company I mentioned earlier in connection with negative ion extraction. Ionex made ion sources for accelerators and supplied us with one of their Cs^+ ion sources. (Incidentally, Ionex had purchased the prototype of their cesium ion source around 1970 from Electro-Optical Systems, a Xerox subsidiary set up in Pasadena, also to develop space propulsion ion source technology. We'll meet Electro-Optical a little later also)

Evaluation of a Cesium Primary Ion Source on an Ion Microprobe Mass Spectrometer

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Charles A. Evans, Jr.

Materials Research Laboratory and School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

P. R. Harvey

General Ionex Corp., Ipswich, Massachusetts 01938

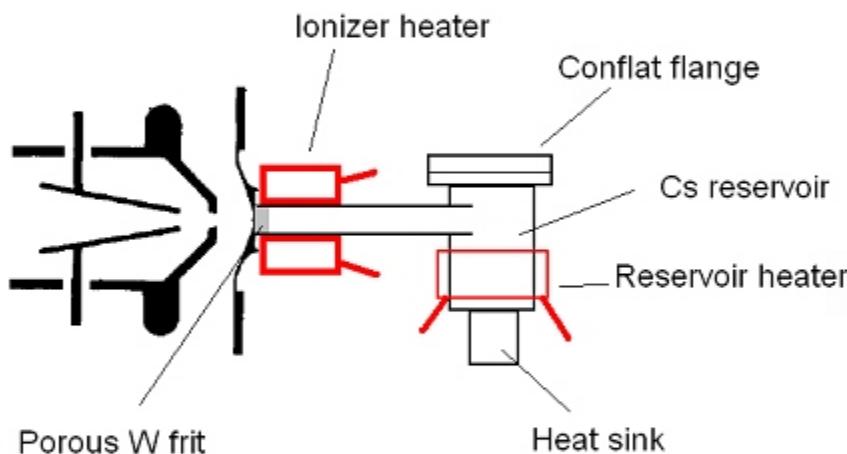
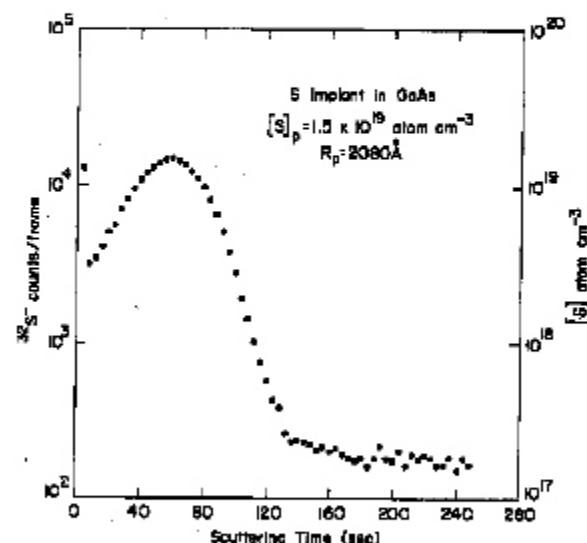
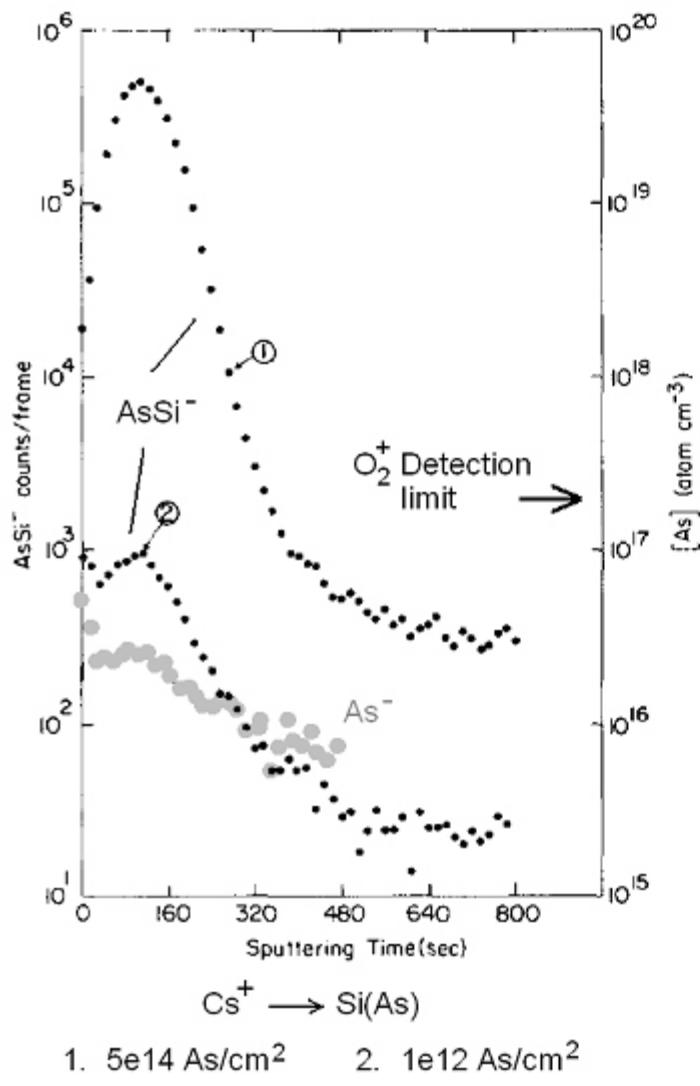


Figure 1. Schematic of cesium ion gun as mounted on AEI IM20 ion microprobe



ANALYTICAL CHEMISTRY, VOL. 49, NO. 8, AUGUST 1977 • 1399

Slide 27: We rapidly adapted the Ionex source to the IM 20 ion microprobe in the fall of 1976. The source had a heated reservoir containing liquid cesium. (Cesium was quite a lot of fun to play with, for those of us with pyromaniac tendencies...). I decided to explore depth profile applications and probably the first Cs^+ negative ion depth profile, of a sulfur implant, is shown here. (Note to current students: the instrument did not have a computer; count rate data were printed out sequentially on a printer resembling a supermarket receipt printer, then plotted by me by hand on semi-log graph paper, and finally given to a draughtsman to turn into a journal-quality figure. And we walked barefoot to the lab every day. In the snow...) The S^- detection limit of around 2 ppm is almost certainly due to an O_2^- background signal. In fact we moved so quickly that we got our paper into print in August 1977 before Howard Storms's paper appeared in November. But I always make it a point to acknowledge that it was Howard's presentation in Hawaii that inspired our work.



Depth profile detection limit of 3×10^{15} atom cm⁻³ for As in Si using Cs⁺ bombardment negative secondary ion mass spectrometry*

Peter Willems

Morris Research Laboratory, University of Illinois, Urbana, Illinois 61801

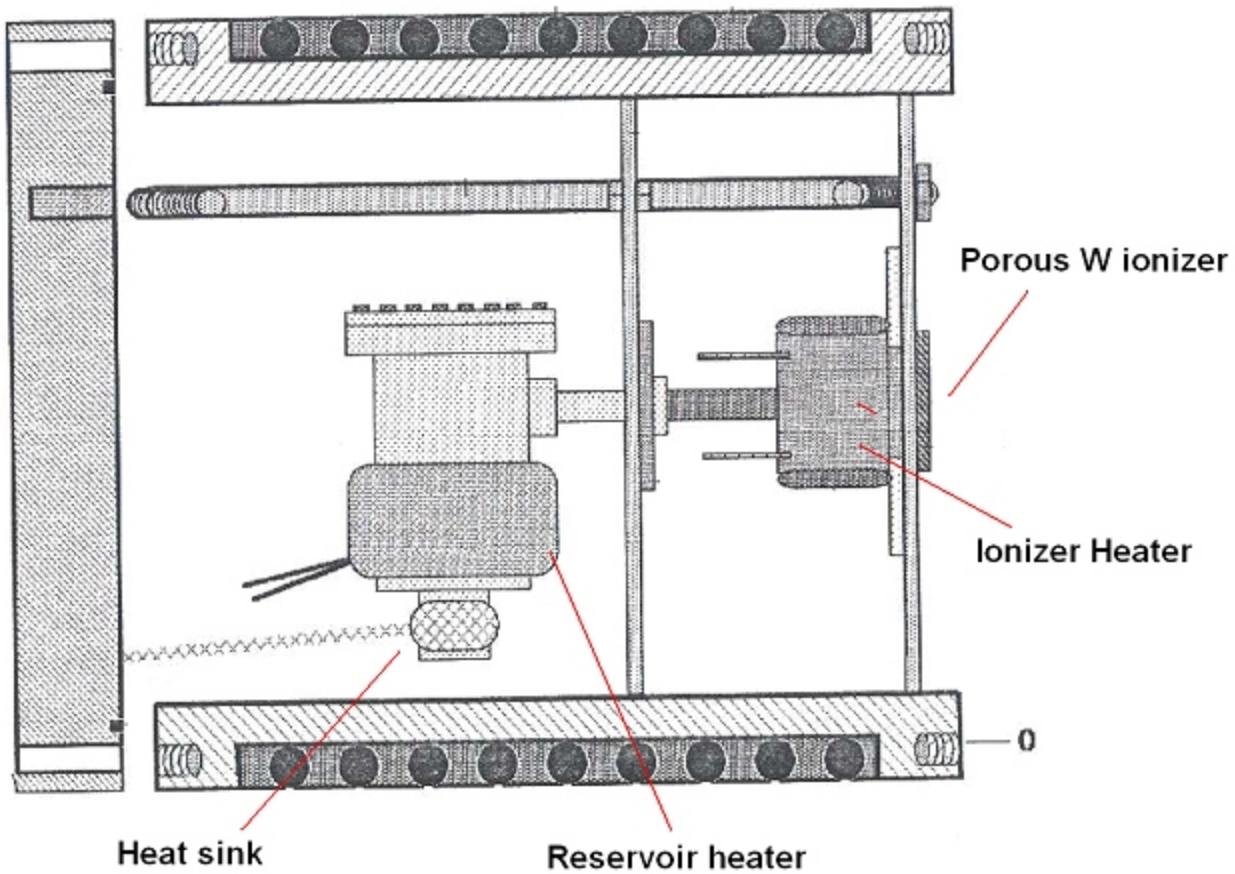
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(Received 24 February 1977; accepted for publication 21 March 1977)

Applied Physics Letters, Vol. 30, No. 11, 1 June 1977

Slide 28: Actually our first Cs source paper came out in June 1977 in APL. In January that year I decided to look at detection limits for As implants in silicon. Using an oxygen primary beam the limit was somewhere in the few e17 atoms/cm³ range due to a silicon-oxygen cluster interference at mass 75. Using an As implant with a dose of 5e14 As/cm² I was able to follow the signal down to a level of ~ 5e16 As/cm³ -- ~ 1 ppm. But this was not an intrinsic limit, just a dynamic range limitation. (The difference between a true background signal limit, as in slide 27, and a dynamic range limit is that in the former case the transition to a level background signal is quite sharp on the semi-log plot, rather than a gradual curve, as in curve 1 here.) Using a 1e12 As/cm² implant with a **peak** concentration of 1e17 As/cm³, the true background limit was shown to be as low as 3e15 As/cm³. Note also that this was the first use of the AsSi⁻ species, rather than the As⁻ atomic ion. I reasoned that AsSi should be chemically similar to CN and should therefore have a fairly high electron affinity. Data for the As⁻ signal for the 1e12 implant are shown as the gray points on the slide, plotted on the current scale on the left. It is clear that the ion yield is a factor of ~3 lower and the background a factor of ~ 10 higher for the As⁻ signal.



