

Two-Dimensional Micro-Colloid Thruster Fabrication
AFOSR Contract No: FA9550-04-C-0064

*Holey Fiber Technology
for Colloid Thruster Emitter Clusters*
- A Phase I Research Effort, Final Report, No.3 -



CAC

Connecticut Analytical Corporation

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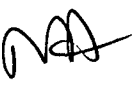
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14. ABSTRACT In the field of electric space propulsion, specifically colloidal propulsion, there have been significant improvements in 1-D micro-fabricated arrays operating in the single Taylor cone per emitter regime. Unfortunately, this arrangement will necessitate the construction of very large colloidal thrusters inefficiently utilizing a very limited amount of area to produce suitable thrust. To maximize the density of individual colloidal emitters per unit area, a 2-D array is required. This utilization of a 2-D colloidal thruster array will provide a much greater thrust density. The current state of the art technology used to create compact 2-D thrusters is to use MEMS based devices. Although very efficient in the use of material, MEMS based devices can be tricky to get "just right", and the associated production costs can be prohibitive. An alternative to creating a 2-D colloidal thruster as a MEMS based device would be to use commercially available fiber-optic cables constructed in such a way as to have a geometrically symmetrical arrangement of uniform holes running the length of the glass optical fiber. These optical fibers are commonly referred to as "Holey" fibers. Connecticut Analytical Corporation has been investigating the properties of these Holey fibers as to their use in ElectroSpray applications.					
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Two-Dimensional Micro-Colloid Thruster Fabrication

Contract FA9550-04-C-0064

Progress Report III

(January 30th 2005 to May 30th 2005)

AF04-T005: Development of Micro-Fabrication Technology for colloid thruster emitter clusters, complete and ready for spacecraft integration

20050804 009

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Report In Accordance with Exhibit A, Reporting Reqmts by AFOSR

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*Connecticut Analytical Corp. Progress Report III
for
Two Dimensional Micro-Colloidal Thruster Fabrication
STTR AF04-T005*

Part I: Research Objectives & Results of Phase I Investigation

Colloidal thrusters are based on the production of beams of charged drops and ions from the tip of an electrified liquid held in a vacuum. The charged liquid meniscus takes a conical shape (Taylor cone; see **Figure 1**), whose tip region emits either a jet (which breaks into drops), a mixture of drops and ions, or only ions [1, 2]. The purely ionic emission regime has been obtained only with organic salts with melting points below room temperature, often called ionic liquids. Within this class of relatively new materials, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) is the only one exhibiting the purely ionic regime at room temperature [1, 2]. Several other ionic liquids attain this regime when heated between 50 and 150 °C [3]. Although not much work has so far been published on the propulsive characteristic of electrosprays of EMI-BF₄, several groups have studied it for the last 3 years. All have confirmed the existence and singular interest of the ionic regime, and examined various characteristics of the emitted spray [1-5]. Another promising ionic liquid that has received extensive attention and tests (including radiation tests at JPL) for propulsion applications in NASA's Disturbance Reduction Program is EMI-Im [Im=bis(trifluoromethylsulfonyl)imide=(CF₃SO₂)₂N]. EMI-Im does not operate in the purely ionic regime at room temperature, but recent work in the laboratory of our colleagues at Yale has shown that it does so at moderately elevated temperatures.

Figure 1: Photo of an electrified Taylor cone formed at the end of a capillary tube. Note the thin jet ejected from the apex



These studies of electrical propulsion based on Taylor cones of ionic liquids have already contributed sufficient basic propulsive information to design practical thrusters, and some are being built at present at Busek Co. Inc. for NASA's DRS program. Operational regimes of EMI-BF₄ have been reported that yield specific impulses of 4000 s at an acceleration voltage of only 1.6 kV [2], with current levels in excess of 4.5 μA per emitter.¹ Time of flight (TOF) mass spectrometry (MS) data showing this performance are shown in **Figure 2**. Post acceleration to 5 kV would provide a specific impulse of 7000 s, with a power of about 22.5 mW per emitter. The current level quoted of 4.5 μA can in fact be increased by more than one order of magnitude by operating in a high-current regime, which is of considerable interest for high power missions. However, this regime is at present not properly understood and appears to have limited energy efficiency (high voltage loss in the process of ion beam formation), and will therefore not be used in our present design. A propulsive system based on individual elements each yielding only 22.5 mW would appear at first sight to be of little practical value in general, and hopeless for high power applications. On the other hand, two key additional parameters determining power density are the size of each emitter and the effectiveness with which multi-emitter systems can be integrated. From that point of view, we will argue that Taylor cone based electrical propulsion enables high power densities, with very attractive overall weight. Each tip could in principle be anchored into a submicron structure, if it were mechanically feasible, without serious effects on the emission physics. The power densities attainable are therefore not limited by the electrospraying phenomenon itself, but by one's ability to integrate a large system of individual emitters into arrays. It is this ability to create a large number of emitters we report.

¹ Reference [2] reports an uncorrected current of 2.1 μA when using three grids with 85% transparency and a fourth screen 75% transparent, with total transmission of 46%

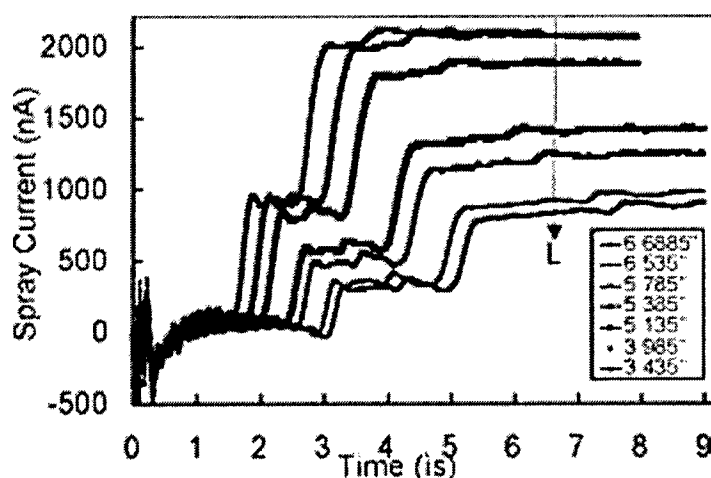


Figure 2: TOF mass spectra of electrosprays of EMIBF_4 in vacuum obtained by gating the ion beam with a set of three grids and measuring the current received at a collector plate connected to a digitizing oscilloscope. The various curves correspond from left to right to increasing TOF distances. The two main steps visible correspond to the monomer ion EMI^+ and the dimer ion $\text{EMIBF}_4\text{EMI}^+$.

Power density and parallelization considerations

The notion that large scale parallelization of electrospray emitters is a realistic option has already been considered in a number of settings, such as biological analysis [6], combustion and energy generation [7], propulsion of microsatellites [8], and very high resolution thrusters for delicate scientific missions [9]. Earlier microsatellite oriented efforts at MIT have been led by Martinez-Sanchez, a renowned specialist in several key areas of propulsion. Martinez-Sanchez has argued that electrospray-based propulsion is almost impossible to match by any known device in its ability to be miniaturized. In the case of plasma thrusters such as Hall thrusters, his argument involves the need to increase the operating pressure as the characteristic size is reduced, which leads to increased erosion rates and lifetime reduction. For the purposes of the present high power application, we will extend Martinez-Sanchez's argument in three directions. The first is to note that his is fundamentally a power density reasoning, which has so far been applied only to small power levels, but which carries naturally to high power systems. This first point will be expanded on below. The second consideration is that high-power applications of electrosprays are in fact considerably simpler technically, than those low power applications involving micro-satellites. Both require dealing with the challenge of high level multiplexing. Micro-satellites offer an environment which is itself very demanding, with low power levels where high specific impulse maneuvers take long periods, and with stringent limitations on the weight of the various systems. For instance, the liquid feed system for a micro-satellite based electrospray thruster is a rather sophisticated component, and the efficiency of conversion of satellite power into high voltage power for the thruster is not trivial either. These challenges become relatively simpler in large spacecraft, where the relative weight of individual thruster components is of less concern, but still remains low. A final advantage to be noted in favor of the present project is that, in the few years since the initiation of earlier Taylor cone multiplexing efforts in micro-satellite propulsion, the purely ionic regime of ionic liquids has been discovered and characterized, with dramatic potential improvements in both specific impulse and in power density with respect to previously known colloidal devices based on drop producing electrolytes of organic liquids. Certain devices are evidently more amenable than others to concentrate energy into a small region. Combustion systems are constrained by the limited energy density of chemical propellants, and by the need to confine high temperature flows within solid structures. They are therefore restricted to low specific impulses. Their miniaturized versions are also restricted by poor flow performance at small Reynolds numbers, and suffer from additional mechanical difficulties due to the existence of rotating parts. Plasma based systems, with or without magnetic confinement, need to provide a continuous medium at high temperature, where the balance between operating pressure and size coupled with the impact of energetic particles on electrodes and grids limit either the lifetime or the power density, as already mentioned.

Establishing high magnetic fields also tends to involve relatively heavy components. The situation of electrosprays is entirely different. On one end, the relatively mature liquid metal ion source technology (Field Effect Electrical Propulsion; FEEP [10]) is in principle capable of high miniaturization. However, liquid metals have a number of inherent difficulties such as the need for moderately heated sources (using In, or higher temperature sources with other metals, unless one is willing to face the chemical challenges of working with Cs), their corrosive properties and reactivity, the difficulty to avoid metal deposition on insulating components, the high contamination risk from metal ion plumes, etc. In addition, the impossibility to produce negative metal ion beams calls for a high-density integration of neutralizing electron beam sources with the metal ion source.

The combination of these technical challenges with the usual ones of miniaturization, as well as other problems which have not been clearly discussed in the literature have led to an easily observable outcome: after many years of development, no practical system involving two-dimensionally integrated liquid metal ion sources have emerged. This limitation alone necessarily confines such thrusters to very low power missions. Furthermore, even the slit-based linear FEEP emitters that have evolved into real thrusters suffer from serious performance problems as soon as they are operated (as they must for any practical mission) past the moderate current regime where the quality of the ion beam is acceptable, and the physics of the ion source has been adequately studied and understood [11].

Against this background, the emergence of ionic liquids as highly inert materials and ability to produce high quality intense beams of both positive and negative ions, offers for the first time a high power density alternative to plasma thrusters. This situation is new, and entirely unexpected. The traditional electrospray source of charged drops has never been capable of high specific impulses. Now it is, when run in the purely ionic regime. This ion source has some interesting advantages over plasma sources. Perhaps the most crucial relates to erosion rates of electrodes and grids, which control lifetime. Each emitter is precisely located in space, and is for all practical purposes a point source. No grids are necessary for ion acceleration, which is typically achieved by one or several perforated electrodes coaxial with the emitter.

As long as the geometry of the system and the operational regimes are such that ion impact on the electrodes is avoided, erosion is avoided entirely. If one or several sources in the array are imperfectly shaped or centered, their extractor electrodes will be rapidly eroded, at which point emission will stop. There is hence a stable scheme to keep this vast array of emitters in tune with each other. As long as the fraction of initially defective structures is modest, their impact on the overall setup will be small. There are evidently stringent tolerance criteria to attain a system free from radiation damage, and these will be discussed in the fabrication section. In particular, it is essential to control the wetting characteristics of the surfaces anchoring each emitter, as random shape variations due to uncontrolled wetting patterns would be detrimental. The important point here is that, in principle, erosion under steady operation can be eliminated in Taylor cone based system, and not in ion thrusters using plasma sources. A certain rate of erosion would probably be unavoidable during the brief periods when the device is started after a period of inactivity. If, as we will endeavor to show, electrospray emitters can be integrated in two dimensional arrays, no need arises to operate them under highly stressed regimes where emission characteristics and spray angles are poor and relatively unknown. We shall also argue that this device density is based on well known fabrication methods and emission regimes, and well below what can be achieved, both from the point of view of ion beam physics (space charge limitations) and of fabrication technology. Consequently, we will be able to show that going to the next level of integration of a much larger array involving groups of positively and negatively charged emitters should pose no serious design or fabrication challenges.

"Holey" Optical Fibers & 2-D Micro-Colloidal Thruster Fabrication

Before beginning this discussion regarding our proposed approach to micro colloidal thruster fabrication, it is important to note that while our approach is not a specifically silicon MEMS device as described in the original Phase I solicitation, we were encouraged by the technical point of contact nevertheless to submit a proposal based on our fused silica Holey Fiber electrospray sources.

In the field of electric space propulsion, specifically colloidal propulsion, there have been significant improvements in 1-D micro-fabricated arrays operating in the single Taylor cone per emitter regime. Unfortunately, this arrangement will necessitate the construction of very large colloidal thrusters inefficiently utilizing a very limited amount of area to produce suitable thrust. To maximize the density of individual colloidal emitters per unit area, a 2-D array is required. This utilization of a 2-D colloidal thruster array will provide a much greater thrust density. The current state of the art technology used to create compact 2-D thrusters is to use MEMS based devices. Although very efficient in the use of material, MEMS based devices can be tricky to get "just right", and the associated production costs can be prohibitive. An alternative to creating a 2-D colloidal as a MEMS based device would be to use of commercially available fiber-optic cables constructed in such a way as to have a geometrically symmetrical arrangement of uniform holes running the length of the glass optical fiber. These optical fibers are commonly referred to as "Holey" fibers, a term coined by the Optical Research Center based in Southampton, England. Connecticut Analytical Corporation has been investigating the properties of these glass fibers for their use in ElectroSpray applications over the past year and a half. One major avenue of research with these fibers is their application as a self-regulating, passive hydrostatic feed source for spacecraft thrusters. The original idea of using a "wick" for a passive hydrostatic feed system was conceived by Dr. John B. Fenn of Virginia Commonwealth University in Richmond, Virginia. Dr. Fenn was awarded the Nobel prize in Chemistry in December of 2002 for his contributions in the field of ElectroSpray Ionization and its applications to Mass Spectrometry. It was Dr. Fenn's suggestion to use a "wick" to supply suitable propellants in the field of Colloidal space propulsion, thus alleviating the requirement of a complex, potentially unreliable, hydrostatic feed system. Connecticut Analytical Corporation has taken the "wick" concept a step further by utilizing Holey fibers as not only the passive hydrostatic feed system for ElectroSpray MS applications, but also for colloidal propulsion (Awarded Phase I & II by NASA-JPL for Capillarity based feed system for Colloidal Thrusters). The advantage is significant. The Holey fibers are constructed from fused silica (glass) and are thus, totally inert. The fibers also contain a 2-D arrangement of small holes that are uniform in size throughout kilometer distances of fiber. The quantity of individual holes contained in a single fiber currently being studied is 168, where each individual hole in the Holey fiber can act as a separate Taylor cone source. Since each individual small hole runs the length of the fibers, each one can be thought of as an individual glass capillary tube. As most people are familiar with capillary action, it will come as no great surprise to learn that the Holey fiber acts as not only the ElectroSpray needle source, but also its own passive hydrostatic feed source. Various size capillary hole structures in the Holey fibers can easily be realized and these fibers are presently being manufactured in kilometer lengths. Experiments have been conducted with have uniform hole diameters from approximately 4 μm to as large as 12.5 μm diameters. The overall fiber diameters are 225 μm in width, and all have 168 individual capillary structures (holes) running throughout their length. The Holey fibers will also allow the testing of higher vapor pressure propellants to be used in space applications as the small hole diameters will isolate a great portion of the liquids surface area from being exposed to the high vacuum environment of space. Where other systems would expose too much surface area of the liquid to the high vacuum of outer space resulting in significant amount of fluid loss, the Holey fiber system would limit this loss to a controlled amount. (If ionic fluids are used, then the point is moot). In an externally wetted wicking system, such as when using a MEMS structure, ONLY an ionic fluid can be used due to its negligible vapor pressure. The Holey fiber thus has been shown to have the potential of being able to use a myriad of possible propellant solutions. Yet another benefit of utilizing Holey fibers to construct a 2-D colloidal thruster array is the fact that each individual Holey fiber is already a 2-D array, and all that is required is construct a larger 2-D array is to combine more individual Holey fibers.

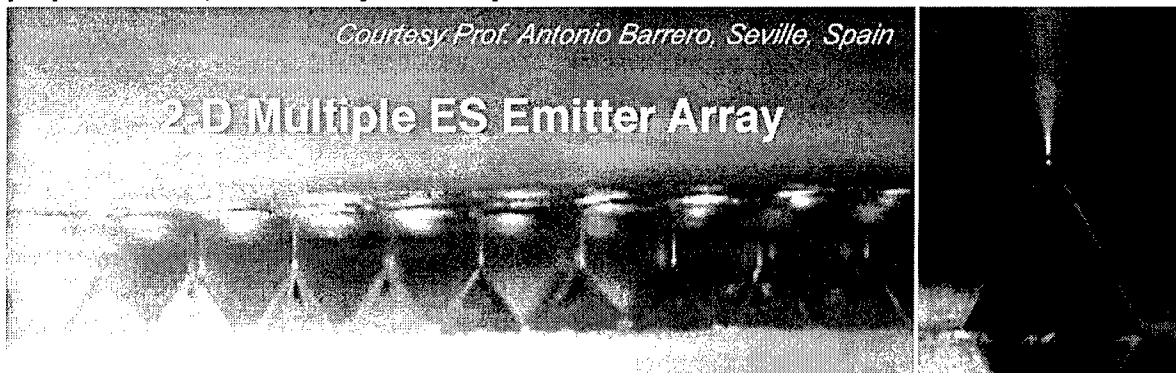
Since each Holey fiber contains 168 individual Taylor cone emission sites, the combination of just 2,401 individual Holey fibers, would yield a total of 403,368 individual Taylor cone emitters, occupying an area of only approximately 27 mm². Still another possible future advantage of utilizing Holey fibers is the fact that custom concentric hole arrangements could be realized that would allow a coaxial flow of two distinct liquids to combine to form "coated" droplets. The individual droplets formed by a volatile propellant (e.g. Formamide) "coated" with a low vapor pressure oil. This specific coaxial arrangement of liquids was proposed by Juan Fernandez de La Mora of Yale University as a means of providing higher amounts of thrust than would be possible by using strictly low weight, low vapor pressure liquids alone. By using Holey fibers with the aforementioned coaxial arrangement, this concept produce a greater amount of thrust for a given colloidal propulsion system. As previously stated, the Holey fibers are commercially produced in kilometer lengths. Therefore, the only real cost would be labor associated with customizing the fiber for colloidal propulsion use. Another drawback of using a MEMS based device is extractor alignment. With several thousand or even several hundred individual Taylor cone emission sites, then it becomes exceedingly difficult to try to "align" the extractor to each individual emission site. Given that the Holey fiber geometry, the individual groups of holes are closely compacted together, and it was found, after several discussions with MIT, that a high transparency grid functioned well, but that by controlling the number of Holey fiber pores and thier geometry, a single annulus or ring electrode will be all that would be required for each Holey fiber bundle, not an individual extractor opening for each individual capillary hole.

Before the Phase I, we had only tested the Holey fibers using water-propanol mixes, taking for granted that the capillary feed system is able to provide the liquid flow rates required for proper operation of the electrospray source using ionic liquids. This was based on the following calculation performed by Dr. de la Mora of Yale for the relevant case of EMI-BF₄. Let us take the capillary to have an inner radius R, length L and be perfectly wetting, so that the capillary pressure drawing the flow is $\Delta P = 2\gamma/R$, where γ is the surface tension of the liquid-vacuum interface. The fluid flow rate Q is in turn given by Poiseuille's law: $Q = \pi R^4 \Delta P / (8\mu L)$, where μ is the viscosity coefficient of the propellant liquid. We take the widest commercial Holey capillary radius, R = 6.25 μ m, the properties of EMI-BF₄ ($\mu = 0.4$ g/cm³, $\gamma = 52$ g/s², $\rho = 1.2$ g/cm³), and the shortest capillary length we can conveniently cut properly at present, L = 1 cm, and obtain $Q = 2.5 \cdot 10^{-8}$ cm³/s. This flow rate is substantial for colloidal propulsion at high specific impulse. It is also high for the standards of purely ionic operation, leading to a current level of 1.4 μ A at a typical mass to charge ratio of 200 amu. Thus far, we have tested Holey fibers successfully using both ionic liquid (EMI-BF₄) and Formamide as propellants.

Phase I: Technical Objectives

The Phase I technical objectives consisted of creating a small fiber bundle consisting of seven individual Holey fibers. The resulting bundle would then be tested in Connecticut Analytical's vacuum chamber to determine the total performance from a single fiber and from a bundle or cluster. The construction of the bundle would be facilitated by commercially used techniques with dealing with optical fiber. The front surface or face of the fiber would be cleaved to a perfectly smooth and flat face, then face would then be treated to make it hydrophobic, thus facilitating the confinement of individual Taylor cone emission sites to the individual fiber pores. Performance using select ionic liquids will be quantified as suitable propellants using TOF.

Multiple Closely packed ES sources have also been proven by Prof. Antonio Barrero of Seville, Spain, as shown below. The emitter surface of such a source is treated with a hydrophobic chemical agent (we have used Hexamethyldisil Azane or HMDS) to maintain the integrity of individual sprays. The array shown below is limited to hydrostatic propellant feed, obviated by the Holey Fibers.



The Phase I work plan consisted of the combining of seven individual Holey fibers into a small bundle. The process would then entail cleaving the bundled fiber to a smooth, flat face and testing propellant candidates in the CAC Time of Flight chamber. After the initial results are obtained, the face of the fiber bundle would be treated to make it hydrophobic, and the same tests would be repeated. The determination of various liquids would be researched to find out which is the best candidate for use.

The Phase I tasks were as follows:

1. Select best ionic liquid propellant for Holey Fiber under Juan de la Mora (Yale)
2. Treat end of fiber to make surface hydrophobic (allows for individual electrosprays)
3. Create Extractors (Annular & thin film holes using microfabrication)
4. Test Extractor Performance
5. Test completed fiber in vacuum
6. Perform TOF on propellants using Ionic Liquid
7. Create Small Fiber bundle
8. Test bundle in vacuum

Issues and Developments Relating to Electrospray Operation

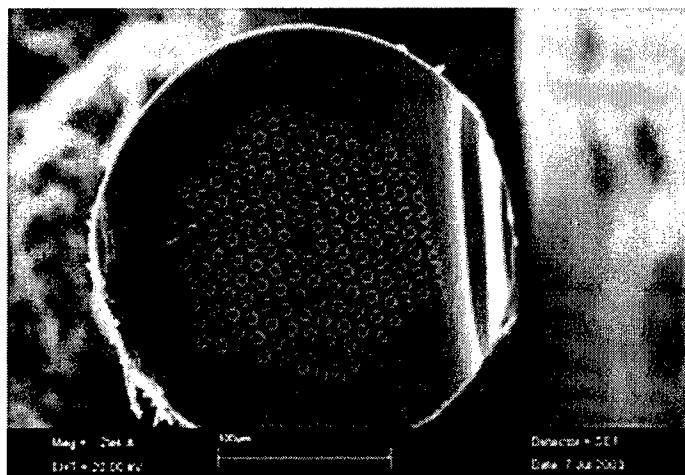
Tests of the kind just discussed with varying geometries and improvements in the overall performance will continue, if necessary, through the duration of the project. In addition, several other studies with longer range implications will be undertaken. One involves *Electrochemical* effects. The MIT group has found that either solid deposits or bubbles form in solid needles with external feeding of EMI-BF_4 in the positive and negative polarity, respectively. We do not encounter these problems with internal feeding, but perhaps they will become manifest at longer time scales, possibly leading to clogging of the emitting nozzles. This is therefore an important subject that must be addressed. In our system the emitting surface is an insulator, so no electrochemical reactions are expected at the nozzle. The high voltage will be supplied to the tip through the liquid from a platinum electrode on the propellant reservoir. Electrochemical reactions would then, if at all present, occur at the surface of this electrode. Solid deposits would not represent a problem.

Alternative Propellants. All Phase I work was primarily based on EMI-BF_4 . However, we have done extensive work with other propellant candidates, and we plan to continue it if more urgent tasks make it possible. Electrochemical problems for one thing will be highly specific to one fuel or the other. Effective use of fuel mass depends vitally on electrochemistry. For instance, if the dimer ion $\text{EMIBF}_4\text{EMI}^+$ is primarily ejected, then what happens to the counter-ion BF_4^- released on the counter-electrode to attain charge neutrality? In a worst case scenario, it will be wasted as a gas or a solid. Martinez-Sanchez and Lozano have argued that this problem can be eliminated by periodically varying the polarity of the beam, whereby electrochemical reaction products would somehow be reconstituted. They have in fact shown that in this bipolar mode neither the solid deposits nor the gas bubbles are formed. All propellant work will be performed under the direction of Dr. Juan de la Mora.

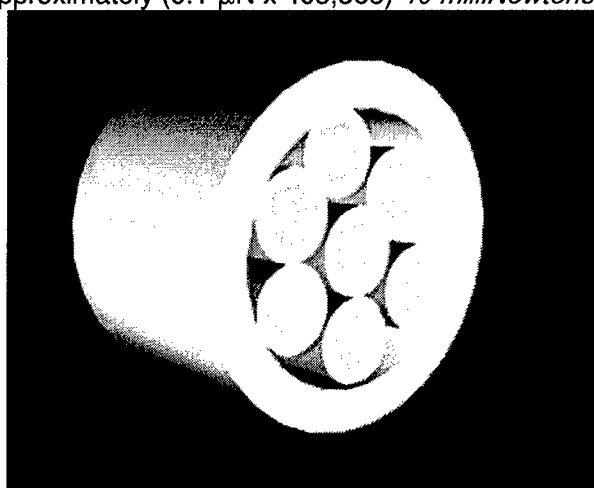
If ion recovery mechanism is not successful in all fuels, it may be in some. Alternatively, one would wish to minimize the percentage of wasted fuel by selecting ionic liquids with a high mass ratio between cation and anion, or vice-versa.

Another important property of the propellant is its **volatility**. Ionic liquids have been highlighted for their essentially null vapor pressure, which ensure no evaporative wastage of propellant to space. However, if a layer of propellant reaches the insulating surfaces of the emitter and creates a short, the device may be seriously damaged. Perhaps this event will be self-healing via Joule heating. This would be a clear advantage of ionic liquids over liquid metals. Alternatively, a very modest volatility would be desirable to avoid entirely such conducting layers. Interestingly, recent work of Angell [12] has introduced a new class of ionic liquids based on the reaction of small amines with acids such as formic acid. These materials have extraordinary electrical conductivities and appeared to us as first rank candidates for ionic propulsion at high specific impulse. We have therefore investigated amine based salts of many ionic liquids, and have found interesting leads for progress (though still no material clearly superior to EMI-BF₄). We note in particular that amine formates are slightly volatile, and probably too volatile for space applications. However, shifting to stronger acids permits controlling the volatility into a range of practical interest. With individual Holey fibers bundled into groups of seven, each bundle would comprise 1,176 individual emitters while only being 1 mm across. This diameter would occupy just under 1 mm² of area. These individual clusters could then be bundled into another larger group to form a total of seven

individual clusters, each having seven fibers in them. This would bring the total amount of individual ElectroSpray emitters to 8,232. This would be approximately 3.5 mm across, and occupy an area of 9.6 mm². If each individual capillary emitter produced a thrust of 0.1 μ N, then the entire large cluster would produce approximately 0.8 mN of thrust. If these larger clusters were combined to form a still larger array comprising a two dimensional grid of 7 x 7, that would give us a total of 49 large clusters (7 fibers per small cluster x 168 holes per fiber x 7 small clusters per large cluster x 49 = 403,368) which would be equivalent to 403,368 individual ElectroSpray emitters. The thrust produced would be approximately (0.1 μ N x 403,368) 40 milliNewtons of thrust from less than 0.75 in² of area.

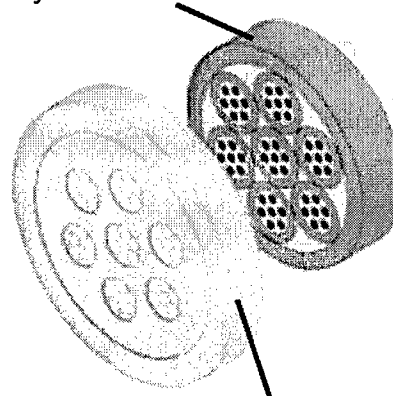


Courtesy of OptoElectronics Research Center, UK



Proposed Holey Fiber 2-D Micro-Colloid Thruster

Holey Fiber 2-D Thruster



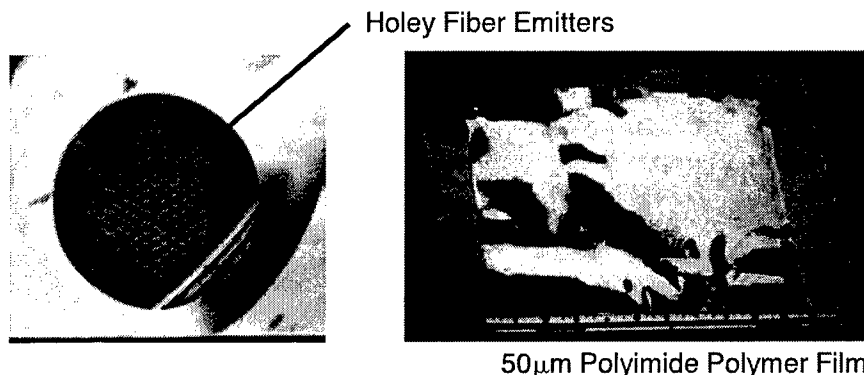
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MicroFabricated Extractor

Part II: Status of Effort / Description of Work Performed

Extractor Design Experiment Tested Under Phase I for "Holey Fibers"

Microfabrication of Extractor electrodes for Holey Fiber Arrays

One of the challenges facing the production of a large array of electrospray sources is to manufacture the extractor electrodes so they are well aligned with the emitters. In the proposed work, the emitters are produced from bundles of holey fibers, that should form perfect hexagonal close packed arrays - in reality, the spacing is not always perfect, and a defect may occur in the packing (a dislocation using crystallography terminology).