ASU Cs⁺ source (Richard Larea PhD Thesis 1985)

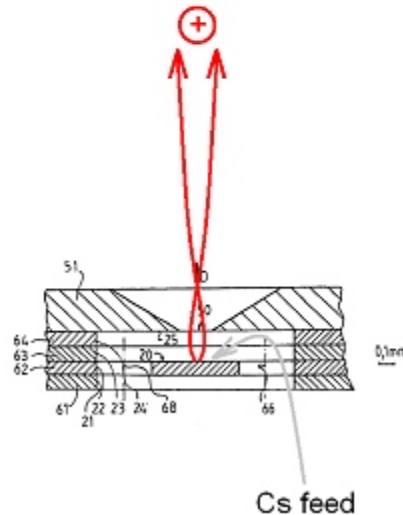
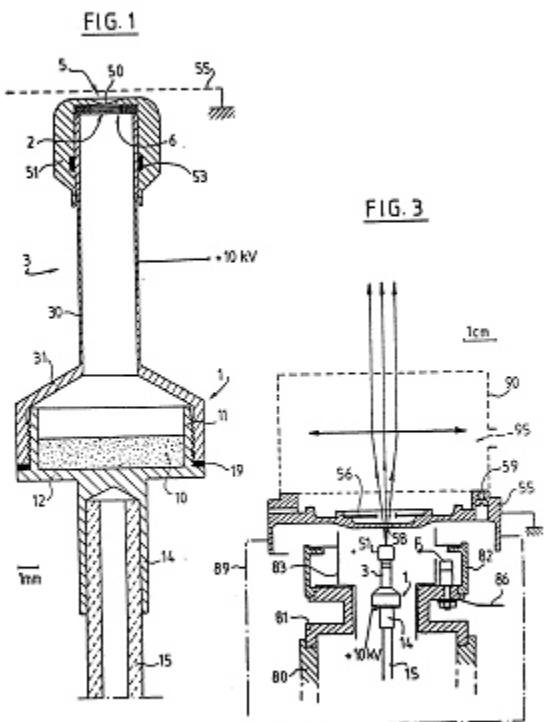
Slide 29: The tungsten frit ion source we developed at Illinois became the standard source for the early Cameca instruments. When I moved to Arizona State and took delivery of my ims 3f there, Richard Larea was my first graduate student and his first job was to design a Cs source for it (I refused to buy one...). The image is from Richard's PhD thesis. He had purchased one of the first Apple Mac computers with the WYSIWYG interface and amazing graphic capability and this image, and the rest of his thesis, was produced on that. (I only had an Apple II computer, so had a severe case of device envy.) This image shows how the source was centered in the housing by two metal plates that also served as radiation shields. One of the things Richard did was to look at the other alkali metal species. By this time we understood that primary species concentration in the sample was inversely proportional to the sputter yield, and we thought that the lighter alkalis would have lower sputter yields and therefore higher surface concentrations, so that maybe the optimum SIMS projectile was not in fact Cs⁺. Richard's work showed that the greater concentration for the light alkalis seemed to be offset by their lower electropositivity, so that in fact Cs⁺ remained the best choice. But it was worth looking at. These data were reported in the SIMS V proceedings.

Cameca Cs⁺ source

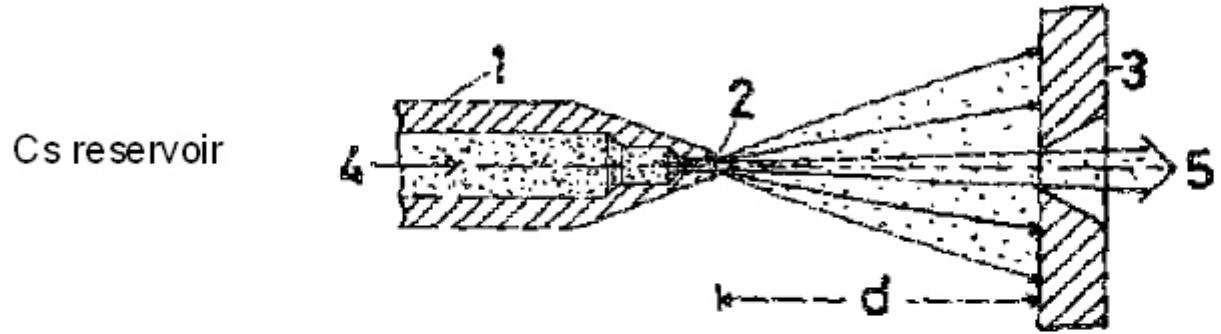
Bernard Daigne, Francois Girard,
Georges Slodzian

European patent filed 1984

Open Cs flow; flat ionizer



Slide 30: In France, Georges Slodzian was developing his NanoSIMS concept, which was going to require an extremely fine focus Cs⁺ beam, and Georges was not impressed by the tungsten frit design. To him it had two problems: (a) the surface of the frit was rough, making it a poor ion optical object for an ion column, and (b) brightness was limited by the slow diffusion of the cesium vapor through the fine pores in the frit. Georges designed a new Cs⁺ source, seen here in an image from his 1984 patent application, with some additions by me (gray and red lines illustrating Cs neutral and ion flow). The source has a small Cs reservoir on a thin mounting stub, so that thermal conduction to the source body is poor and the reservoir can be heated by electron bombardment. The Cs vapor flows up a thin tube to the ionizer head, which is shown in greater detail at the lower right. The Cs ionization is supposed to occur on the flat surface of a small tungsten button, and ions are extracted by field penetration through a Wehnelt electrode at the same potential as the button. Cs vapor flow is through channels around the button so that the current is not flow-limited. With some minor changes this source is standard on Cameca instruments and, on the NanoSIMS column, beam diameters as small as 30 nm are achievable. The commercial source was initially supplied with a cesium chromate feed material to avoid working with metallic cesium. One possible problem with this design is that in practice the Cs ions are not just formed on the tungsten button. Since the entire head region of the source is heated (by electron bombardment), ionization can take place everywhere and probably the entire small volume shown contains a vapor of Cs ions. In fact Slodzian is aware of this and has made efforts over the years to heat just the central region of the button, with a focused electron beam or a laser, to localize the emission site, but this has turned out to be difficult.



Cs+ Capillary source: H. Liebl & B. Senftinger 1988

Brightness ~ 10x tungsten frit designs

Slide 31. In 1988 Helmut Liebl published a source design based on a capillary geometry. Cs vapor flows readily through the heated capillary, avoiding the flow limitation of the frit design. Liebl made the end of the capillary a fine needle to have a high extraction field to reduce space charge effects. He measured the source brightness to be about a factor of 10 better than the frit design, but I'm not aware of any SIMS results with the source.

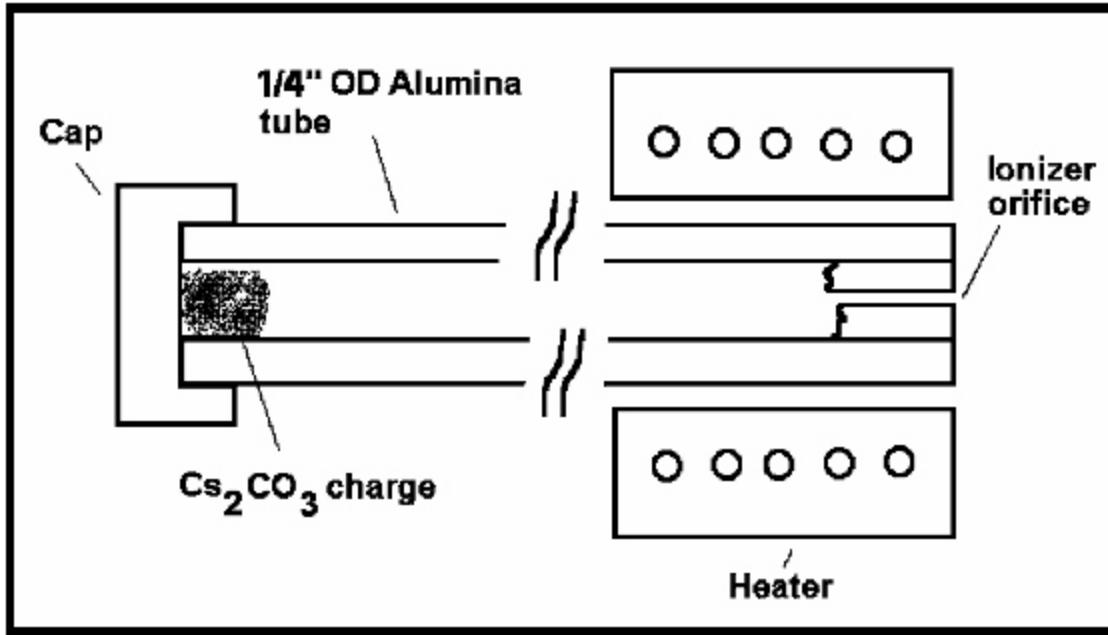
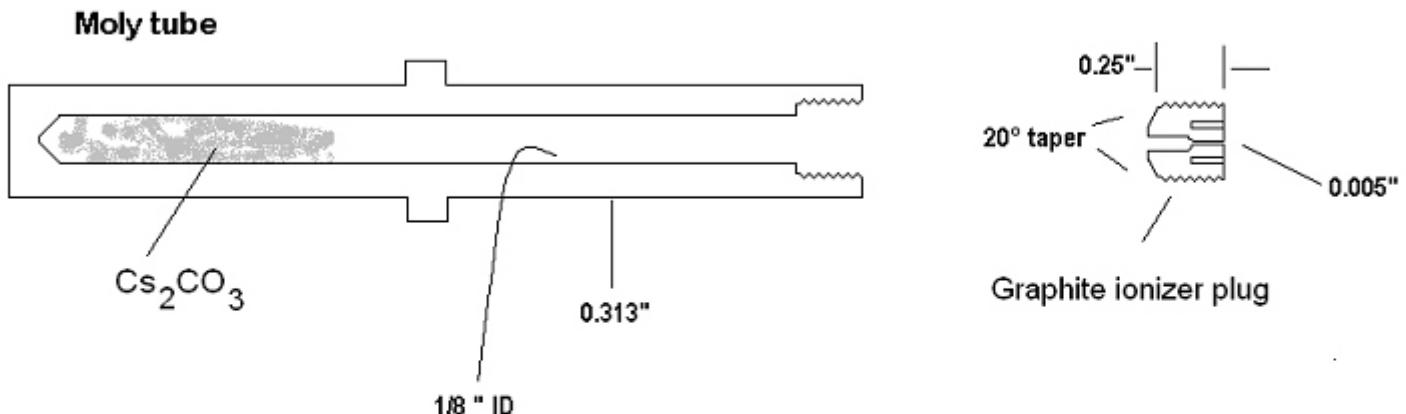


Fig. 2. Alumina tube cesium source design

P. Williams, H. Abdulkawi, R. Hervig, SIMS XII 1999

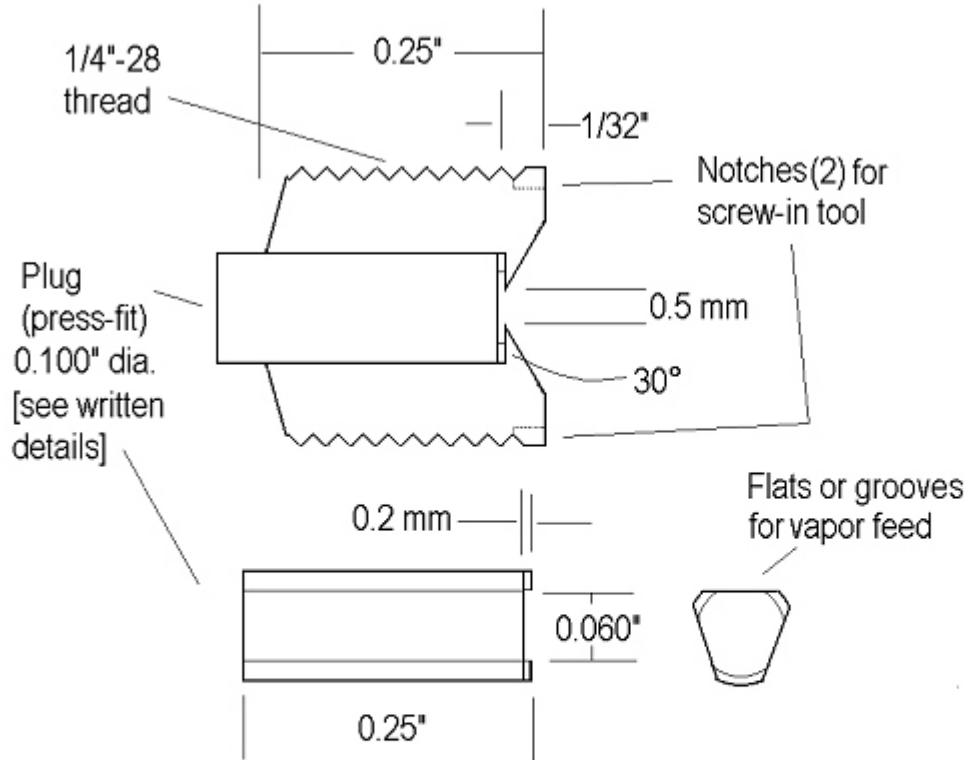
Slide 32: I was not aware of the Liebl paper when I decided a decade later to do much the same thing. To avoid expensive machining, I decided to make the source from ceramics: a $\frac{1}{4}$ inch OD alumina tube was sealed at one end with a blob of ceramic cement. After drying, the cement was friable enough to polish off the face and to drill easily with the smallest available drill size, around $250 \mu\text{m}$ diameter. We loaded the source with Cameca-standard cesium chromate and it ran rather well. Electrical conductivity in the heated ceramic was high enough and a reasonable beam current and size were obtained in our ims 3f primary column. However, when we opened up the source after some days of running we discovered that the chromate had apparently reacted with and softened the alumina so that the central part of the tube was a semi-melted blob. However, the chromium had apparently diffused into the alumina so that the melted blob was a beautiful ruby color! Clearly we needed another feedstock. I considered cesium halides, but I was worried about decomposition and spraying iodine or bromine atoms into the vacuum system. Cesium oxide was the desirable choice but that was probably going to be deliquescent, so we chose cesium carbonate. This will decompose into the oxide upon heating. Cameca was happy to seize on this idea as they were getting worried about toxicity issues with chromium.

1.75 "



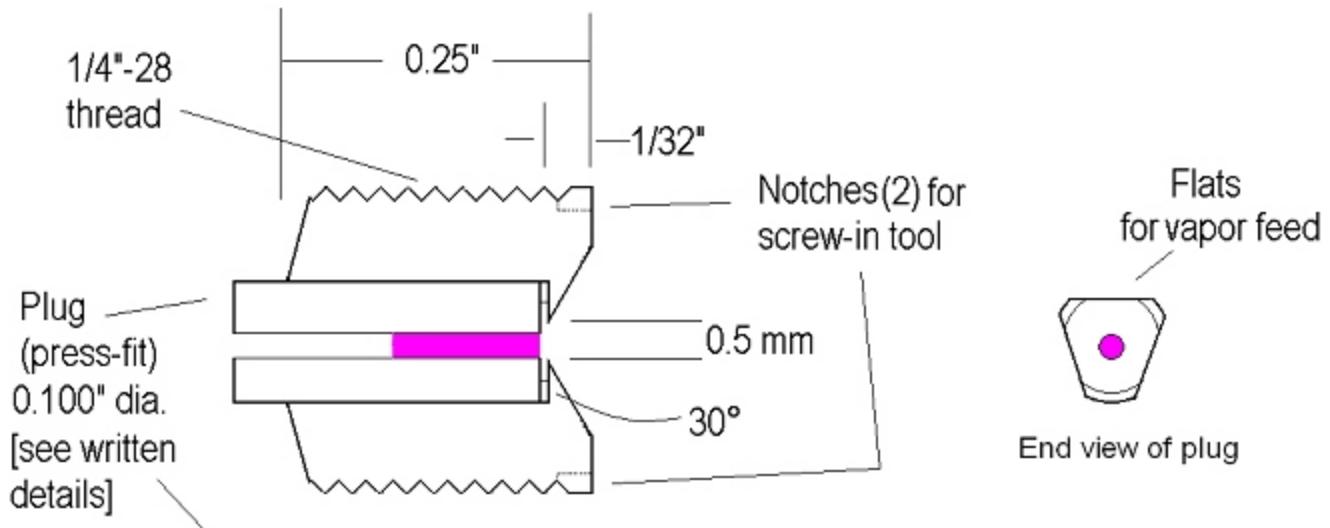
Current ASU Cs⁺ source
(uses resistive heater)

Slide 33: Our present capillary Cs⁺ source is shown in this slide. The source body is a molybdenum tube, machined to be held in the mounting structure shown in slide 29 for the liquid cesium frit source. The ionizer region is a threaded graphite plug with a tiny capillary channel drilled with the smallest drill bit our shop possesses. Graphite is an excellent material for this as it is quite soft so a very fragile drill can be used. Sealing occurs by the knife-edge shoulders at the base of the moly tube screw threads biting into the chamfered shoulder of the graphite plug. I have measured the aperture on a used graphite ioniser since returning from the workshop and it seems to be closer to 0.009"; I don't know if this is what we settled for or if the aperture erodes slightly with use. In any event, this source runs reliably for many months with a cesium carbonate charge in our ims 3f and can readily be refilled.



Slodzian ionizer fabricated in graphite

Slide 34: I've also engineered a version of the Slodzian source geometry in this graphite format. This is fabricated in two pieces. The screw-in portion contains the Wehnelt electrode geometry, then the ionizer is a press-fit graphite plug that pushes up against the base of the Wehnelt. A ridge machined around the rim of the plug maintains the specified 200 micron spacing of the Slodzian ionizer button, and the sides of the plug are ground away to allow vapor feed channels. All of this machining is trivial to accomplish in graphite. The graphite work function is variously reported in the range of 4.5 – 5 eV, at least as large as tungsten (4.54 eV). Interestingly, this source gave about a factor of 2 lower current in our column than the simple capillary source, so we have reverted to that geometry for everyday work.



Graphite Slodzian ionizer with LaB_6 insert for negative ion generation

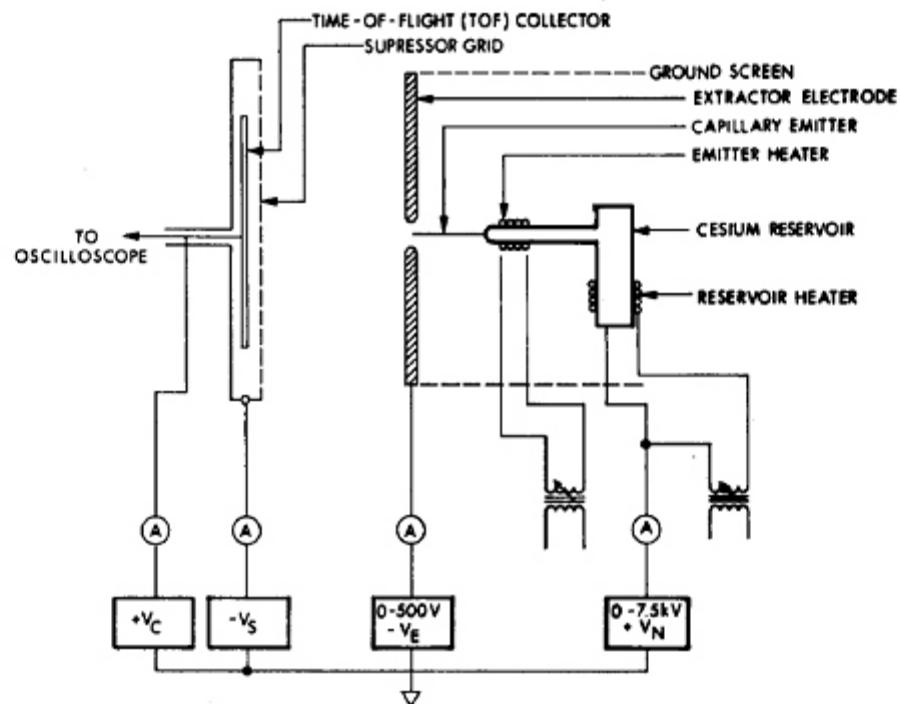
Slide 35: We've also made a graphite source version with a press-fit LaB_6 plug in the center of the ionizer with a view to generating thermal negative ions. Brief trials with this design and a CsI loading gave about 10 nA of I^- , but LaB_6 really needs to operate at a significantly higher temperature than we use for Cs^+ and we were reluctant to sacrifice our source heater so this work hasn't gone very far.

Liquid Metal Field Ion Sources

Electrohydrodynamic Ion Source*

JOHN F. MAHONEY, ARTHUR Y. YAHIKU, HOWARD L. DALEY, R. DAVID MOORE, AND JULIUS PEREL
Electro-Optical Systems, Pasadena, California 91107

ELECTROHYDRODYNAMIC ION SOURCE

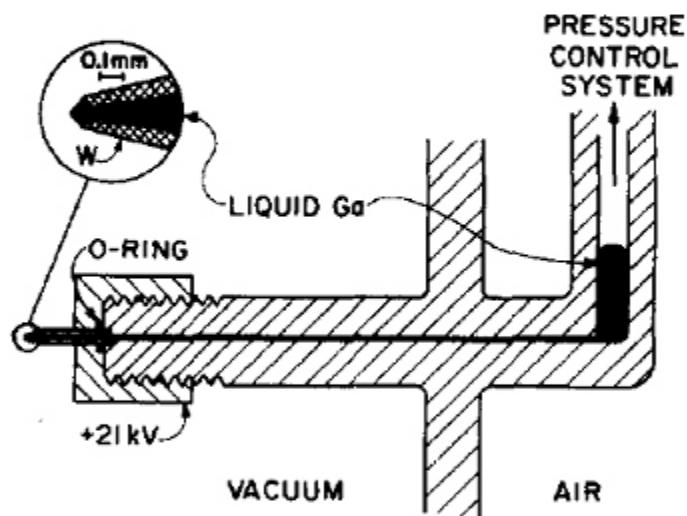


Cs⁺ field ion source

Slide 37: Liquid metal field ion source technology also originated in the space propulsion field. The Cs field ion source shown here is from a subdivision of Xerox in the 1960s, Electro-Optical Systems. Cs vapor from the heated reservoir condenses again as it nears the cooler capillary tip and is drawn to the tip by capillary action. Two of the authors here, John Mahoney and Julius Perel took their various ion source technologies (they also had a glycerol electrospray technology) to their own company, Phrasor Scientific, shortly after this paper was published, and we'll meet them again later.

Ion source of high brightness using liquid metal*

V. E. Krohn and G. R. Ringo



Applied Physics Letters, Vol. 27, No. 9, 1 November 1975

Slide 38: The earliest suggestion to use field ion sources for SIMS appears to have been from Victor Krohn, whom we have met earlier. This slide shows a source he reported in 1975 with Roy Ringo, also at Argonne. The source is a capillary design again, and not a particularly simple design. The authors charmingly comment in their paper that in the morning to start up the source it was usually necessary to tap it with a hammer! Presumably this breaks up any surface oxide layers that have formed. Krohn and Ringo had plans to incorporate this source into an ion microprobe SIMS design, but the source was sufficiently troublesome that they didn't get too far with the entire design. But once again Krohn had a vision that was ahead of the rest of the field.

MINIATURE ION SOURCES FOR ANALYTICAL INSTRUMENTS

R. CLAMPITT and D. K. JEFFERIES

UKAEA Culham Laboratory, Abingdon, Oxon, England

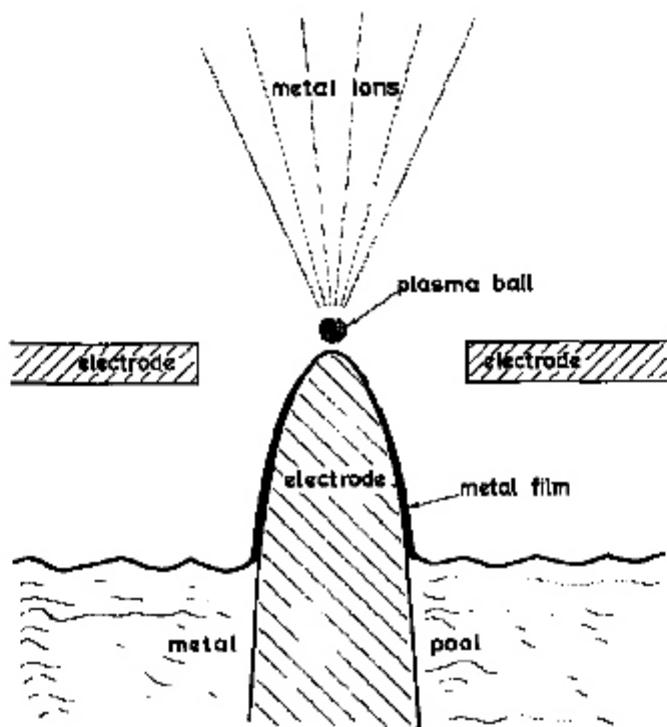
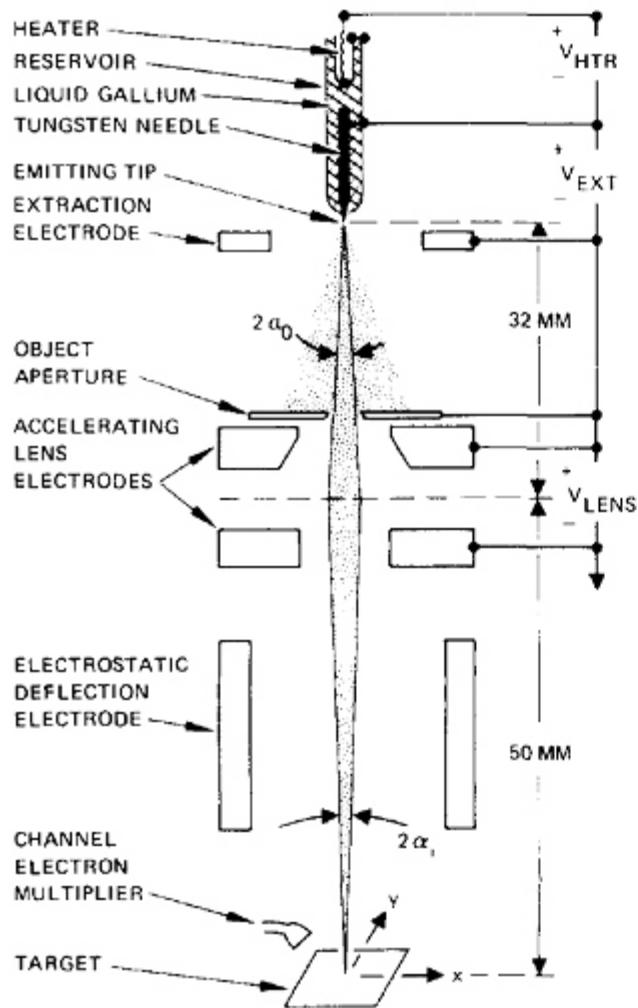


Fig. 3. Schematic of single needle ion source.