We proposed two methods to produce micromachined extractor electrodes that perfectly match the emitter arrays by using an in situ production process.

The first approach was an additive strategy, where a thin metallized film was used, the emission from the electrospray should erode the thin metal layer in front of each emitter, creating a template that can be used to produce a robust electrode. Once the template had been formed, it was removed from the system, and a thick coating will be electroformed over the existing metallization - the electroformed layer can be highly conductive and resistant to electrospray erosion. This process was to serve to reduce the size of the holes produced in the template, as it is likely the thin metallization will have been eroded excessively. Electroforming in this manner is routinely used to produce LIGA and LIGA-like structures for MEMS. David LaVan (Yale) led these unusual electroforming techniques (Ref below) and was responsible for the production of the extractor electrodes. The resulting extractors were not as sharply defined as hoped.

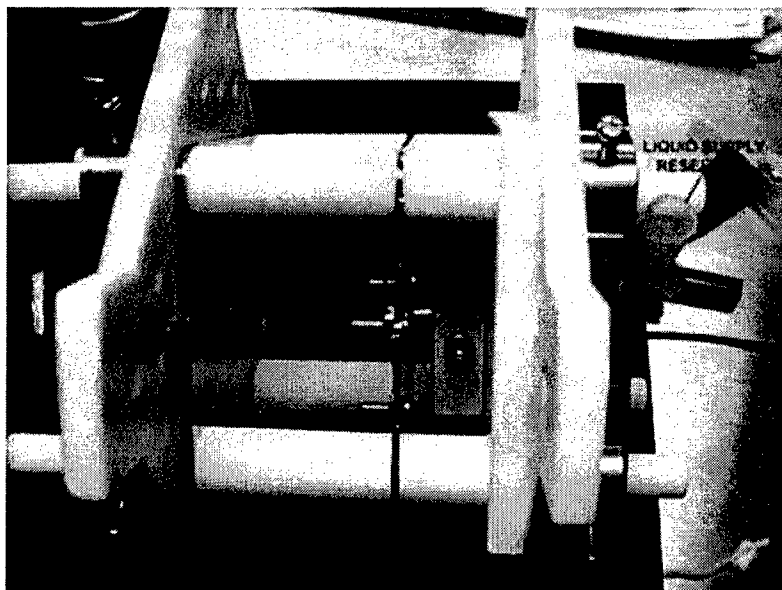
The second approach was a subtractive strategy, based on a similar concept. A thin metallized film was used to form a template with the exact locations of each emitter captured in the nature of the holes "burned" through the metallization. Rather than try to work with this film directly, it was used as an etch mask to form a mechanically robust extractor electrode using a conductive wafer (doped silicon or a polished metal substrate). The wafer was coated with photoresist; the photoresist will be exposed to UV light (using a mask aligner) through the template formed by operating the electrospray emitter array. The exposed area of the photoresist will be removed in the developing process, and the wafer / metal substrate etched to form a hole in the exact same location as each of the original emitters - capturing any small variation in location. This worked much better, but was still a labor intensive process.

Reference:

LaVan, David A.; George, Paul M.; Langer, Robert. Simple, three-dimensional microfabrication of electrodeposited structures. Angewandte Chemie, International Edition (2003), 42(11), 1262-1265.

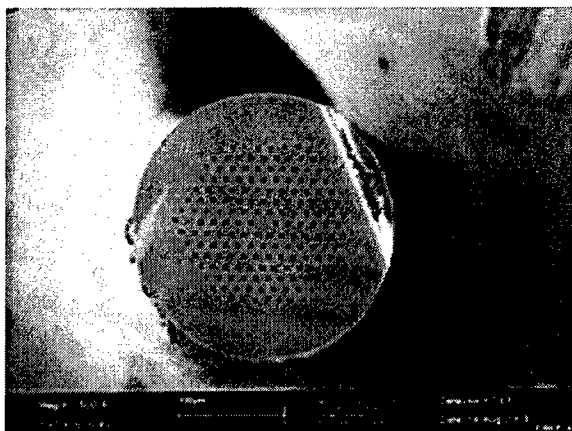


First free standing emitter array on copper sheet –
Film produced by transferring pattern with lithography and etching pattern in sheet.

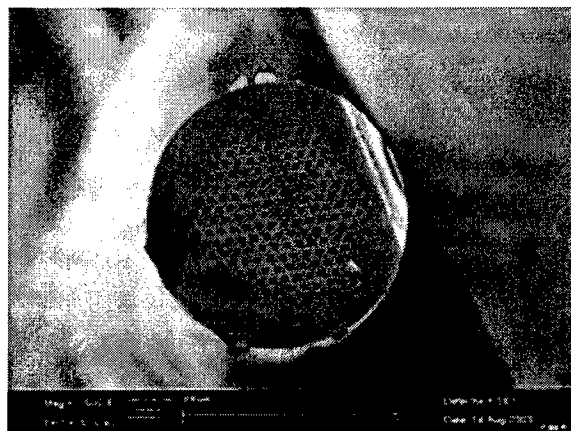


Holey Fiber in Time-of-Flight fixture with 90% transparent grid extractor
Similar arrangement used with annular ring extractor and center holes blocked off

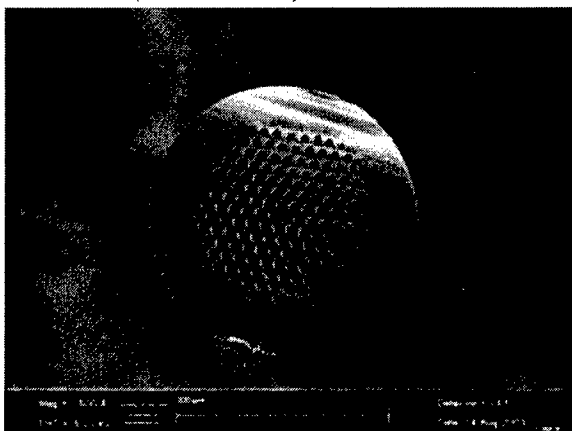
Preliminary tests with the Holey fibers were done utilizing a solution of 50/50 Water/ 1-Propanol mixture at room temperature, and then under vacuum using ionic liquid and Formamide. The six types of holey fibers are detailed in the following SEM micrographs – starting with the smallest diameter holes [Fiber A] and ending with the largest diameter holes [Fiber F]. Work is continuing with ionic liquids.



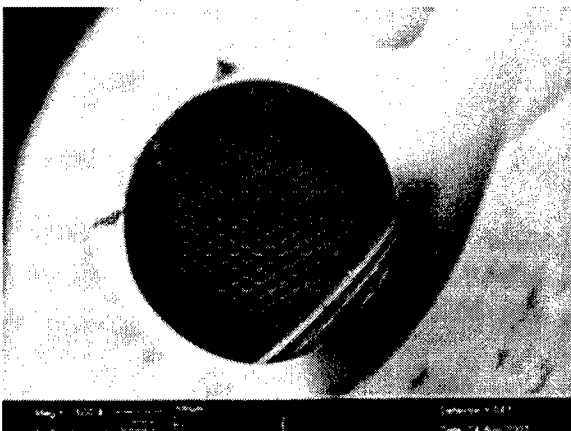
Fiber A (4.1 μm holes)



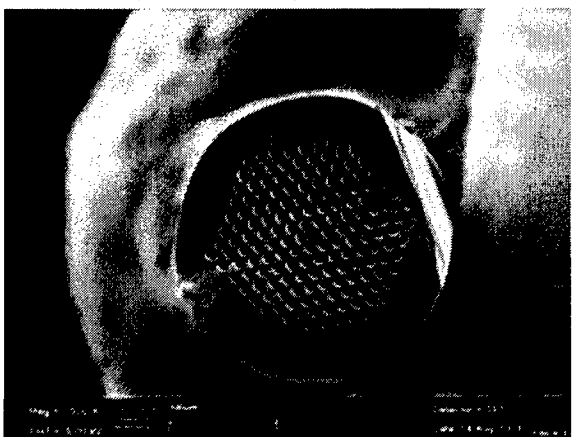
Fiber B (5.0 μm holes)



Fiber C (7.4 μm holes)



Fiber D (7.5 μm holes)



Fiber E (8.0 μm holes)



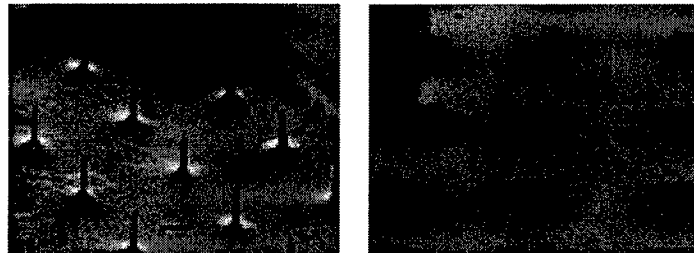
Fiber F (12.3 μm holes)

Advantages of Holey Fibers Over Conventional 2-D MEMS Colloid Thrusters

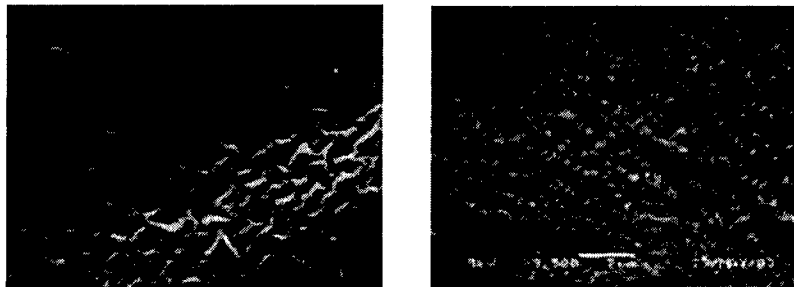
Shown below are two types (volcano-like and pencil-like) of MEMS based 2-D electrospray emitter arrays produced by MIT under NASA-JPL and CAC support. These arrays have performed admirably using ionic liquids. Both arrays utilize capillarity based feed of ionic liquid via a plasma etched surface employing the wick feed system conceived by John Fenn. Because of the large surface area of this wicking surface, the evaporative losses for any propellant other than an ionic liquid would be prohibitive. Large arrays require an alternate propellant feed system to deliver propellant to the wicking surfaces for long missions.

The volcano-like emitters on the right exhibit multiple jets which can possess jet expansions exceeding 20-30°, necessitating large extractor orifices, unnecessary for a Holey Fiber source. Holey Fibers are not constrained by limited propellant supply, as each fiber can lead directly to the propellant reservoir. As enclosed wicks, Holey Fibers do not offer a large evaporative surface area, and therefore are compatible with propellant other than ionic liquids. Holey Fibers also offer the potential for wick-fed coaxial jets, further enhancing their applications.

SEM images provided by
Luis Fernando Velasques of MIT

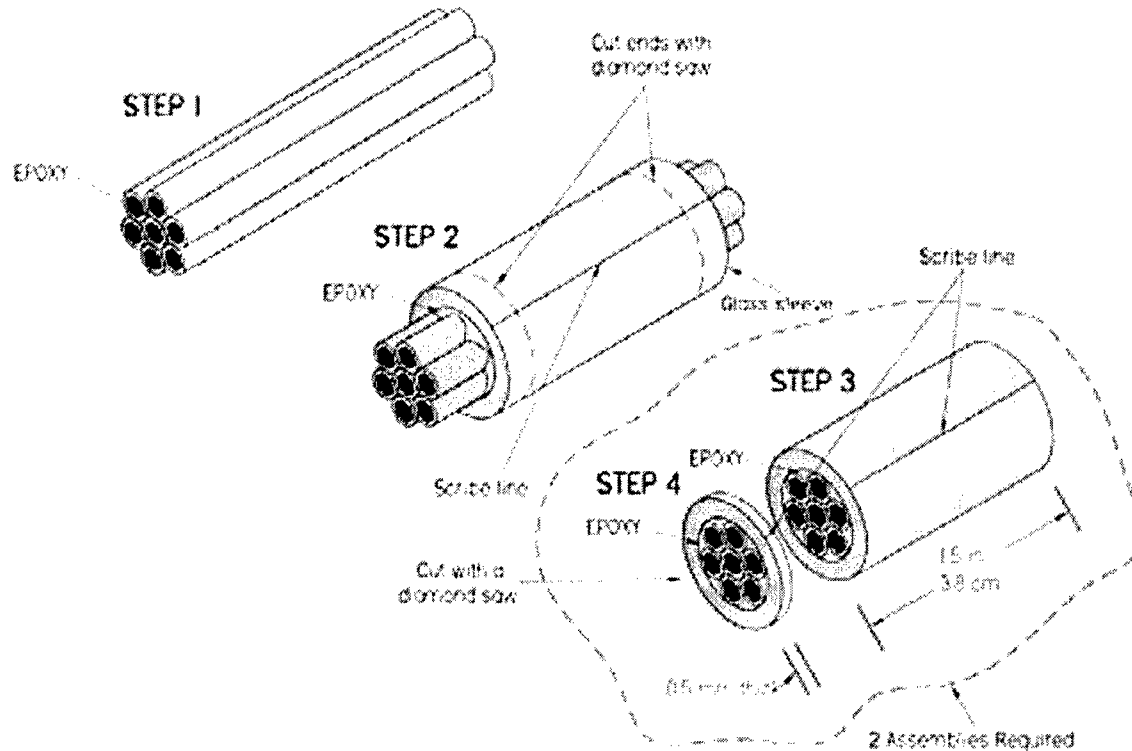


MIT tested the wetting properties of several materials such as bare Silicon (with various roughnesses), Silicon Oxide (SiO_2), Silicon Nitride (Si_3N_4), Aluminum and black Silicon to the ionic liquid EMI-BF₄ (1ethyl-3methylimidazolium-tetrafluoroborate). Qualitative results showed that EMI-BF₄ had difficulty wetting Silicon oxide (SiO_2), Silicon and Aluminum. Rougher Si surfaces were easier to wet than polished Si surfaces (no surprises here). To modify the wetting properties of regular Silicon, a surface modification technique was used. Surface modification techniques can be of physical, chemical or radiative nature. In this case we used a plasma (radiative) to modify the surface roughness and wetting energy. In particular, MIT experimented with black Silicon. Black Silicon results from exposing a regular Si wafer to a plasma dry etch with a chlorine chemistry. The end result is a strong roughening of the surface. The process is conformal thus translating into good step coverage for microfabricated structures. Figure 1 shows two SEM (scanning electron microscope) pictures of black Si for a 5 and 10 minute exposure to plasma.