NUCLEAR INSTRUMENTS AND METHODS 149 (1978) 739-742

Slide 39: Modern liquid metal field ion technology derives from work by Roy Clampitt in England. He introduced the idea of using a tungsten needle wetted by the liquid metal to anchor the field emission, rather than trying to form a Taylor cone in the liquid metal itself.



A high-intensity scanning ion probe with submicrometer spot size

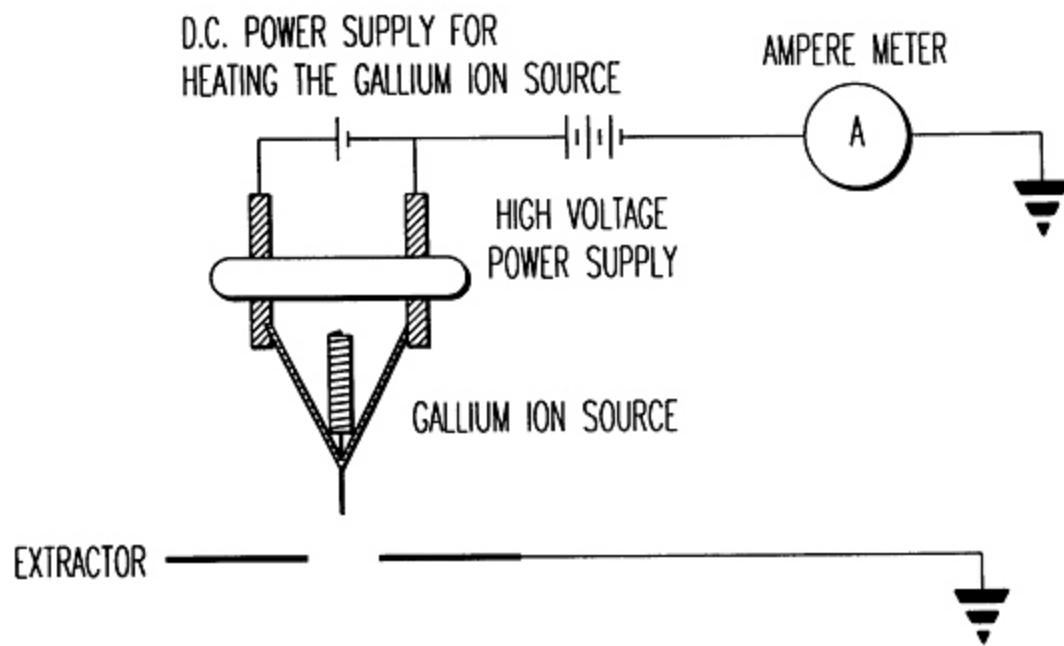
R. L. Seliger, J. W. Ward, V. Wang, and R. L. Kubena

Hughes Research Laboratories, Malibu, California 90265

(Received 9 October 1978; accepted for publication 11 December 1978)

FIG. 1. Schematic of the 57-kV gallium scanning ion probe.

Slide 40: The first implementation of the Clampitt approach on an ion column, that I've been able to find, was in 1978, shown here in a paper from Hughes Research Labs.



Modern FEI Ga⁺ field ion source

Slide 41: The modern liquid metal source design, available from FEI, is extremely simple. The tungsten field emitter is mounted on a heater loop with a gallium reservoir behind.

Ion Sources for Organics

Early history

Sloane & Press (1938): Found organic (contaminant) cluster emission (-ve ions)
(Hg⁺ primary ions)

Benninghoven (1969) Introduced "Static SIMS" (Ar⁺ primary ions)

Evans (~ 1973-75): Mass spectra of organics (Ar⁺ primary ions)

Torgerson & MacFarlane (1974): Discovered molecular ion ejection by MeV projectiles (eventually ²⁵²Cf fission fragments: "plasma desorption mass spectrometry, PDMS). Up to 45 kDa proteins

Barber (1981): Introduced fast atom bombardment of glycerol solutions ("FAB" – Ar⁰ projectiles). Up to ~ 25 kDa proteins

-- Later: "Liquid SIMS" using Cs⁺ primary ions

Slide 43: Early developments in the organic field are summarized here. Sloane and Press in 1938 had already found that sputtering can eject small organic clusters. In the late '60s Alfred Benninghoven started to use SIMS for surface studies and later realized the importance of keeping the primary ion dose below the "static SIMS" limit to ensure that each primary ion has a high chance of impacting a pristine sample region. Drew Evans, when I joined him in Illinois in 1974 was trying dynamic SIMS studies of organic targets, with some success. In 1974 a breakthrough came from a most unlikely source when two radiochemists at Texas A&M, David Torgerson and Ron Macfarlane, discovered accidentally that high energy nuclear decay products passing through organic films could desorb intact organic molecules, and later biomolecules. They pushed this to use extremely high energy fission fragments from ²⁵²Cf – for example, a 100 MeV Iⁿ⁺ projectile – and started to demonstrate mass spectra of highly polar molecules that had long been considered impossible for mass spectrometry. On the assumption that the dense ion-electron plasma produced by the passage of the fast fission fragments was the source of the ions, they named their technique "plasma desorption mass spectrometry" – PDMS. In 1981 Michael Barber at the University of Manchester, UK, had the idea of sputtering a sample dissolved in liquid glycerol. The glycerol is vacuum-compatible, and the beam impact on the liquid tends to stir the surface, removing damaged material and continually renewing a surface layer of undamaged sample molecules. To couple a sputtering source readily to the high-voltage ion source of his magnetic mass spectrometer, Barber had the idea to use a beam of fast neutral atoms, and they gave their approach the trendy name (for the era) of "FAB" – fast atom bombardment. The fast neutrals were produced by allowing Ar⁺ ions from a conventional ion source to charge exchange in an Ar gas collision chamber. Both PDMS and FAB eventually had the capability to produce molecular ions of proteins above 10 kDa. Eventually organic mass spectroscopists realized that there was nothing magic about neutral atoms and later used heavier Cs⁺ projectiles and the technique started to be called "liquid SIMS".

Simplest fast neutral source: the “Capillaritron”

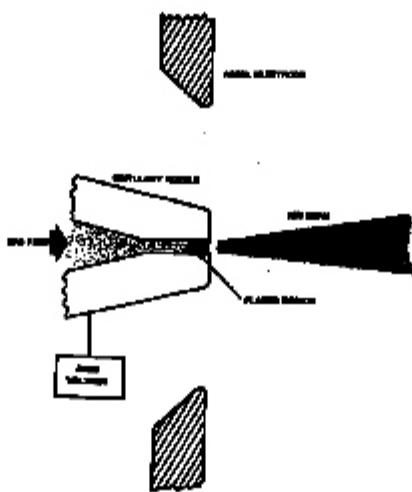


FIG. 1. Capillaritron ion source.

(and fast neutral)

Capillaritron: A new, versatile ion source

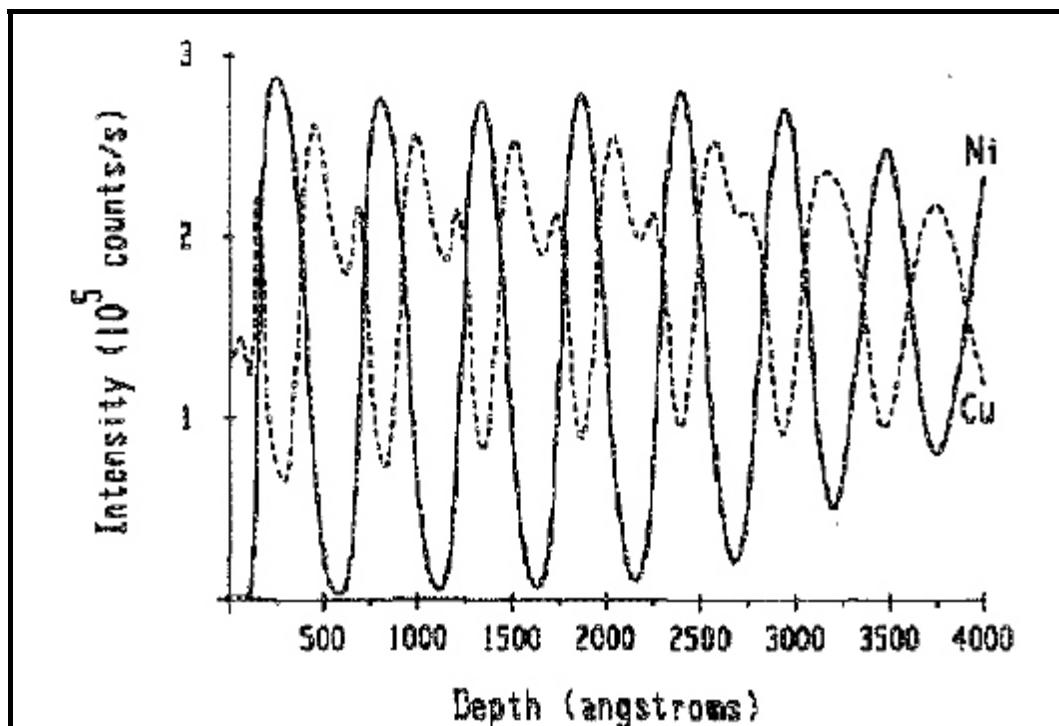
John F. Mahoney, Julius Perel, and A. Theodore Forrester^{a)}
Phrasor Scientific, Incorporated, Duarte, California 91010

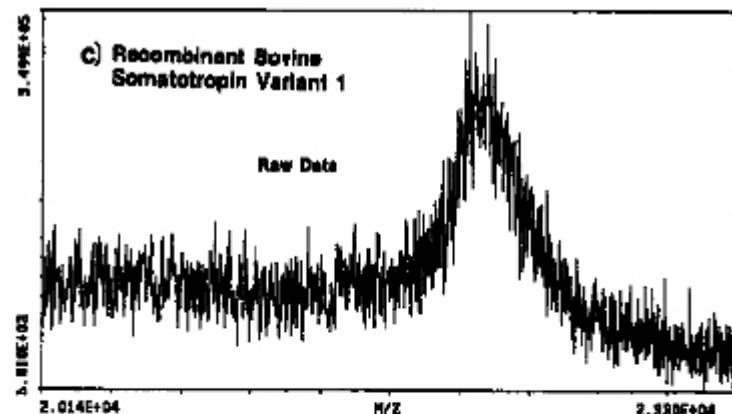
(Received 29 September 1980; accepted for publication 8 December 1980)

Slide 44: I skipped over this slide in my talk in the interest of time, but it's one of my favorites so I'll describe it now. In 1981 Mahoney and colleagues at Phrasor Scientific described an ion source they called a "Capillaritron" which consisted of simply a fine nozzle with Ar gas flowing through at atmospheric pressure, and an applied voltage of several kV – the world's simplest ion source. I mentioned Mahoney above as one of the people who took the electrospraying technology from Electro-Optical Systems into their own small company. They discovered the Capillaritron one day when they were electrospraying glycerol clusters from the nozzle in vacuum and pressurizing the glycerol flow with argon. Eventually they noticed that the glycerol was all gone, but the current was still there. When this paper came out I *had* to try the source in my first Cameca ims 3f. The capillary is easily obtained from the semiconductor wire bonding tool industry – the upper image at left shows one of these tips. Wire bonding of semiconductor chips to their substrate packaging is accomplished by feeding fine gold wire through the tool tip. My source is shown in the lower image. To my surprise I was able to get very little of the several μA of Ar^+ ions from the tip to the sample in the ims 3f. A little thought revealed that this is really a *terrible* SIMS ion source because it produces ions with a HUGE energy spread. The ions exiting the nozzle are accelerated through a fairly high pressure of

neutral argon where resonant charge exchange is highly likely. So new positive ions are produced and accelerated most of the way down the accelerating potential drop, producing ions with an energy spread amounting to almost the full potential drop – no good. But at the same time there is a corresponding production of fast neutrals, so this is also the world's simplest fast neutral source. Making lemonade out of lemons, I mounted a Capillaritron on the organic mass spectrometer at Arizona State when I moved there in 1981, where it operated for several years as an effective FAB source. The Phrasor people subsequently had a nice little FAB source business for several years until the advent of MALDI and ESI around 1990 took over the biomolecular MS business. At one point I mounted a capillaritron in the sample chamber of my Arizona State ims 3f, pointing at the sample and operating in such a way that only fast neutrals and not ions could hit the sample. The idea was to see the effect of sputtering insulating samples with a fast neutral beam, and whether the sample would charge. The result was that the ion signal faded and disappeared after just a few seconds as the sample began to charge: from the oxide target the positive ion yields were 10% or higher so that even with only neutrals impacting, a sizeable positive ion flux was leaving the sample.

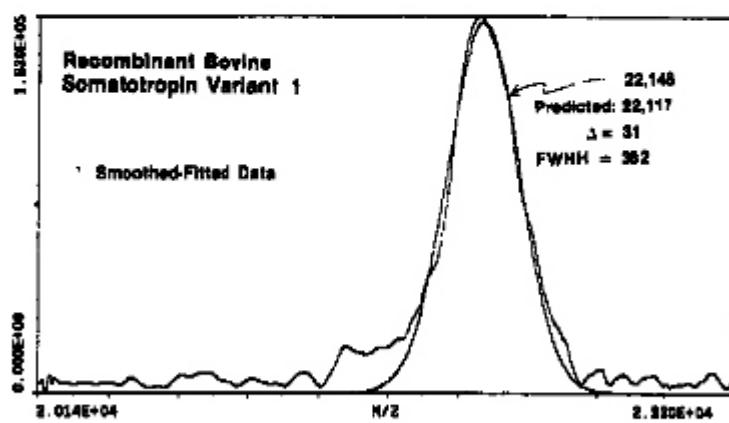
Greg Gillen and Steve Hues at ASU built a neat little multi-element sputtering assembly using several capillaritrons each pointing at a different metal target. Each source could be switched on and off instantly just by switching the high voltage on and off and they were able to demonstrate the production of a sputtered metal multilayer film. To achieve the cheapest possible system, high voltage feedthroughs were made from automotive spark plugs. Currents up to 500 μ A were obtained from each capillaritron. The figure below is a depth profile of a Cu/Ni multilayer film (O_2^+ primary beam) produced in this sputter deposition system, showing the matrix effect artifacts typical for such films.





Ultimate performance of "liquid SIMS" (thioglycerol/glycerol matrix),
35 keV Cs⁺

Bovine somatotropin, MW 22 kDa



Anal. Chem. 1990, 62, 1536-1542

Liquid Secondary Ion Mass Spectrometric Analysis of Natural and Recombinant Proteins and Monoclonal Antibody Light Chains with Molecular Weights between 16 000 and 25 000

Marshall M. Stegel,* Rushung Tse, Vivian W. Deelting, and Irwin J. Hollander
American Cyanamid Company, Medical Research Division, Lederle Laboratories, Pearl River, New York 10565

Slide 45: I included this slide to remind the audience, and the reader, that there is no intrinsic barrier to sputtering very large biomolecular ions with an atomic primary ion beam. This shows the ultimate performance of liquid SIMS. With a 35 keV Cs⁺ beam a molecular ion peak of a 22 kDa protein was detectable, albeit with terrible signal/noise and almost certainly very low efficiency.

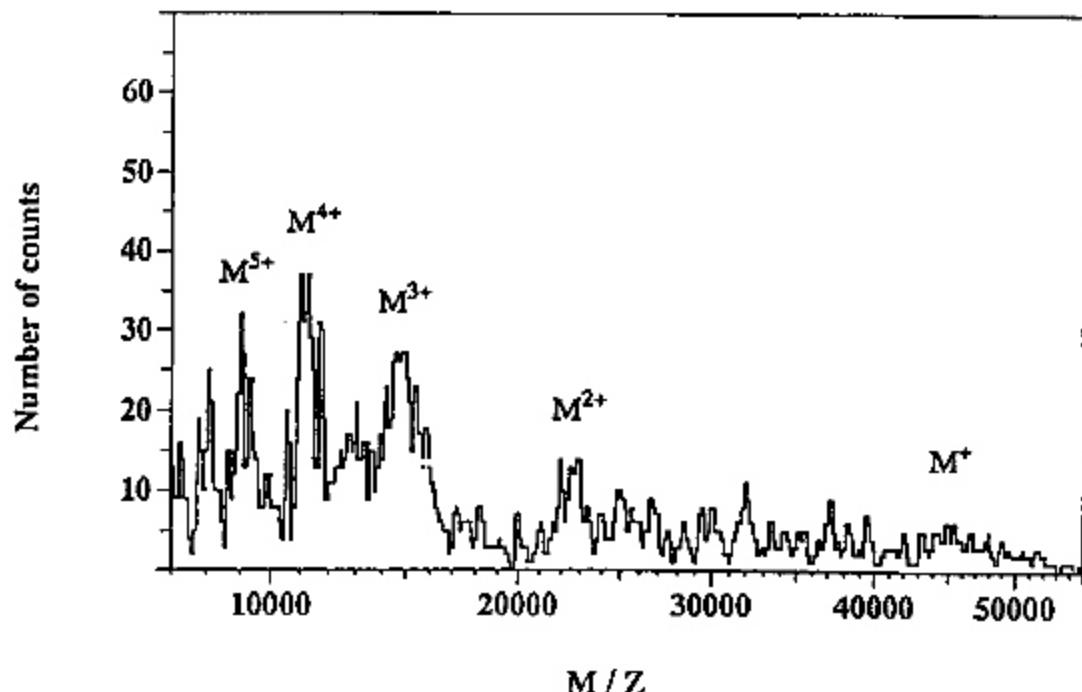


Figure 2 PDMS spectrum of positive ions from ovalbumin (45 000 u) illustrating intact ejection of whole molecular ions in PDMS [21]

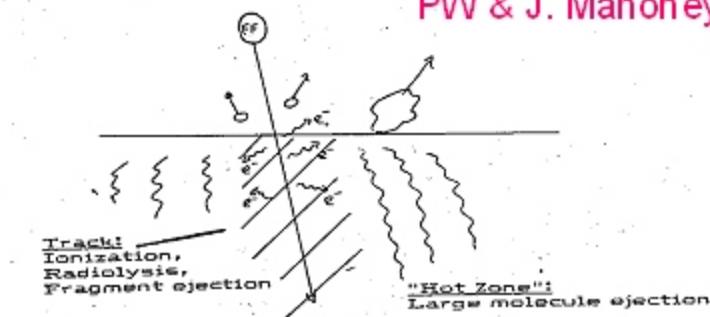
Ultimate performance of “PDMS” (^{252}Cf fission fragments): Ovalbumin, 45 kDa

G Jonsson, A. Hedin, P. Håkansson, B.U.R. Sundqvist, H. Bennich and P. Roepstorff,
Rapid Commun. Mass Spec. **3** (1989) 190.

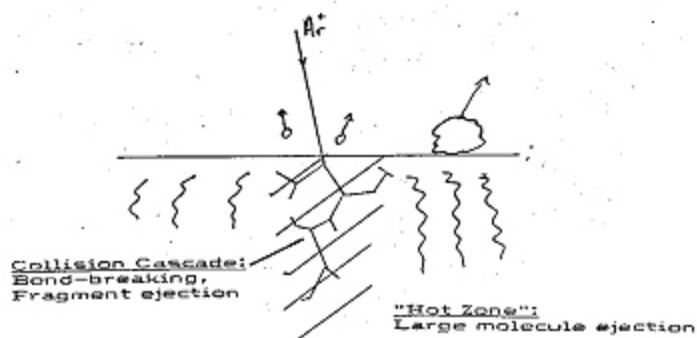
Slide 46: This slide similarly shows the upper limit of “PDMS”. With a 45 kDa protein target, peaks for multiply charged ions were detectable showing that intact molecular species were ejected. (Although it does seem to be a bit of wishful thinking to label the noise in the 45 kDa region as an M^+ signal...)

MCI Concept (1983)

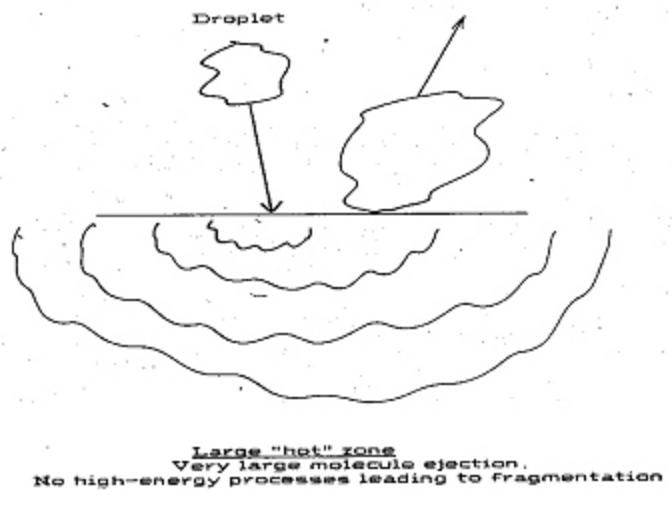
PW & J. Mahoney (Phrasor)



A. Fission-fragment (ff) impact, leading to extensive ionization and radiolysis around the particle track. Small fragments are ejected near the point of impact. Large molecule ejection can occur in the "hot zone" initiated by the atomic motion in the track.

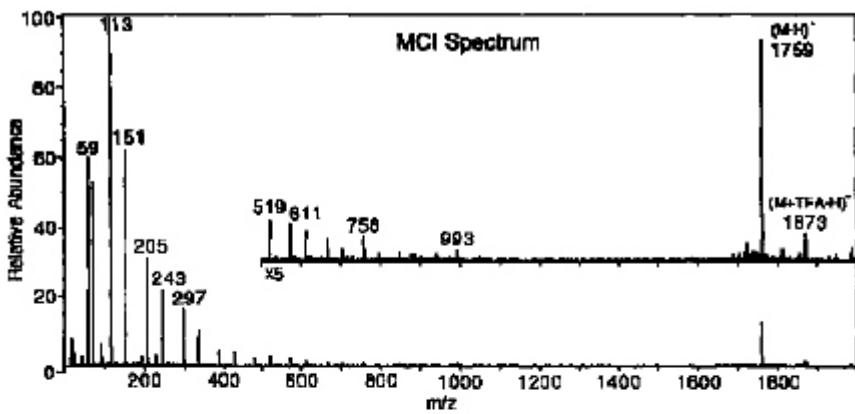


B. Fast ion impact, leading to bond-breaking in the atomic collision cascade. Small fragments are ejected near the impact point, while large molecule ejection can occur in the "hot zone" initiated by the atomic motion in the cascade.



C. Large droplet impact. No collision cascade develops because individual atomic velocities are too low to break bonds. The impact creates a very large "hot zone" from which very large molecules can desorb.

Slide 47. This slide is taken from an NSF proposal I wrote in 1983 with John Mahoney of Phrasor. Looking at the similarity of the mass spectra from keV and MeV projectiles, one can draw pictures of the impact sites in the two regimes (left). The direct impact site is subjected to very high energy deposition -- $\sim 10^4$ eV/nm for fission fragments and a factor of ~ 5 less for 10 keV Ar^+ . Clearly molecule survival along this central track is unlikely, and the dominant noise background of both MeV and keV spectra must arise in this region. Intact molecules must originate in a hot annular zone where the temperature is high enough to desorb intact (desolvated) molecules but too low to cause much fragmentation. I reasoned that it was desirable to create the hot zone directly, by impact of a much larger projectile with much lower energy per nucleon, and avoid the high-energy events leading to fragmentation. Mahoney had the technology to make such projectiles, by electrospraying massive glycerol clusters in vacuum (a space propulsion technique), and we wrote what I thought was a pretty nice, creative proposal. Unfortunately we ran into the type of NSF reviewer for whom nice creative proposals were anathema, who stated that "obviously" what we suggested couldn't work (and implied that we were stupid for suggesting it – I've never had a more insulting review).