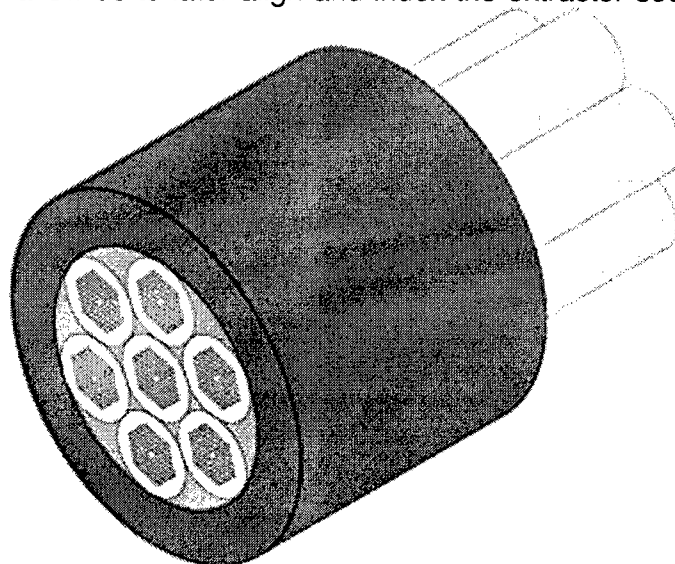
Black Silicon SEM (scanning electron microscope) structure detail.
Left : 5 min. exposure, right 10 min exposure.

Initially, the intent of this research was to form a cluster of seven individual Holey fibers. The resulting cluster would look as detailed below;

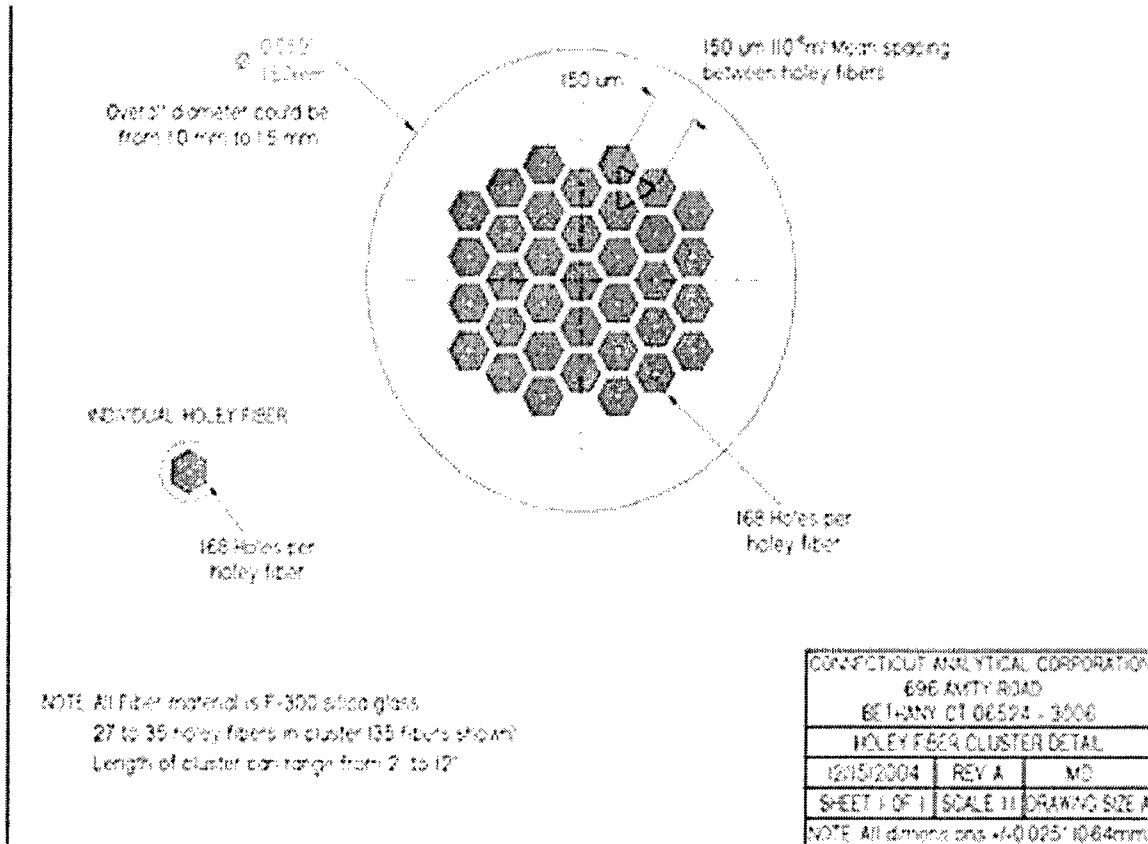


CONNECTICUT ANALYTICAL CORPORATION

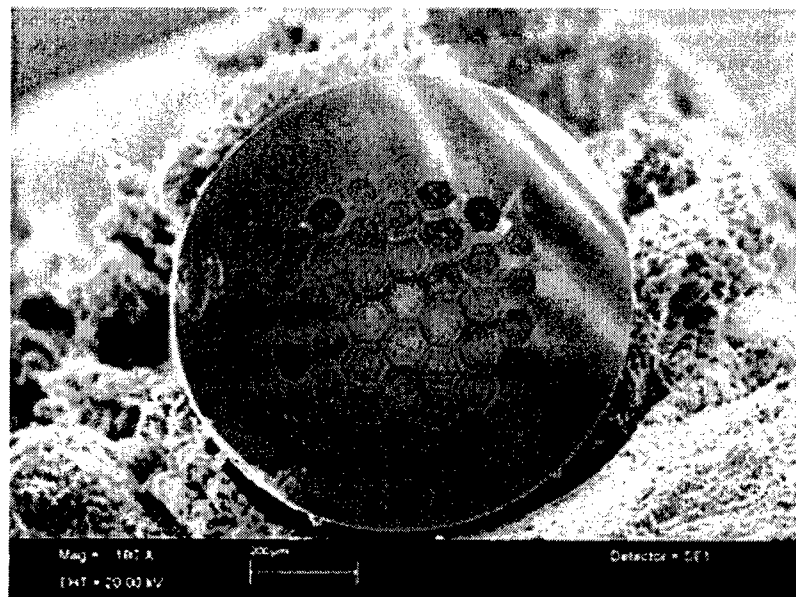
The individual Holey fibers are approximately 200 microns (10-6 m) in diameter, with individual capillary holes around 5 microns in diameter. Each Holey fiber having a neat geometrical arrangement of 168 capillary holes running through the length of the fiber. The scribe line would allow us to later align and index the extractor section to the main cluster assembly.



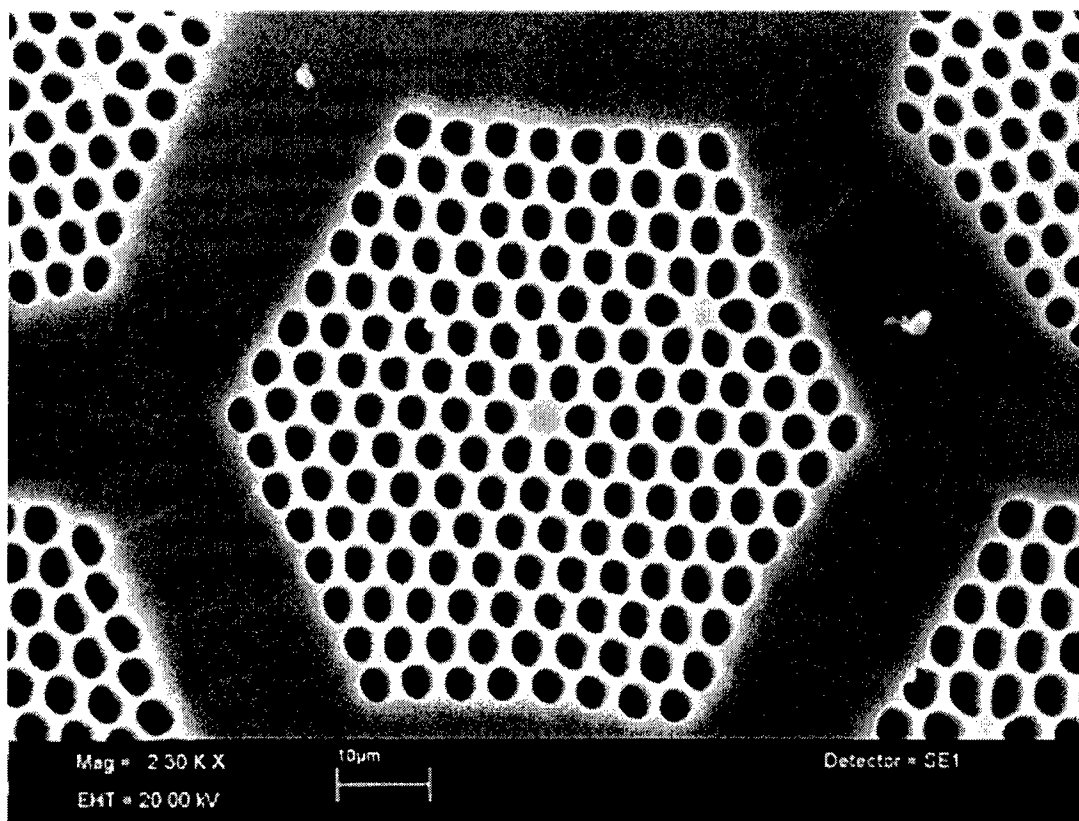
After additional discussion with the Optoelectronics Research Center (ORC) in Southampton, England, it was determined that a full draw could be done in which the cluster would essentially become a single, homogenous structure. Since this was feasible, a detailed drawing was given to the ORC consisting of the following;



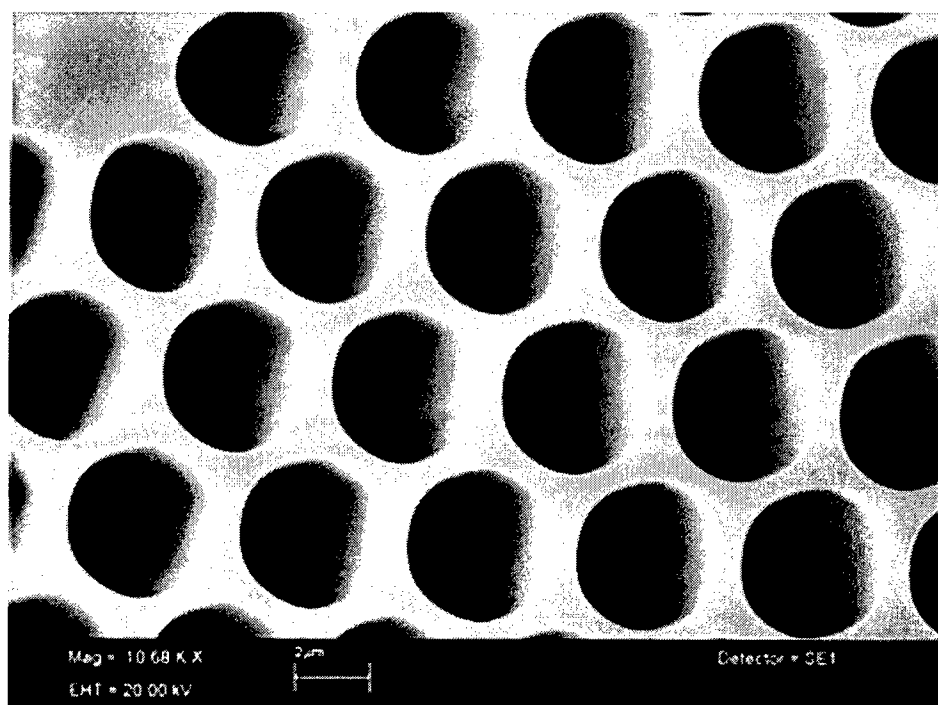
The ORC was able to produce was a glass "cane" consisting of thirty-three individual Holey fibers. The individual Holey fibers were supposed to have 168 individual holes, but do to a slight imperfection; there are only 167 individual capillary holes in each Holey fiber. This still leaves us with 167 * 33 emitters, or 5,511 individual emitters!



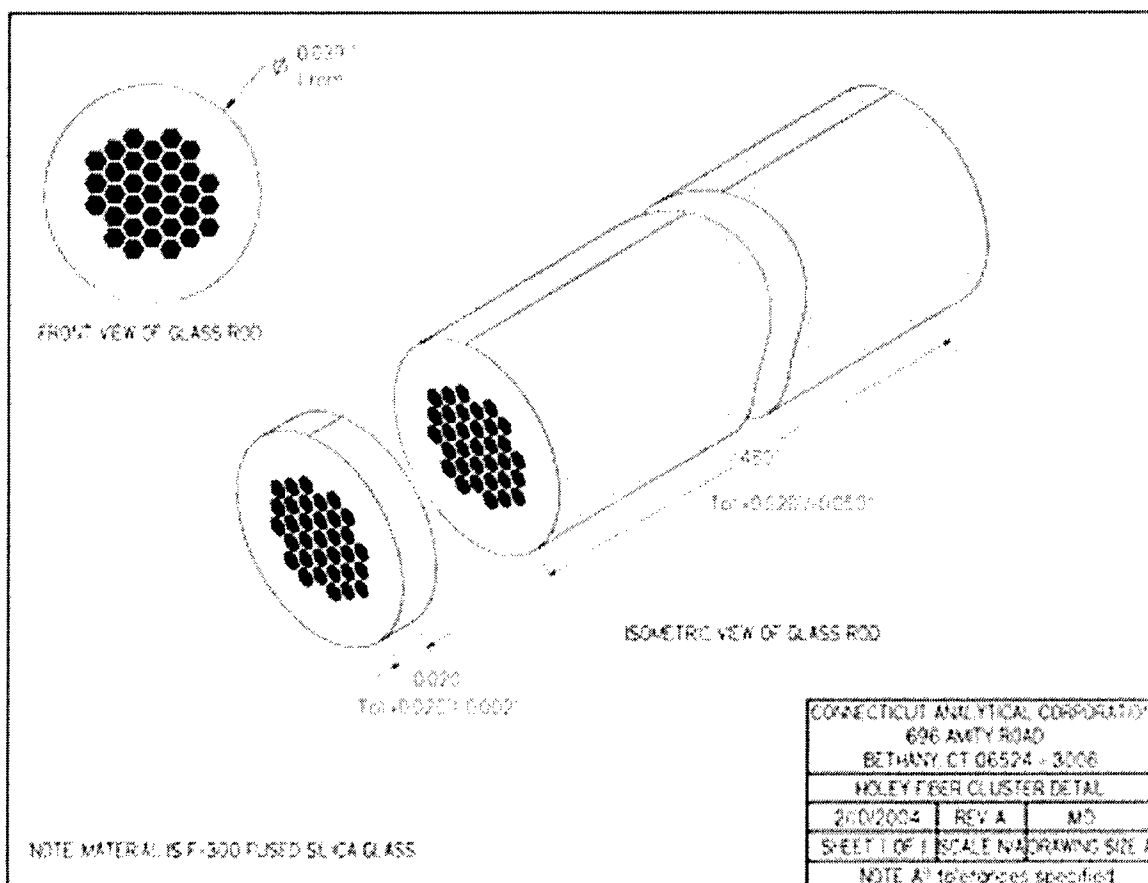
As one looks closer at each Holey fiber section, the slight defect is readily apparent; however, this does not matter as we still have over 5,500 emitters.