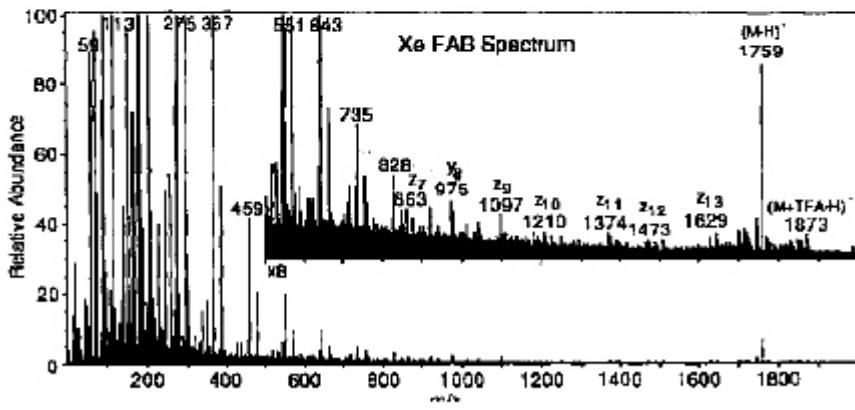
Shock Wave Model for Sputtering Biomolecules Using Massive Cluster Impacts

John P. Mahoney and Julius Perl
Primer Sciences, Inc., Danville, California, USA

Terry D. Lee and P. A. Martin
Division of Immunology, Beckman Research Institute of the City of Hope, Duarte, California, USA

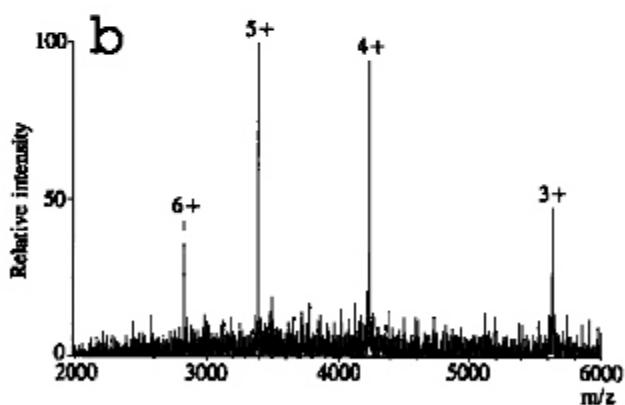
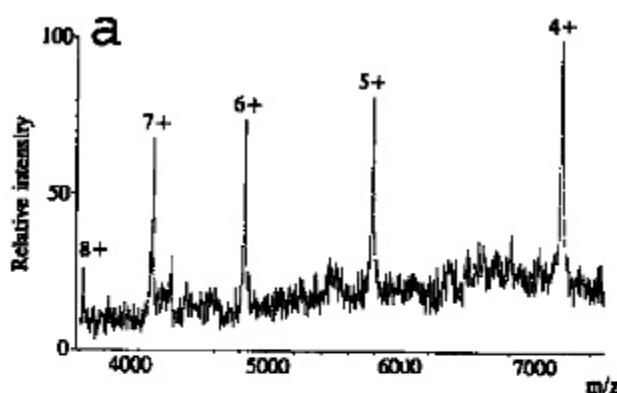
Peter Williams
Department of Chemistry, Arizona State University, Tempe, Arizona, USA

J Am Soc Mass Spectrom 1992, 3, 311-317



Slide 48: My ims 3f arrived around the same time as the negative review, so I had other things to occupy me, but Mahoney stuck with the idea and later hooked up with Terry Lee, an organic mass spectroscopist in Los Angeles. In 1991 they showed that the approach worked EXACTLY as I'd predicted: comparison of the MCI spectrum with a Xe FAB spectrum of the same analyte (in a glycerol matrix) showed a relatively intense parent peak and much smaller amounts of fragmentation. (There is some feeling that the few fragments seen in the MCI spectrum arose from residual glycerol molecular ions in the cluster flux, so that the cluster performance should be even better than shown here.) In fact Mahoney and colleagues didn't include me in their first publication (he later told me he forgot that it was my idea...) but we hooked up a year later to write the mechanism paper shown above. A typical cluster projectile is estimated to contain up to a million glycerol molecules and 100 – 200 proton charges; with 10 kV acceleration the cluster energy is 1-2 MeV, but energy per nucleon is only a fraction of an eV. We attributed the molecular ejection to shock heating by impact of the supersonic glycerol cluster and vaporization of both the cluster and a comparable volume of the target.

Ultimate (?) performance of MCI
(limited by MS mass range)



JOURNAL OF MASS SPECTROMETRY, VOL. 30, 149-151 (1995)

Massive Cluster Impact Ionization on a Four Sector Tandem Mass Spectrometer

D. Fabris, † Z. Wu and C. C. Jenekhe
Structure Biochemistry Center, University of Maryland Baltimore County, 3400 Wilkens Avenue, Baltimore, MD 21228,
USA

Figure 1. Positive ion spectra of: (a) bovine carbonic anhydrase II (29 021 Da); (b) horse heart myoglobin (16 951.5 Da).

Slide 49: Unfortunately, by 1991, MALDI and ESI were taking over the biomolecular mass spectrometry world and MCI was an orphan technique. Fabris and colleagues did report these spectra in 1995: (multiply-charged) molecular ion peaks with excellent signal/noise were obtained for myoglobin (~17 kDa) and carbonic anhydrase (~ 29 kDa).

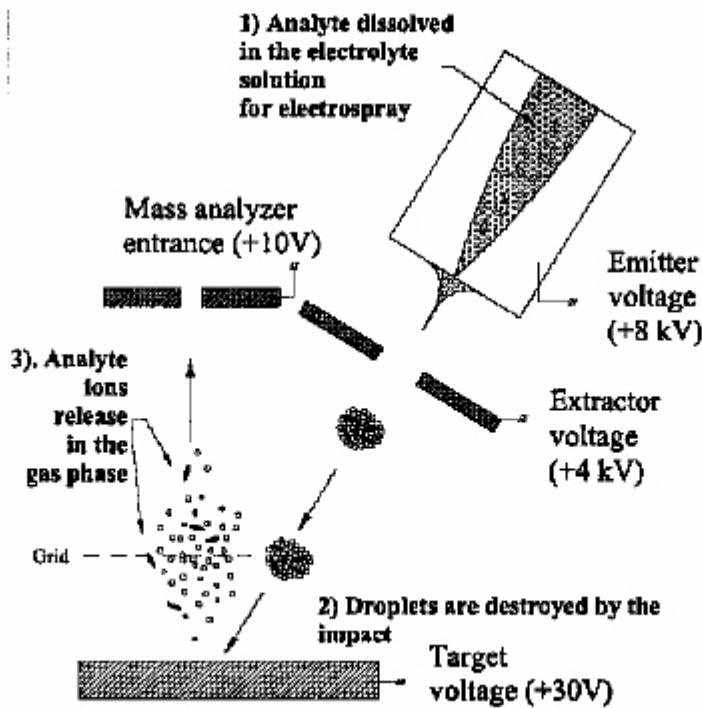
Impact desolvation of electrosprayed microdroplets – a new ionization method for mass spectrometry of large biomolecules

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Received 15 August 2001; Accepted 2 September 2001

SPONSOR REFEREE: Dr. John B. Fenn, Virginia Commonwealth University, Richmond, VA, USA



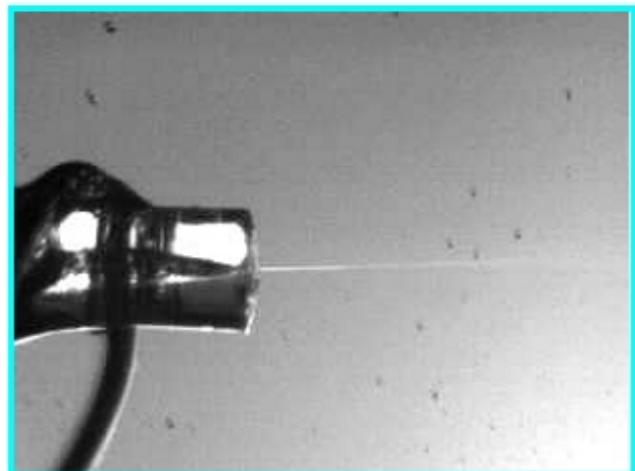
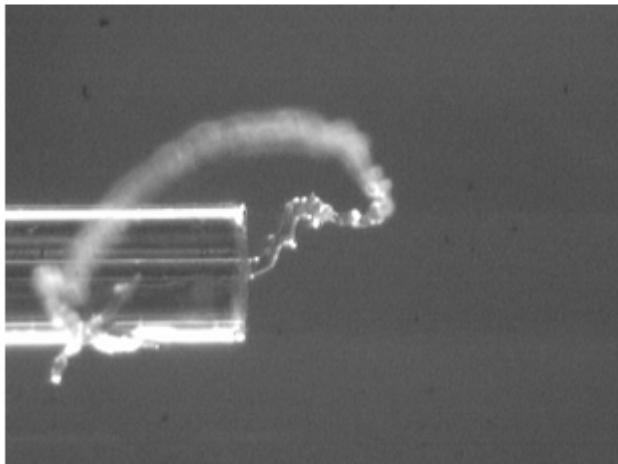
Slide 50: (I omitted the next few slides from the talk in the interest of time, but have re-inserted them here.) I finally got some funding to explore MCI around 2000, from the NIH Human Genome Project. The idea was to explore the technique for DNA mass spectrometry and sequencing. If we could generate molecular ions of DNA with a low extent of multiple charging it might be possible to read out Sanger sequencing mixtures in a mass spectrometer, much faster and with much greater accuracy than by gel electrophoresis. As sometimes happens with me, between the time the proposal was written and the funding arrived, a throwaway concept in the proposal had grown to lead importance. The idea was to include the analyte in the electrosprayed clusters themselves and explode the clusters in the shock impact event. The resulting ions were analyzed in an orthogonal TOFMS. We hoped that this approach would provide more facile coupling to liquid sample handling for the rapid sample throughput needed for DNA sequencing. The acronym for the approach is IDEM (I have never had the knack of generating sexy acronyms, like FAB or DESI, possibly because I like to stick close to the physics of the process). We did have a fairly distinguished sponsor referee – John Fenn about a year before he went to Stockholm.

Massive cluster spraying (in vacuum)

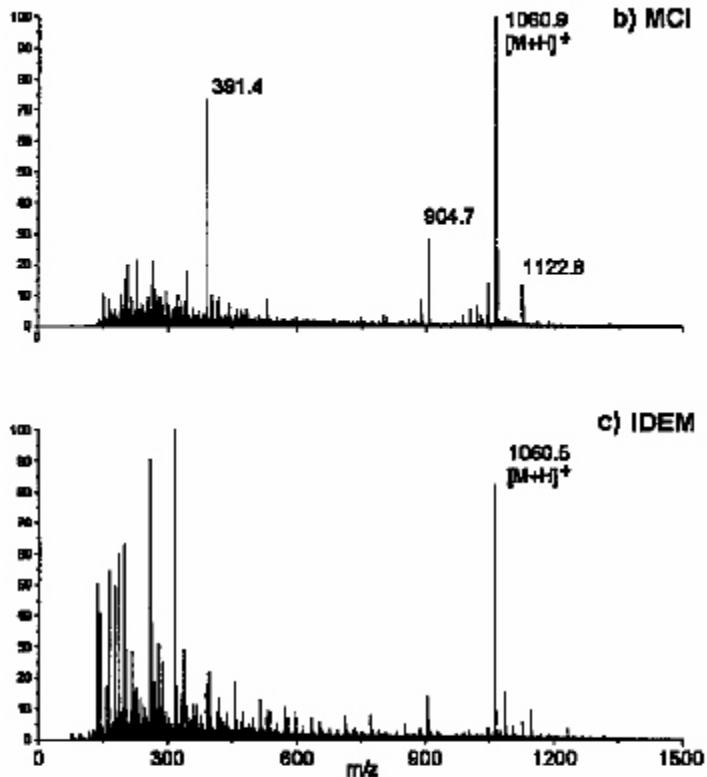
Involatile liquids (e.g. Glycerol) are messy and coat the ion column

Volatile liquids (e.g. Water) evaporate and freeze (need heating). Hard to stabilize

Ionic liquids??? (Fujiwara SIMS 18)



Slide 51: The IDEM approach called for aqueous sample solutions, and electrospraying a volatile liquid like water in vacuum has some problems due to evaporative freezing (left image). However, by heating the emitter a fairly stable spray can be achieved (right). As an alternative, some Japanese workers have suggested using an ionic liquid spray, with the thought that if the spray does coat the column, the coating will be conducting...