The remaining holes are very uniform in diameter...

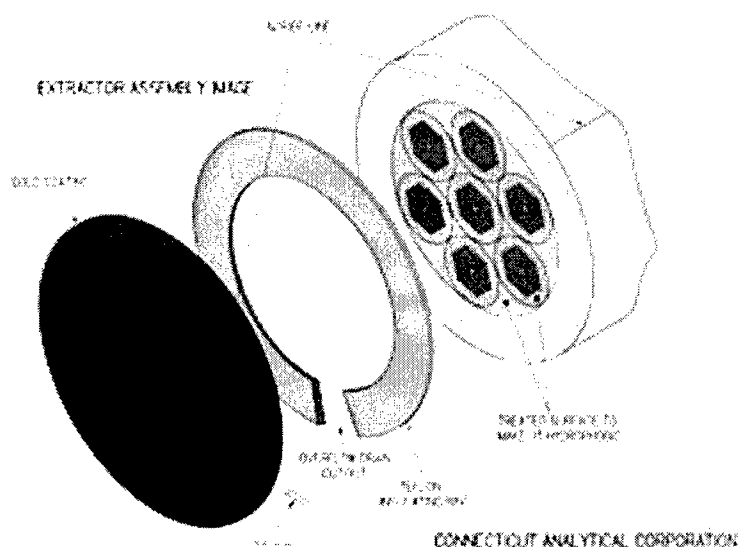


The next step was to cut the cane into appropriate lengths for testing. The extractor section was planned to be first sliced off. This was designed to guarantee that each hole is precisely aligned with the extractor to allow the cluster to produce the 5,511 individual emission sites.

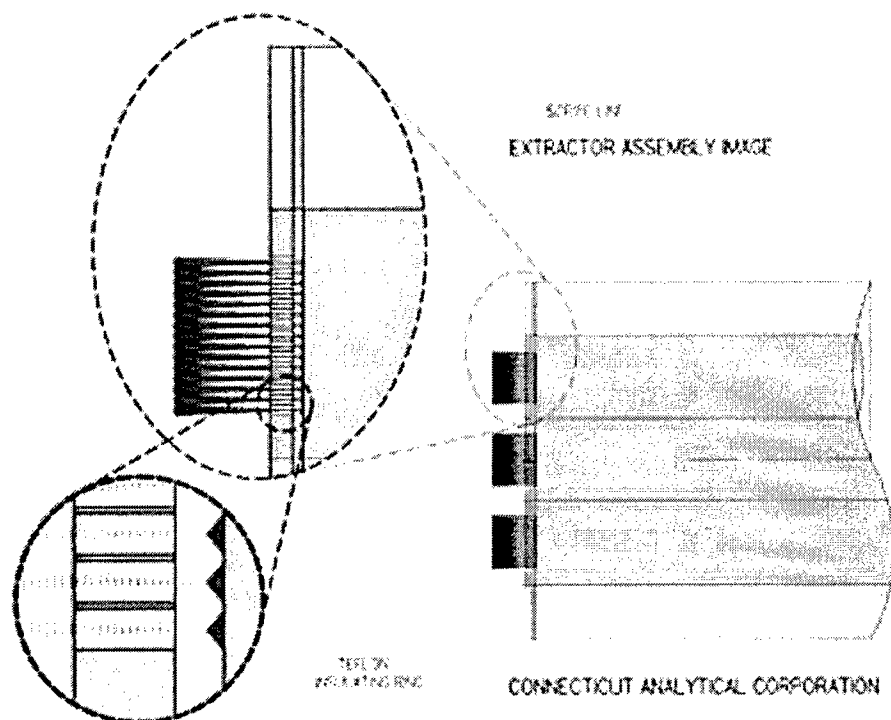


Once the extractor section is sliced off from the cane, it was to be plated with gold by sputter coating and then permanently attached to the cane section with an insulating washer to provide the necessary gap. The Teflon washer will have a small cut to allow for removal of any accidental buildup of liquid.

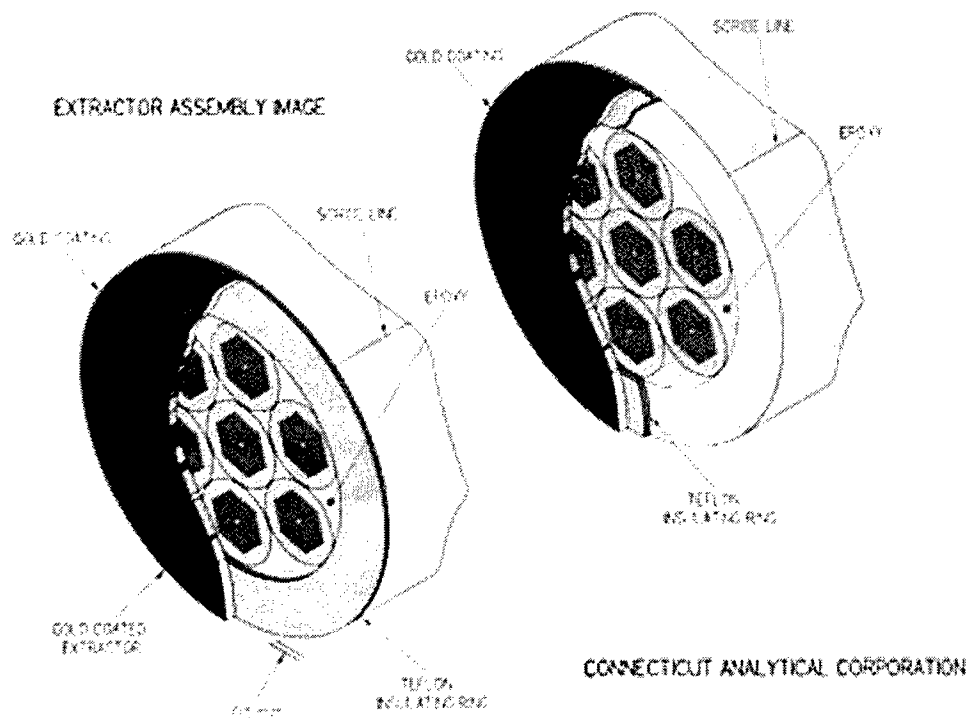
(This approach was obviated by the use of first the a high transparency grid, followed by an annular ring where the geometry of the fiber pores and the annulus were tailored by computer simulation to effect a uniform field across the source face.)



The end section of the planned completed unit (gold coated extractor, Teflon washer, and cane) looks as follows...



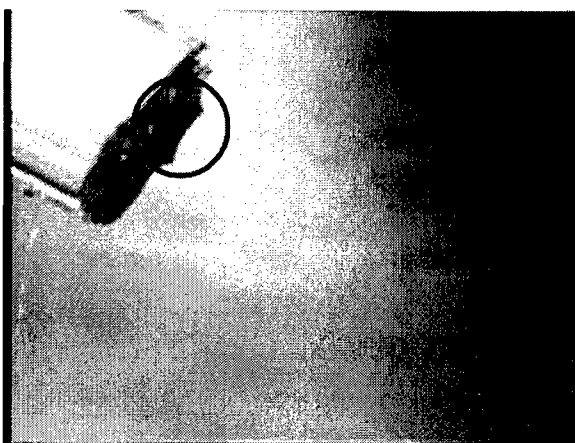
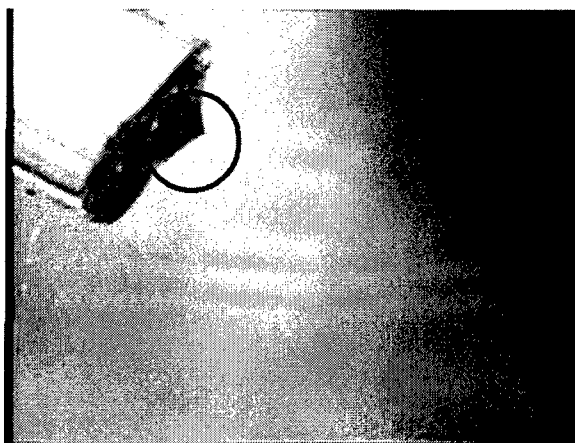
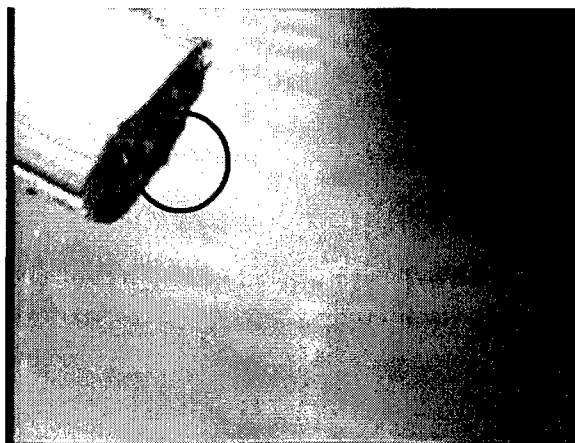
A cutaway view of the assembly was planned as follows...



Several methods were found to permit individual electrosprays from each Holey Fiber pore.

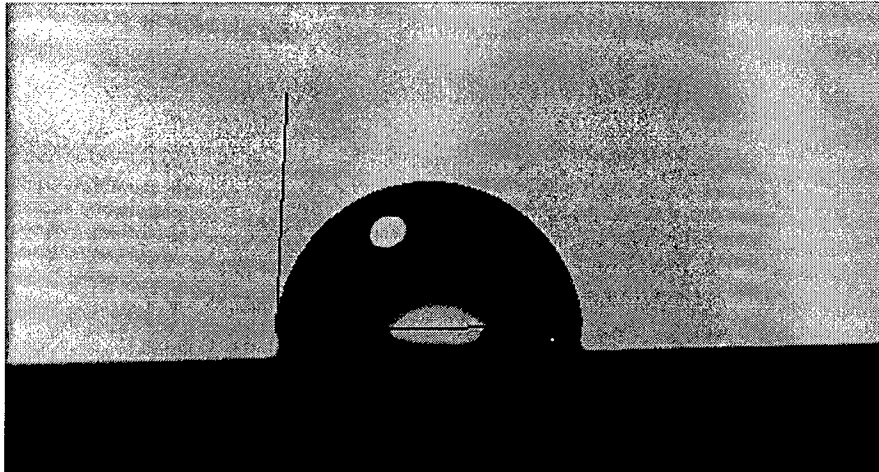
Note without treatment below, Holey Fiber Tips without chemical or other surface treatment to prevent wetting during electrospray.

Several unstable spray points can be observed...

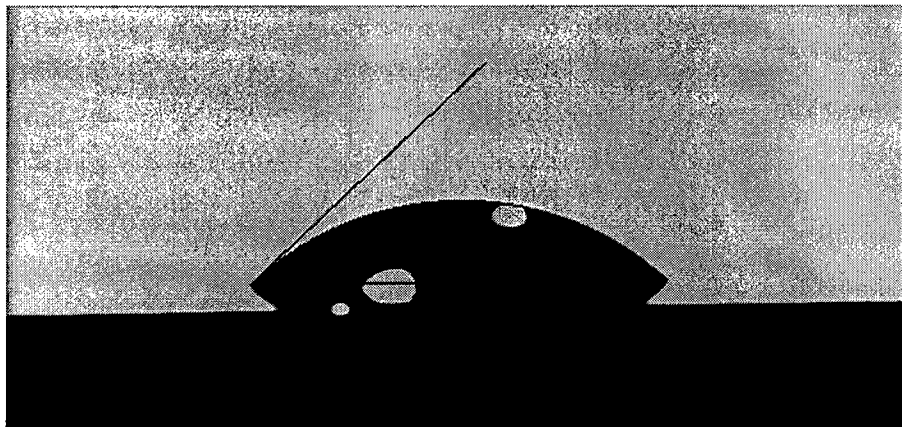


Teflon & Diamond Treated Surface to reduce wetting on Holey Fiber Tip

Teflon and Diamond coating are being evaluated to prevent wetting of the emitter. Teflon can be deposited onto many surfaces, the diamond coating can be deposited onto surfaces that (in general) form an intermediate carbide. Both techniques were found successful during Phase I.



Contact Angle – EMI BF4 on amorphous diamond – 86.1 degree



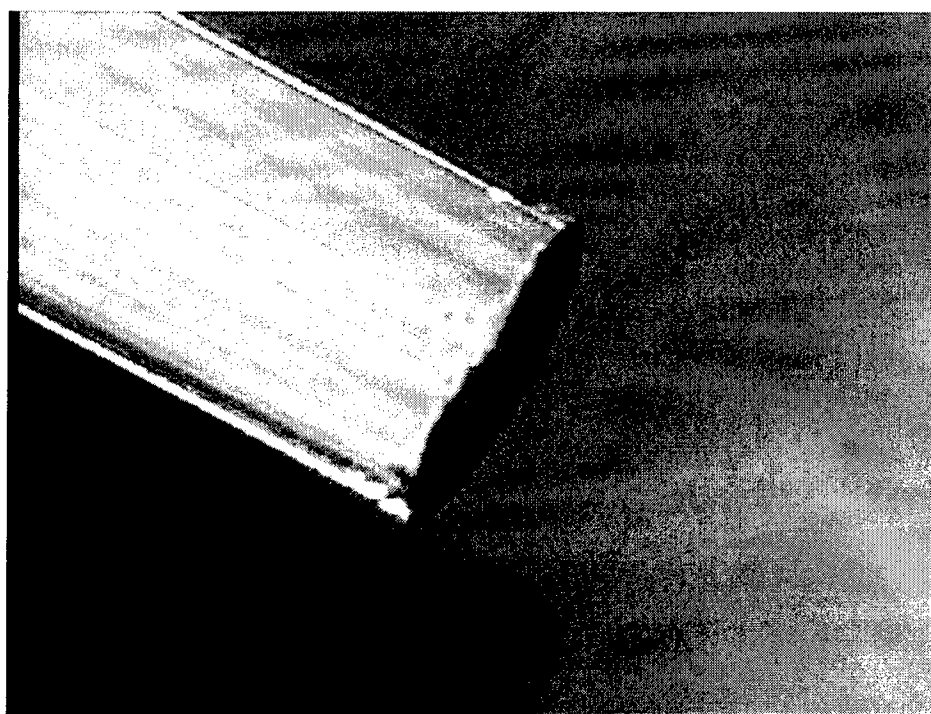
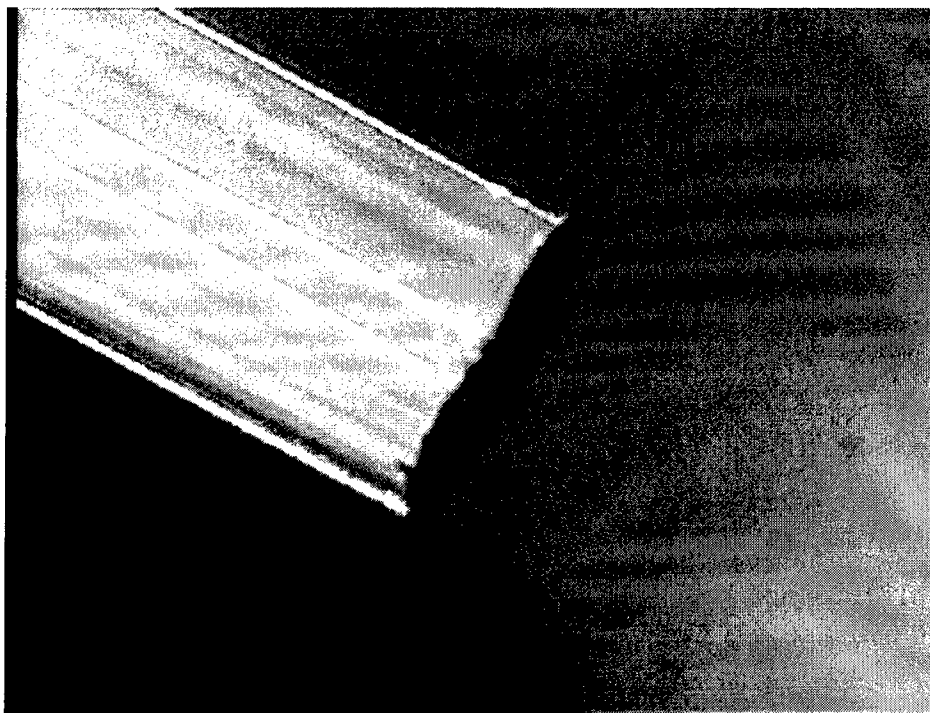
Contact Angle – EMI BF4 on Silicon – 42.2 degree

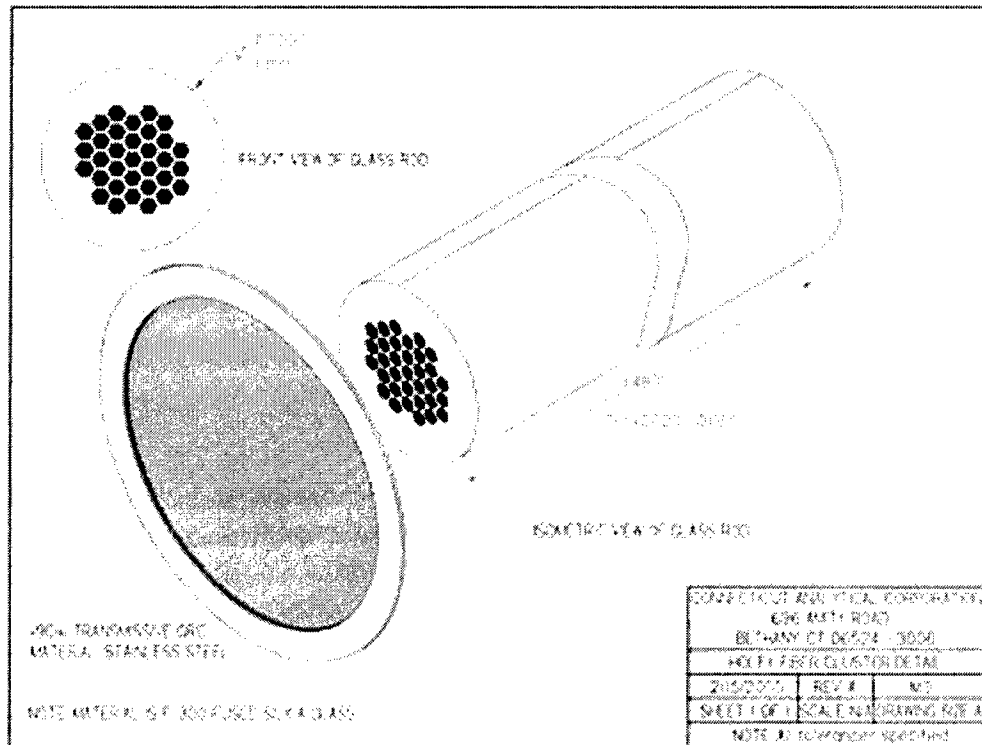
Teflon Treated Surface to reduce wetting



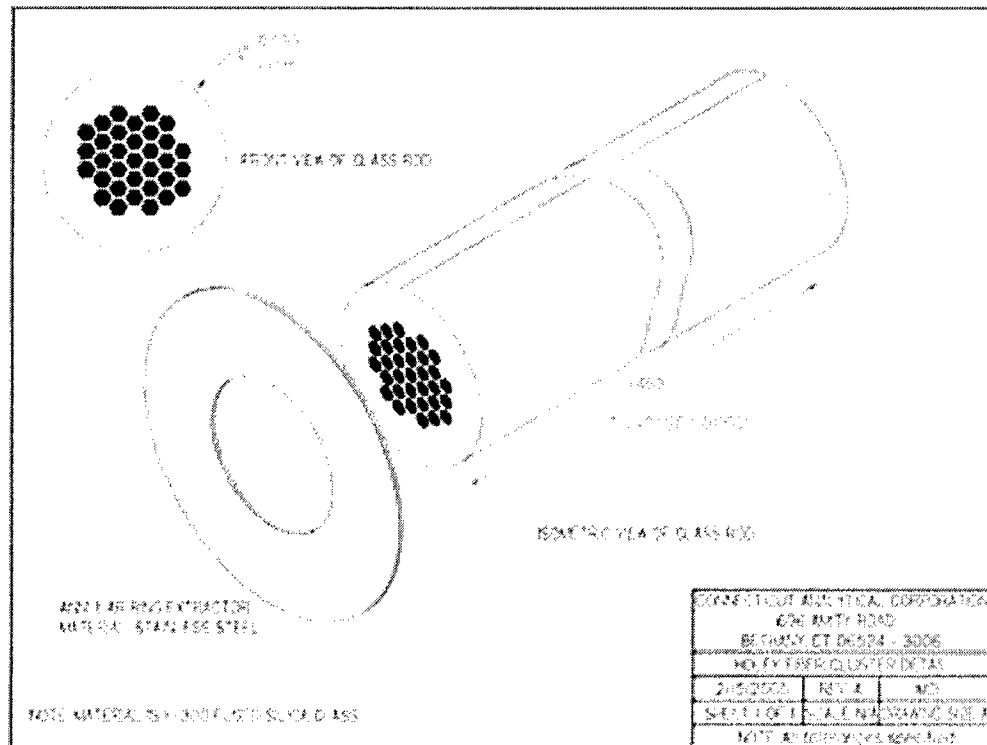
Contact Angle – EMI BF4 on Teflon – 85.1 degree

**Chemically treated Holey Fiber Tip during Spray - Individual Taylor
Cones, no pooling of Propellant**



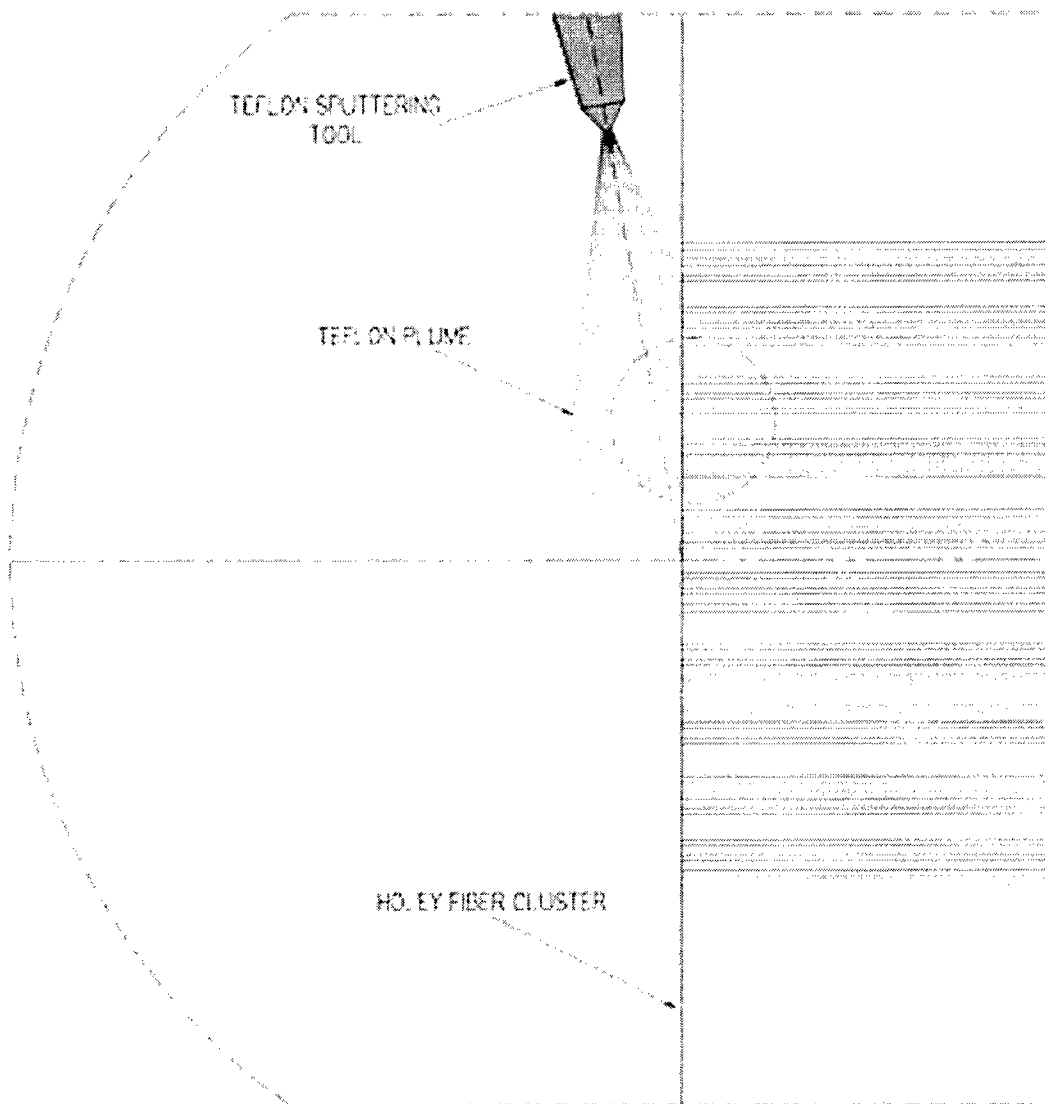


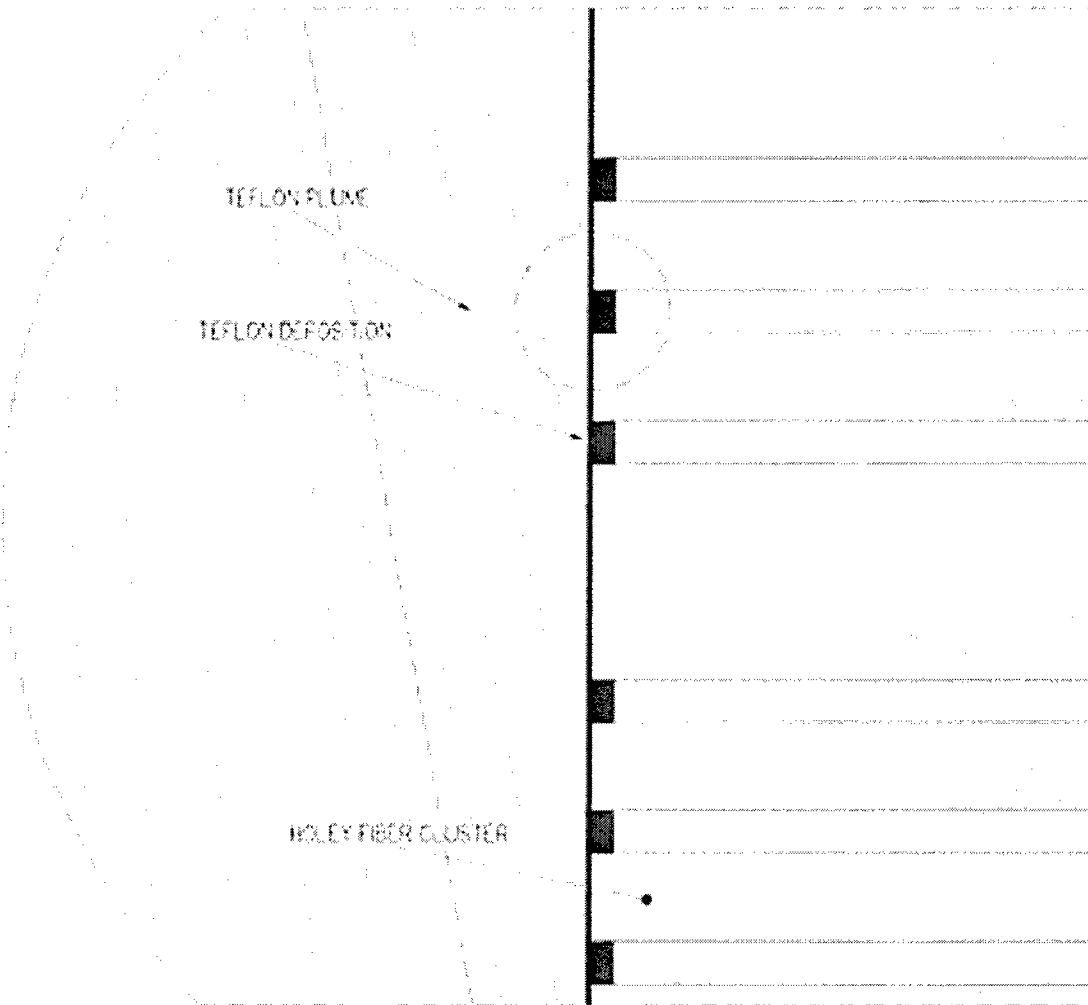
90% Transparent Grid Arrangement Used as Extractor in Phase I