Comparison of MCI (cluster impact on solid target) and IDEM (analyte dissolved in cluster) for bradykinin

Slide 52: This shows a comparison of MCI and IDEM for a bradykinin analyte (a dried solid target for MCI) – one of the few MCI spectra I've managed to obtain in all these years.

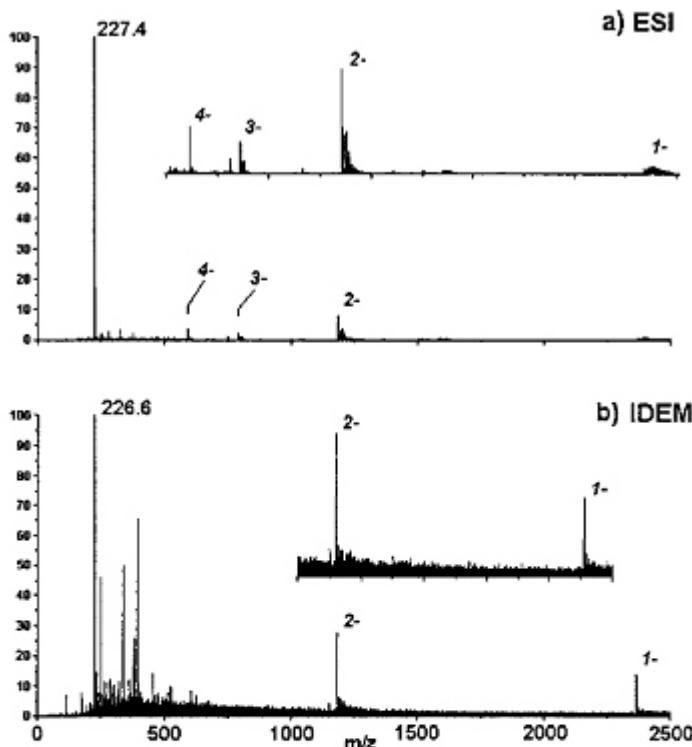


Figure 5. Oligonucleotide (dT)₈ negative ion mass spectra produced by (a) ESI and (b) IDEM. Typical IDEM spectrum is presented. The peak near m/z 227 is a thymidine derivative remaining from oligonucleotide synthesis.

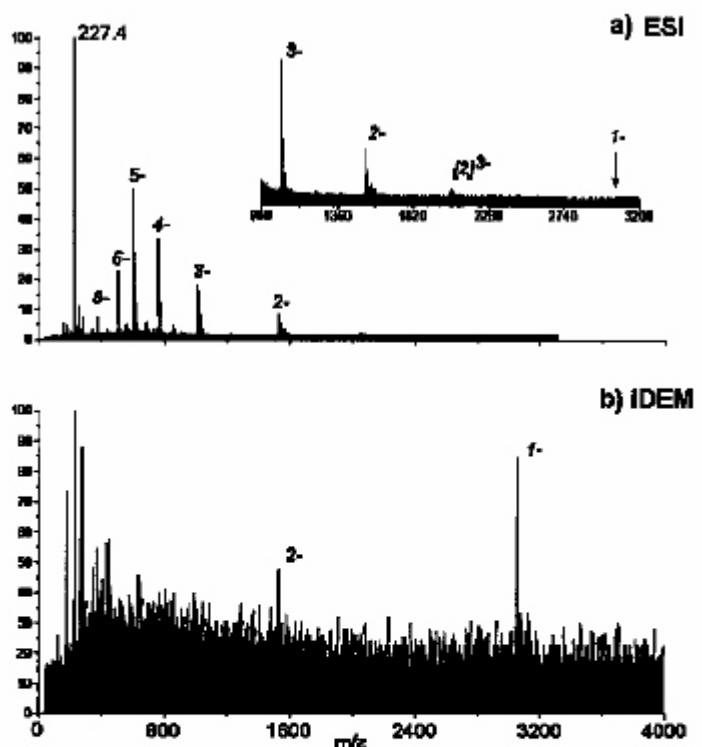


Figure 7. Oligonucleotide 10-mer (GACTGACTGA) negative ion mass spectra produced by (a) ESI and (b) IDEM. Typical IDEM spectrum is presented. The m/z 227.4 peak is a thymidine derivative remaining from oligonucleotide synthesis.

IDEIM performance for DNA compared to ESI. Poly-T nucleic acids are relatively stable; mixed-base analytes are more challenging. Note the dominance of lower charge states compared to ESI, giving the possibility of mixture analysis

Slide 53: IDEM performance for DNA wasn't too bad. Poly-T DNA is relatively robust and many sudden energy input approaches can readily eject intact molecular ions (left). Mixed-base DNA has a greater tendency to fragment but we were able to detect the intact singly-charged ion of a 10-mer, near the upper mass range limit of our mass spectrometer. We suspected that the high noise background arose from small clusters and molecules that were hard to eliminate from our cluster spray. As we had hoped, the extent of multiple charging was significantly less than for ESI, allowing the possibility of mixture analysis. But by this time, next-generation DNA sequencing technology was beginning to zoom ahead, in our lab and others, and mass spectrometry ceased to be competitive in this field.

Electrospray clusters in air: inject through ESI interface with no desolvation

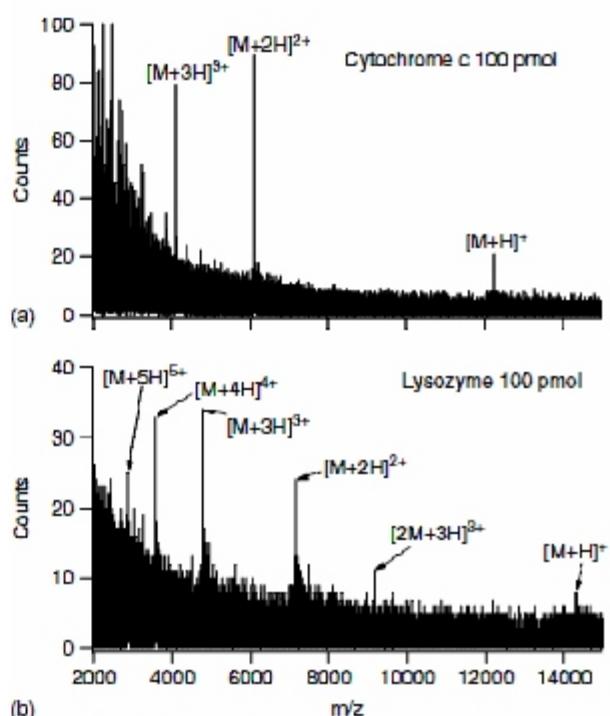
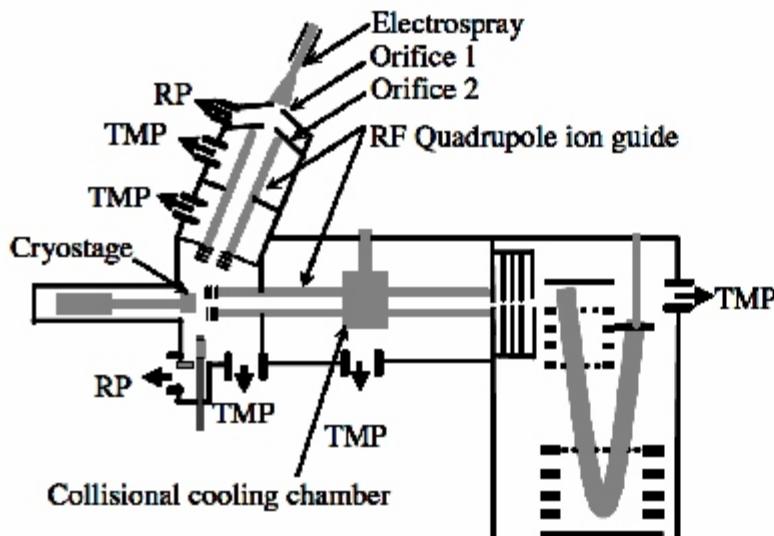


Figure 8. EDI mass spectra for dry 100 pmol cytochrome c (a) and lysozyme (b). Data acquisition time: 2 min.

Fundamental aspects of electrospray droplet impact/SIMS

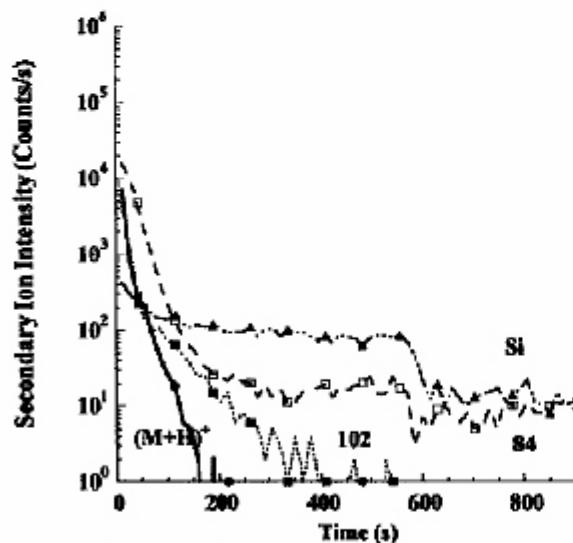
Kenzo Hiraoka,* Kunihiko Mori and Daiki Asakawa *J. Mass Spectrom.* 2006; **41**: 894–902

Slide 54: Interest in the MCI approach has grown in Japan in the past decade. Hiraoka and colleagues had the nice idea of doing the electrospray in air, where control is easy and evaporation is not an issue, and then transporting the resulting clusters into vacuum through an electrospray vacuum interface without heating. He has demonstrated spectra for sizeable proteins, but it is hard to achieve much intensity in the cluster beam with this approach.

Preliminary Evaluation of an SF₅⁺ Polyatomic Primary Ion Beam for Analysis of Organic Thin Films by Secondary Ion Mass Spectrometry†

Greg Gillen* and Sonya Roberson

Ar⁺ Depth Profile of Glutamate Film



SF₅⁺ Depth Profile of Glutamate Film

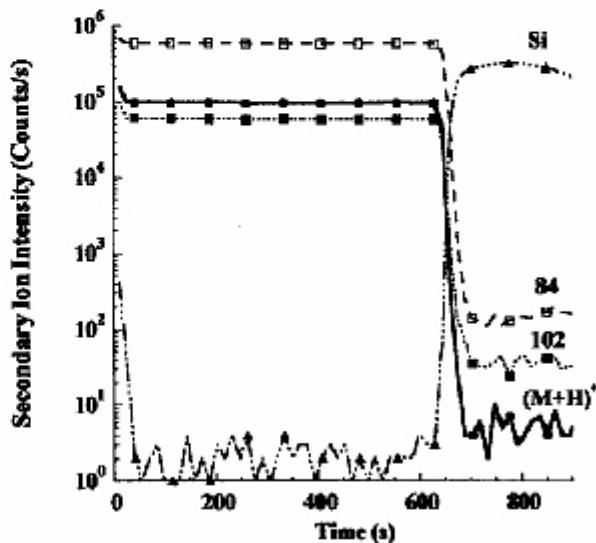


Figure 5. Comparison of depth profiles obtained from an 180 nm thick, vapor-deposited glutamate thin film using Ar⁺ and SF₅⁺ primary ions under dynamic SIMS conditions. The SF₅⁺ primary ion dose required to reach the silicon was $\sim 1.4 \times 10^{15}$ ions/cm² (8.4×10^{15} atoms/cm²).

Slide 55: SIMS interest in cluster projectiles began to take off in 1998 with this lovely demonstration by Greg Gillen and Sonya Roberson that a fairly small SF₅⁺ cluster beam allowed stable depth profiling of a glutamate film.

C_{60}^- ion source (IONOPTIKA)

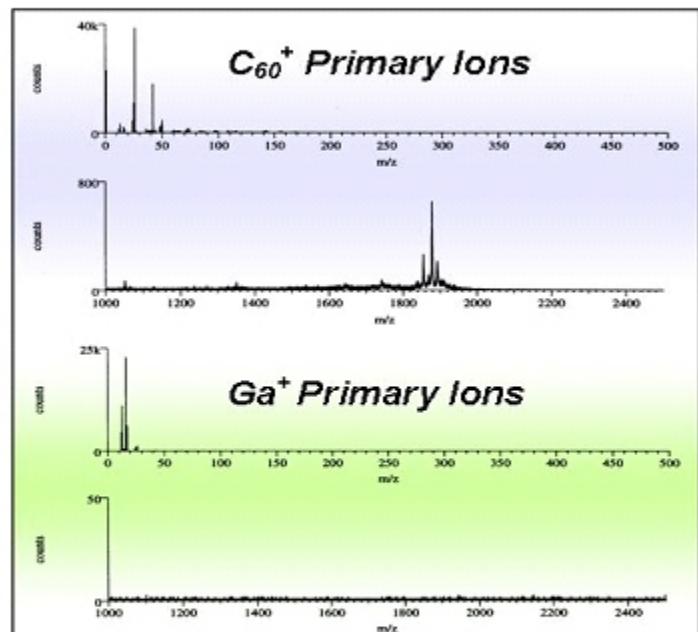


Figure 1. Spectra of Gramicidin D under Ga^+ and $C60^+$ bombardment. Ga^+ dose is 10x $C60^+$ dose. Data courtesy of SARC, University of Manchester.