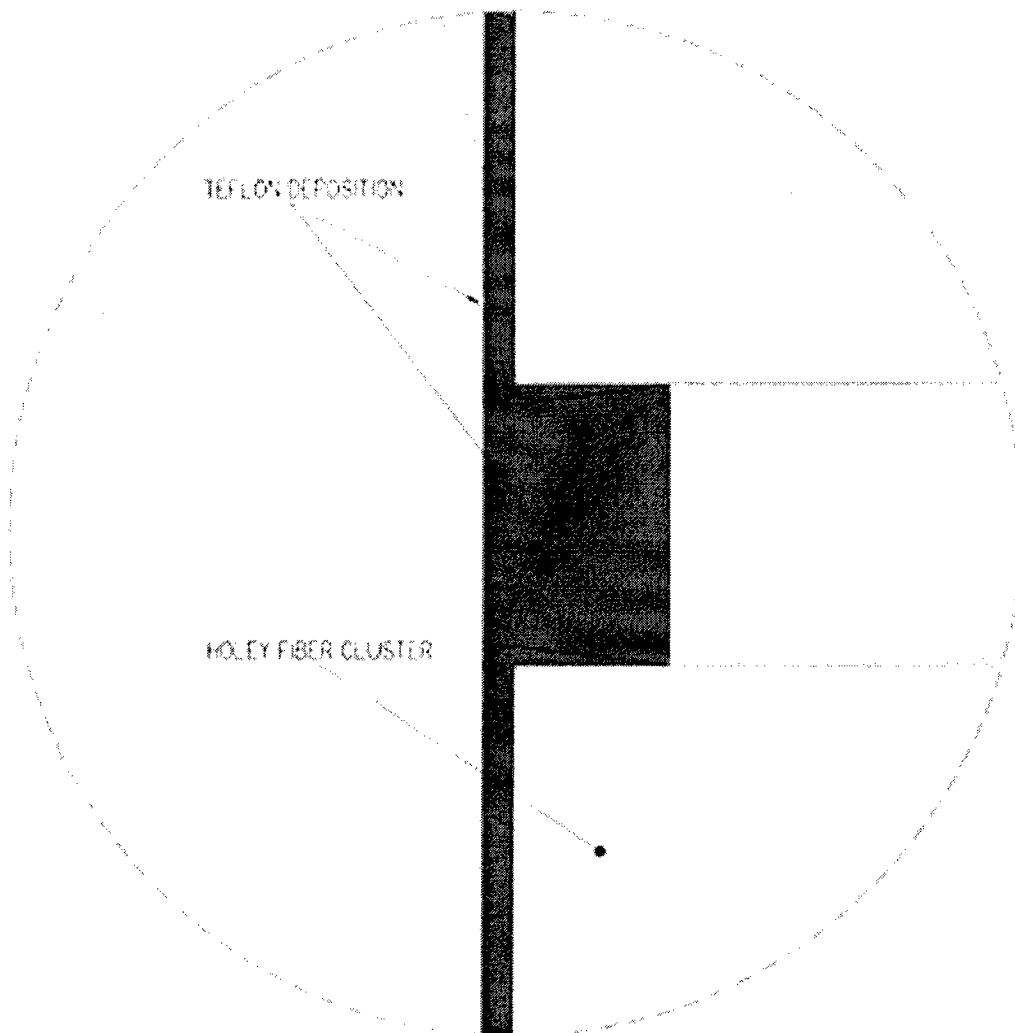


Annular Ring Used as Extractor in Phase I

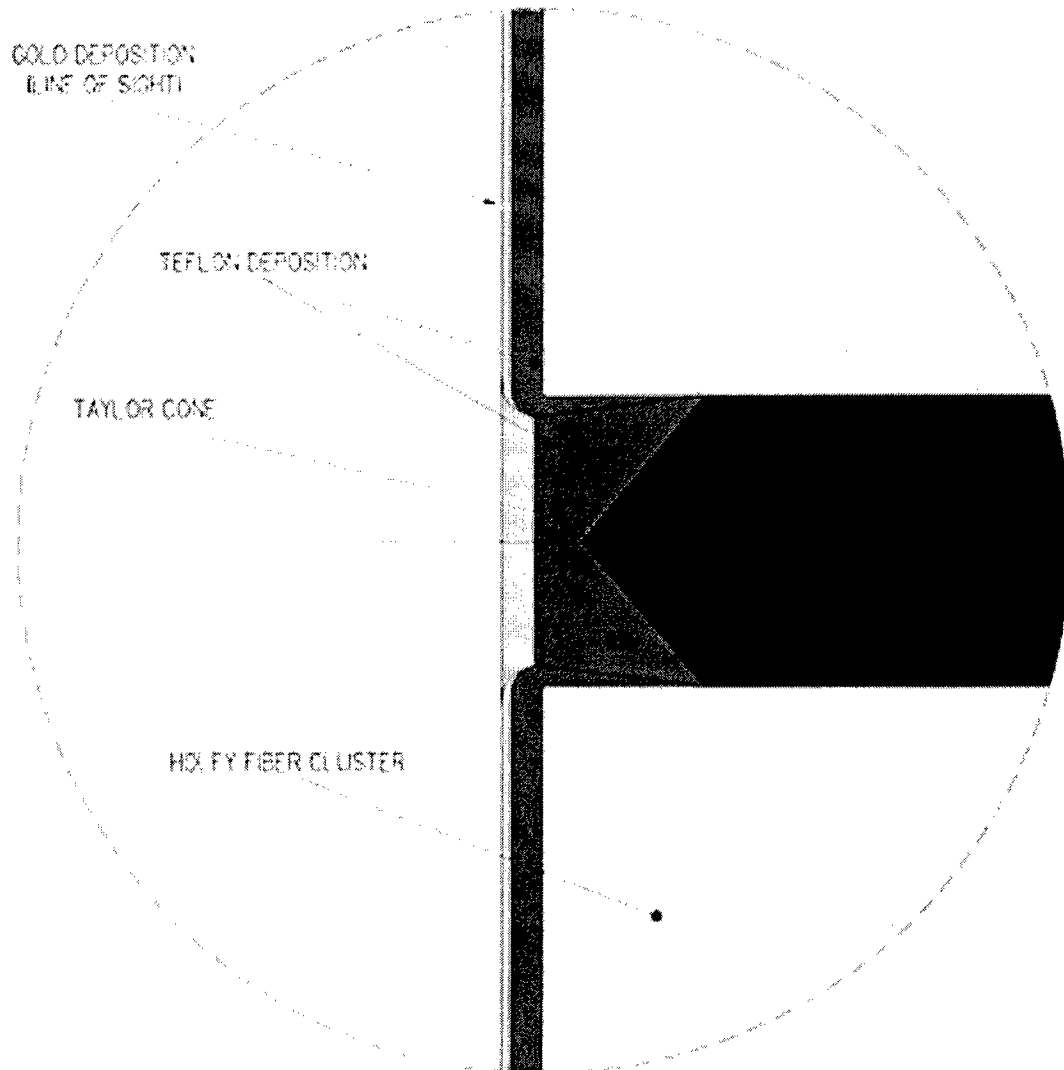
New Concept For Deposition of Insulator As Part of Conformal Extractor Design



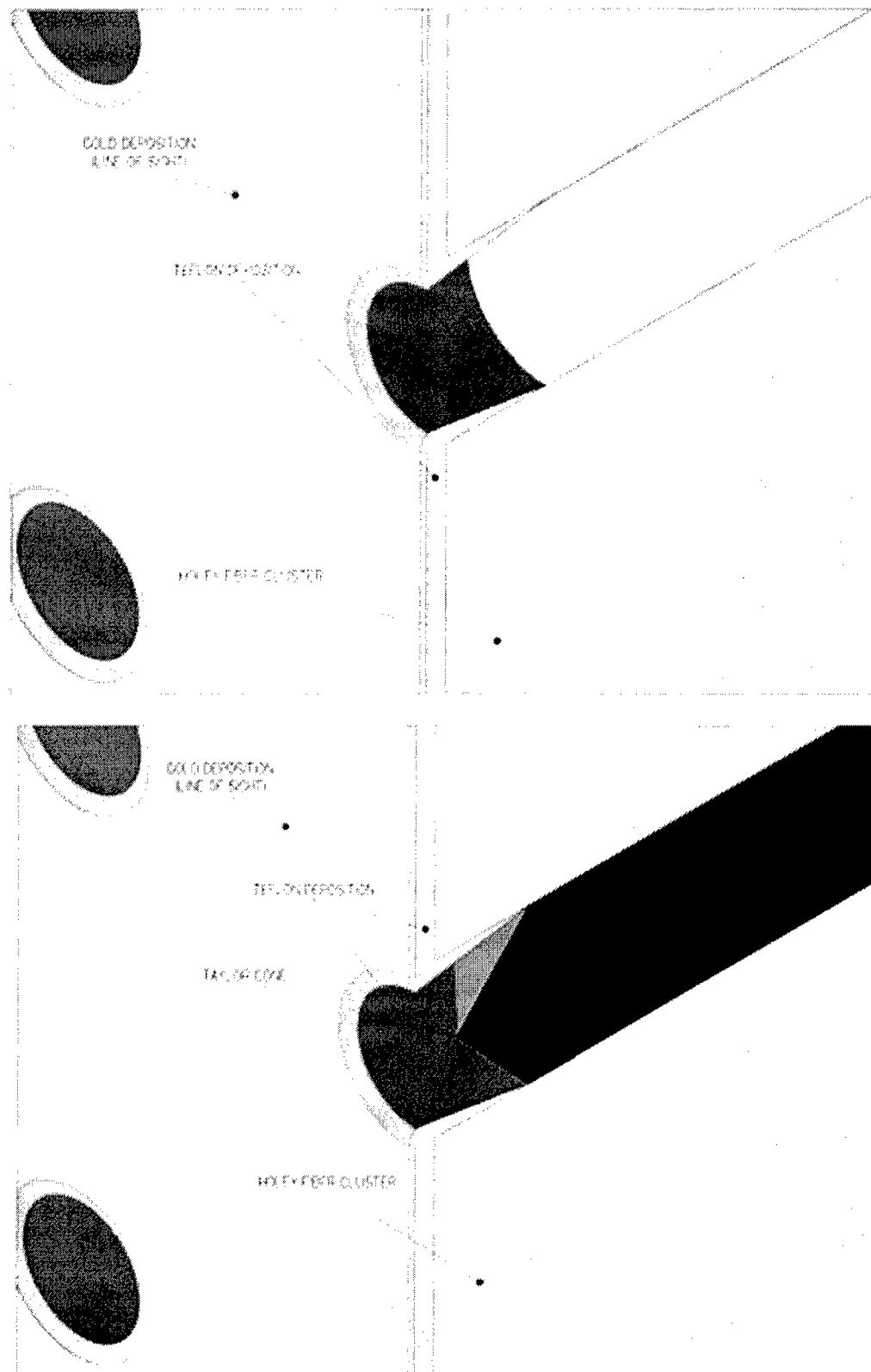




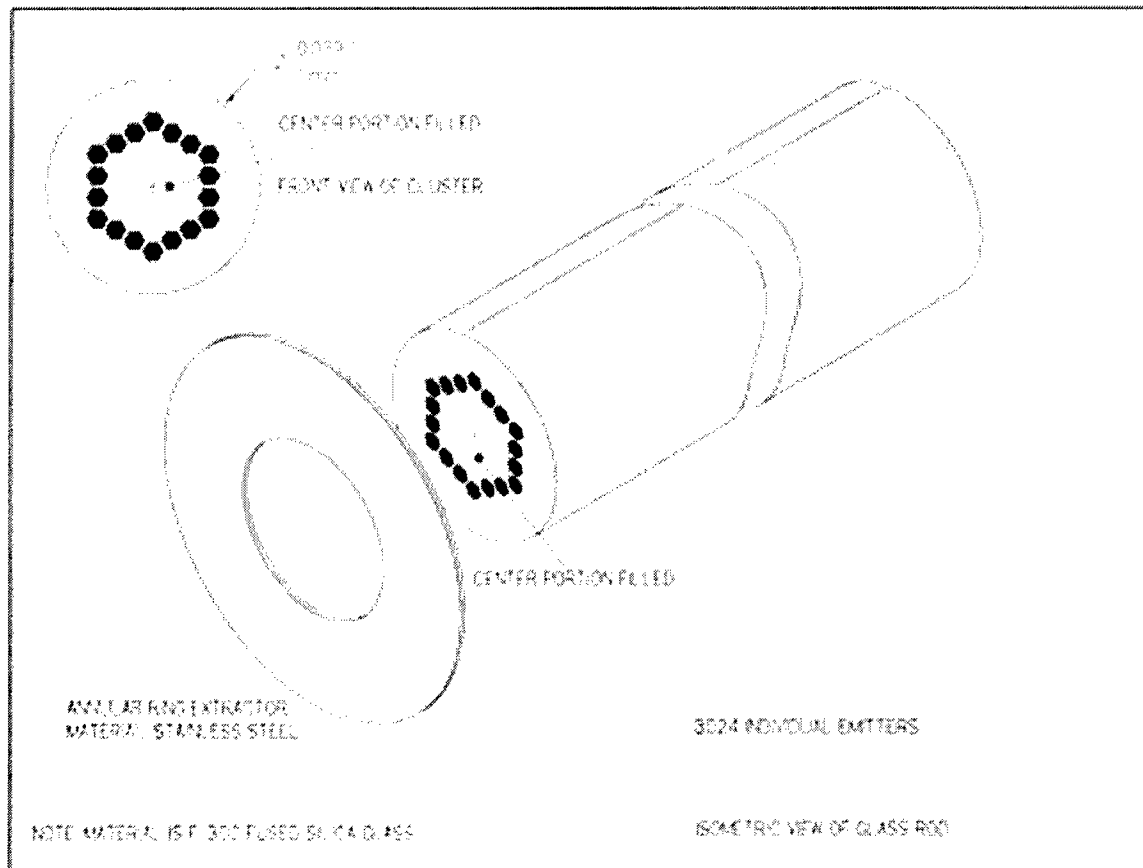
Conformal Extractor Conductor Fabrication