Slide 56: Since the NIST paper, a commercial C_{60}^- source from IonOptika has spawned many papers from the Vickerman and Winograd groups, and others.

Gas cluster ion source (Matsuo et al.)

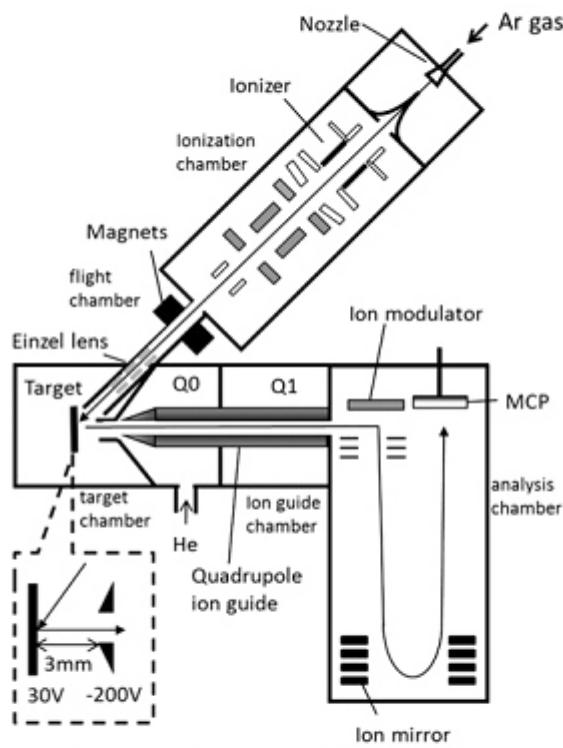


Figure 1. Experimental setup for oa-TOFMS with GCIB irradiation.

Ar gas cluster ion beam coupled to orthogonal TOF (Matsuo et al. SIMS 18)

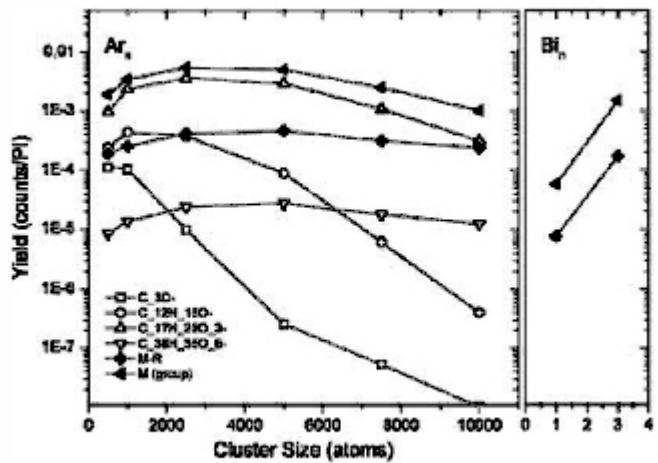
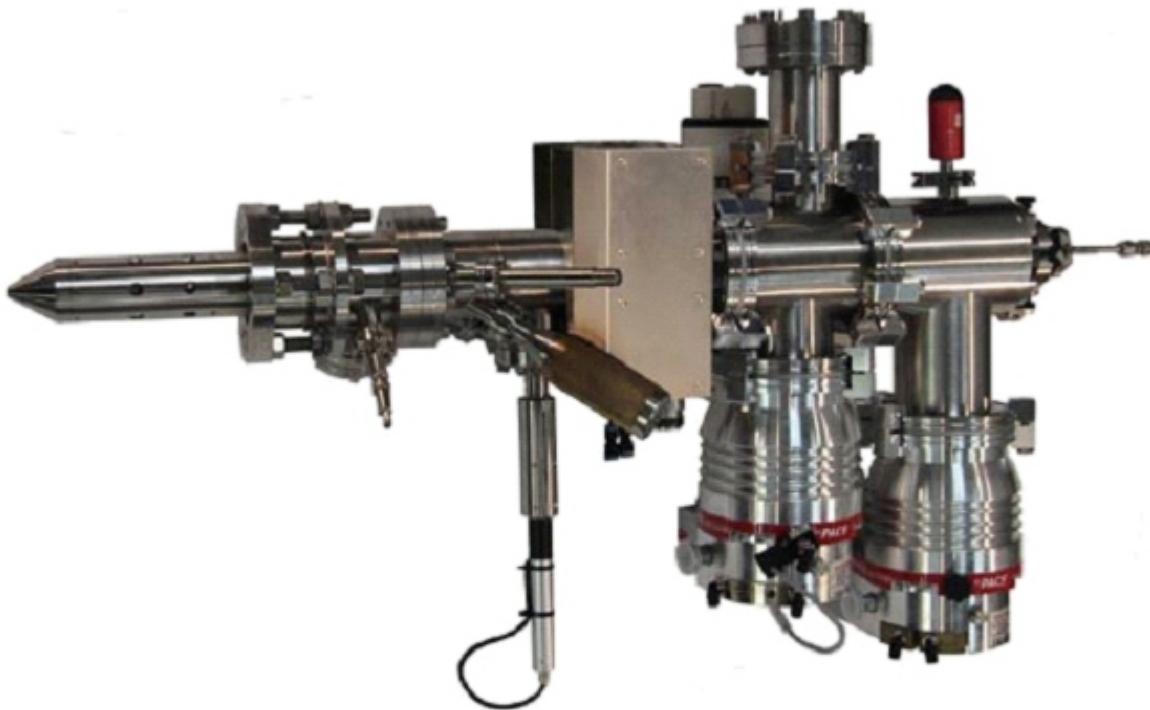


Figure 3. Negative secondary ion yield (Y) as a function of cluster size for argon and bismuth at 20 keV ion energy on Irganox 1010.

Irganox ion yields as a function of cluster size (Kayser et al. SIMS 18)

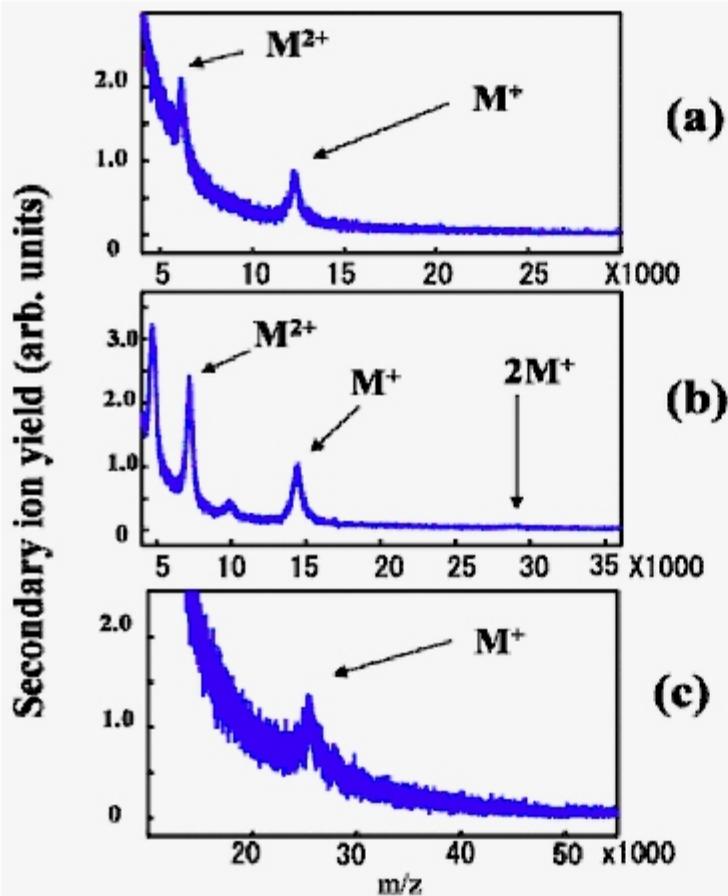
(Is ionization efficiency dropping for larger cluster size?)

Slide 57: More recently the Kyoto University development of a practical argon cluster source has most of the SIMS field very excited, particularly since they have been able to reduce the size of their source (the size of a couple of large refrigerators when I first saw it) to something that we can imagine adding to a SIMS instrument without knocking down walls to accommodate it.



“Compact” Ar GCIB source (IONOPTIKA)

Slide 58: I couldn't find an image of the Kyoto source but here is one from IonOptika. It amazes me that they seem to have a fair mass of equipment, including a couple of turbopumps, hanging off what seems to be just a 6-inch flange.



Ar clusters can desorb (some) intact proteins
(Moichi, Univ. of Hyogo 2011)

Figure 6: Secondary ion mass spectra of cytochrome C (a), lysozyme (b) and chymotripsin (c) by the bombardment of Ar_{1500}^+ at 5 kV.

Side 59: Argon clusters also perform quite well in producing molecular ions for moderate-sized proteins, as seen in these data from Moichi and colleagues, although the background levels are high.

A look forward:

- O⁻ : Will RF source exceed duoplasmatron performance?
(- Probably)
 - Cs⁺ : Can the brightness/spot size be improved? (- Difficult)
-- maybe we can lower the price...
 - Field-ion: Any further improvements? Watch for He⁺ (Ne⁺) ion beams with sub-nm widths (!)
 - Clusters: GCIB will have “massive” success (but what is the ionization efficiency??). Efficiency (intact molecular ions ejected per molecule sputtered) is CRUCIAL for imaging
 - Massive clusters: Need a way to produce these reproducibly and couple with imaging and TOF MS
-

Molecular depth profiling:

-- largely solved (GCIB)

Molecular imaging:

-- the jury is still out...

Slide 60: So what can we look forward to in the near future?

The duoplasmatron has probably reached the limits of its performance; we continue to tweak our sources but the incremental improvements are maybe 50% or so, not an order of magnitude. The future almost certainly lies with the RF source. NanoSIMS users know the frustration of trying to image with a ~200 nm O⁻ beam after seeing the impressive performance of the sub-50 nm Cs⁺ beam, and a comparable 50 nm O⁻ beam would be a great improvement.

It's not clear that the brightness of the Cs⁺ source can be much improved, although after developing this talk I'm inspired to go back and make an effort to adapt our capillary source to the NanoSIMS because I suspect our ion emitting volume may be smaller. In any event, perhaps we can lower the price by making sources that are user-refillable.

Are there improvements in field-ion sources? Watch for adaptations of He⁺ and Ne⁺ field-ion microscopes to SIMS use. These fascinating sources use **single atom** field emitters to provide an extremely bright source of ions, and can achieve **sub-nanometer** beam sizes. Ion yields will be an

issue of course, but we know how to spray oxygen or cesium onto our samples. The other challenge is efficient collection of sputtered ions from these tiny volumes.

Argon cluster beams are going to be increasingly widespread, especially since they are now commercially available. They will almost certainly take over the organic depth profiling field. The clusters are relatively difficult to pulse or to focus, but the former issue can be addressed with DC beams and buncher-type mass spectrometers, and the latter, possibly, with direct-imaging mass spectrometers, even magnetic SIMS imaging instruments, which can have a mass range as high as 1000 – 2000 Da. The big question for imaging concerns the ionization efficiency of the intact molecules sputtered.

Massive clusters continue to be explored. There are major instrumental challenges, but there is a possibility that ionization efficiency may be better than for smaller, lower-energy projectiles, so I'm not counting them out just yet.

Overall, my view is that the molecular depth profiling issue is very largely solved with the advent of gas cluster sources. For molecular imaging, at least two significant issues remain. One is which projectile species will give us the highest efficiency, i.e. the ratio of molecular ion signal to the number of intact molecules sputtered to obtain that signal (*not* the ratio of molecular signal to primary ion flux, which is a much less useful parameter). The other question concerns the molecular complexity of biological tissue, which is the primary target of imaging. Many species of interest are present at low abundance and to detect them unambiguously (assuming we can generate enough ions) will require efficient MS-MS approaches.