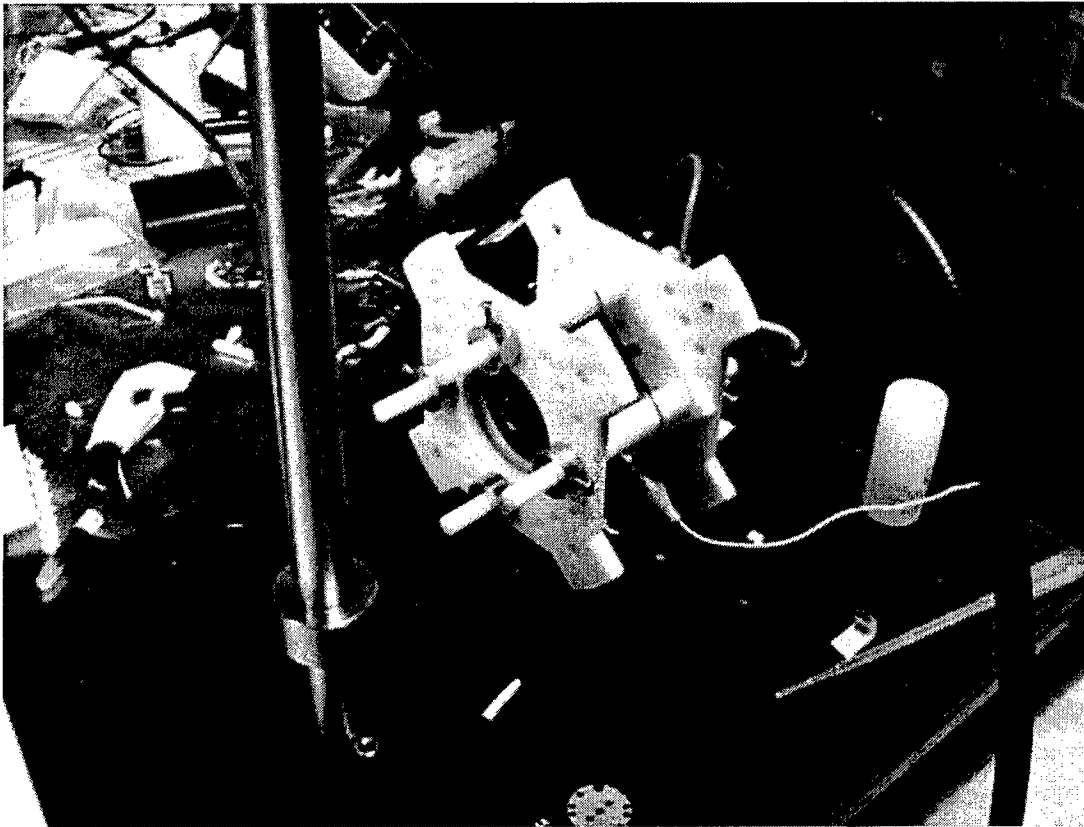
Detail of Conformal Extractor

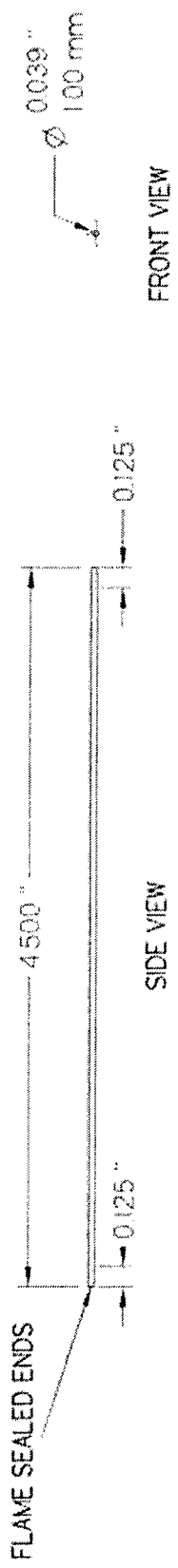


Detail of Ring Emitter with Annular Extractor



Ring Emitter with Annular Extractor Thruster Fixture as Tested

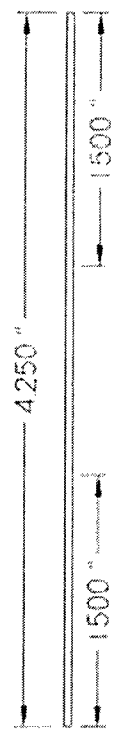




STEP 1) CLEAVE OFF 1/8" ENDS OF GLASS ROD AND CREATE SCRIBE LINE (DISCARD TWO CUT 0.125" ENDS)



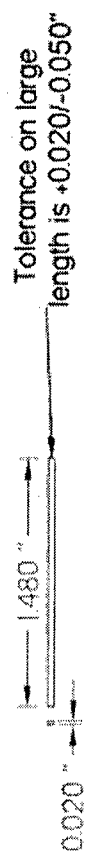
STEP 2) CUT TWO 1.5" SECTIONS OF GLASS ROD FROM THE ENDS (SAVE REMAINING 1.25" SECTION)



STEP 3) CLEAVE OFF SECTION OF GLASS ROD FROM THE ONE END (KEEP CUT END WITH ORIGINAL SECTION)



STEP 4) PLACE EACH CUT SECTION OF GLASS ROD WITH ITS OWN SLICE

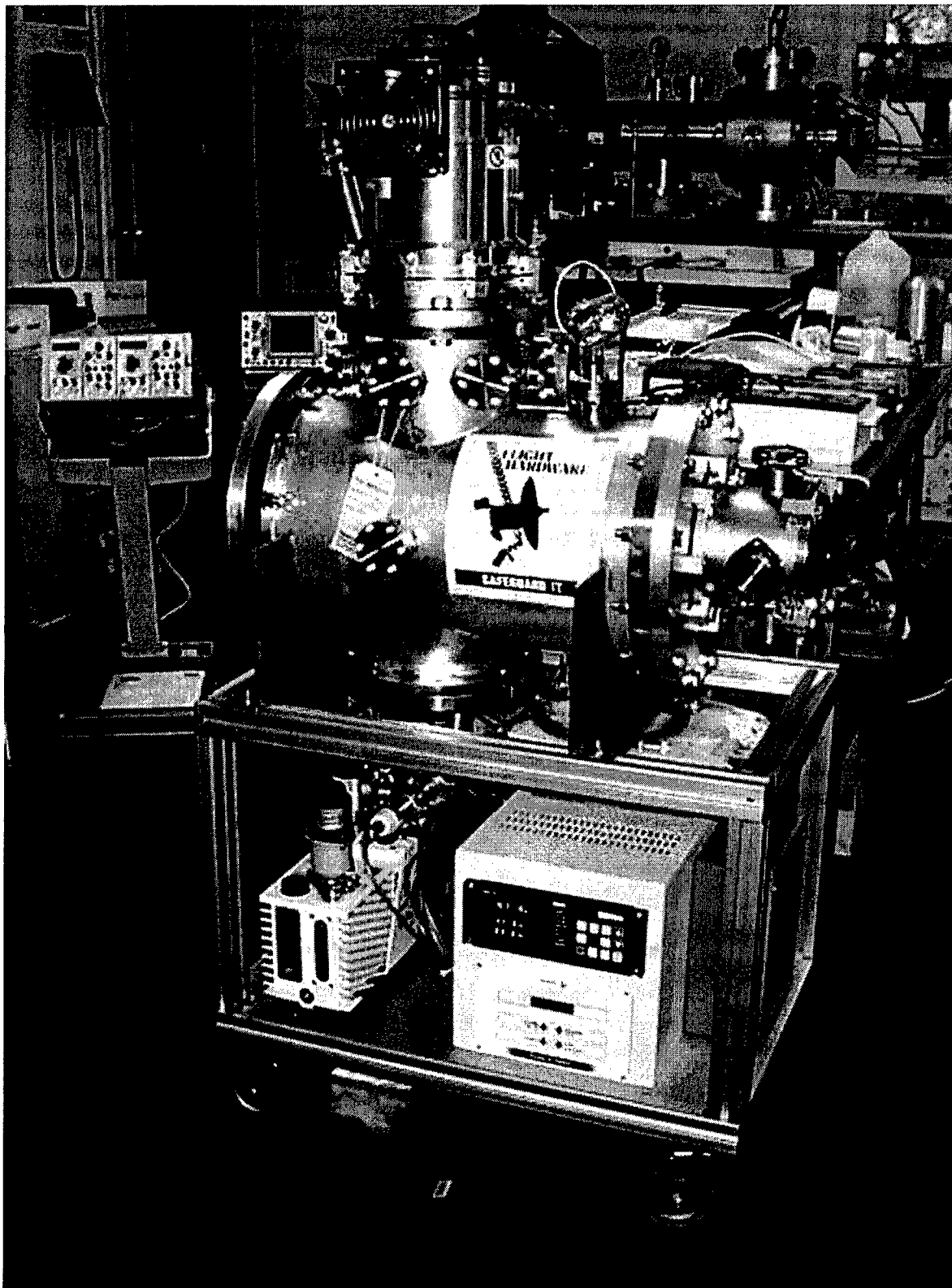


(TWO PIECES NEEDED)

NOTE GLASS ROD MATERIAL IS FUSED
SILICA UNCOATED GLASS

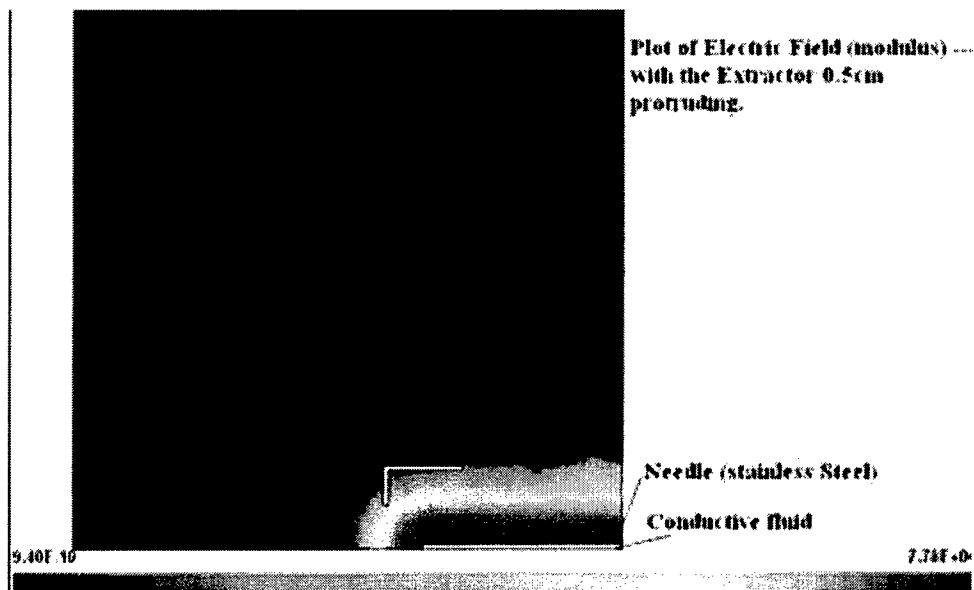
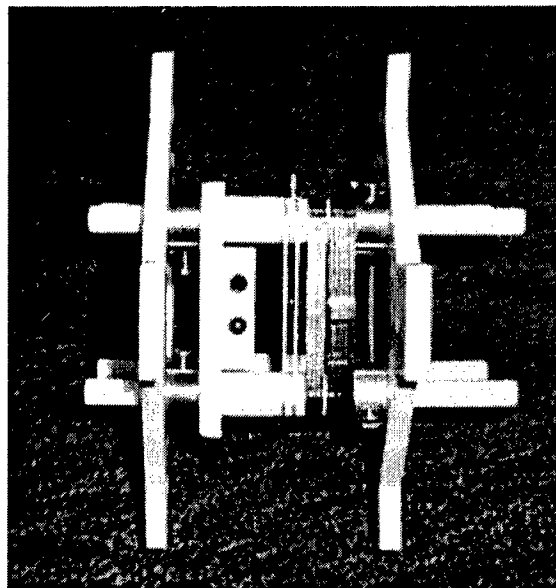
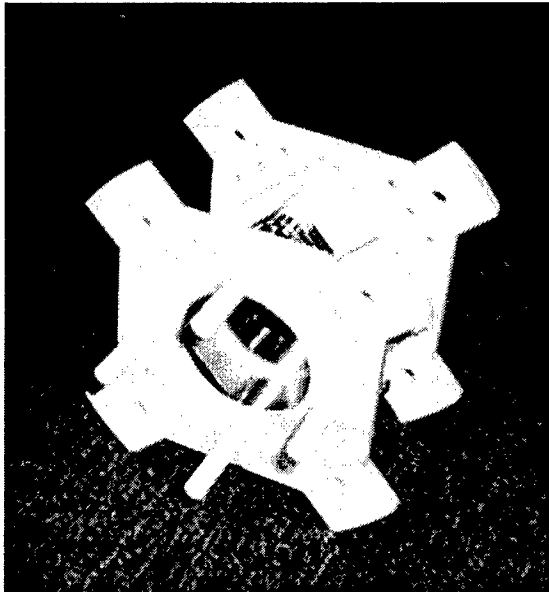
CONNECTICUT ANALYTICAL CORPORATION			
696 AMITY ROAD			
BETHANY, CT. 06524			
INSULATED NEEDLE & TARGET SPINDLES			
02/10/2004	REV. A	MD.	
SHEET 1 OF 1	SCALE 1:1	DRAWING SIZE A	
NOTE: All dimensions +0.020"/-0.002"			

CAC Time-of-Flight System Employed in Phase I



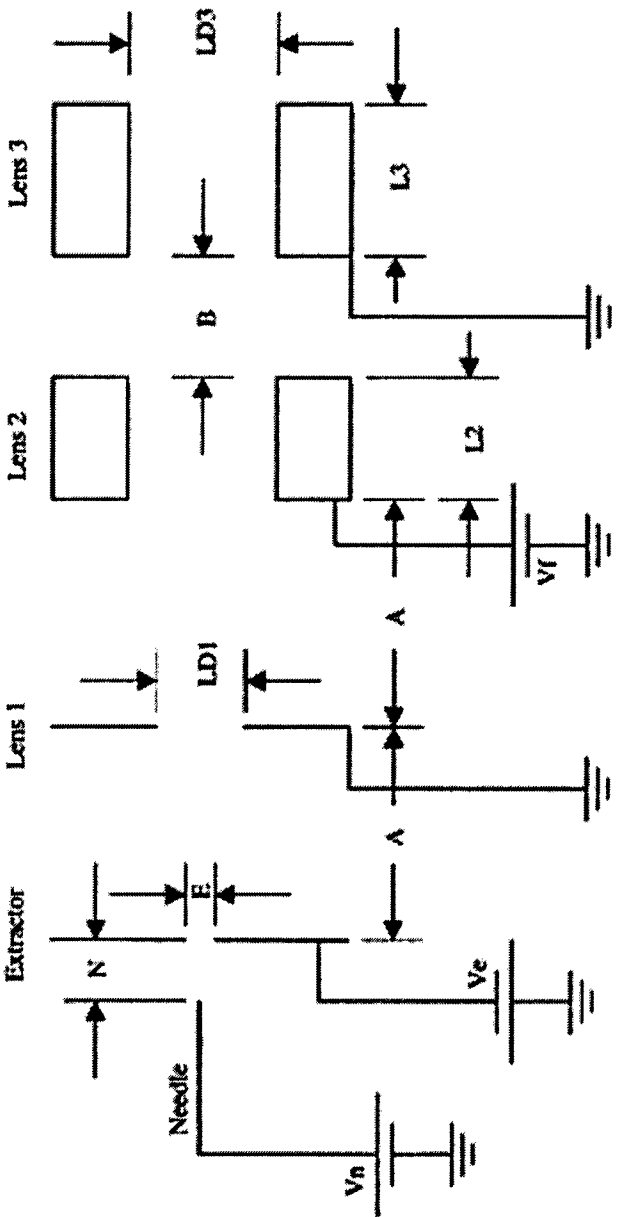
Detail of Thruster Assembly/Electrode Support

Holey Fiber thruster assembly used in CAC Time-of-Flight. The design of the thruster permits one to insert different electrospray sources, and through the use of multiple stacked electrode plates, one can configure electrostatic lensing as desired.



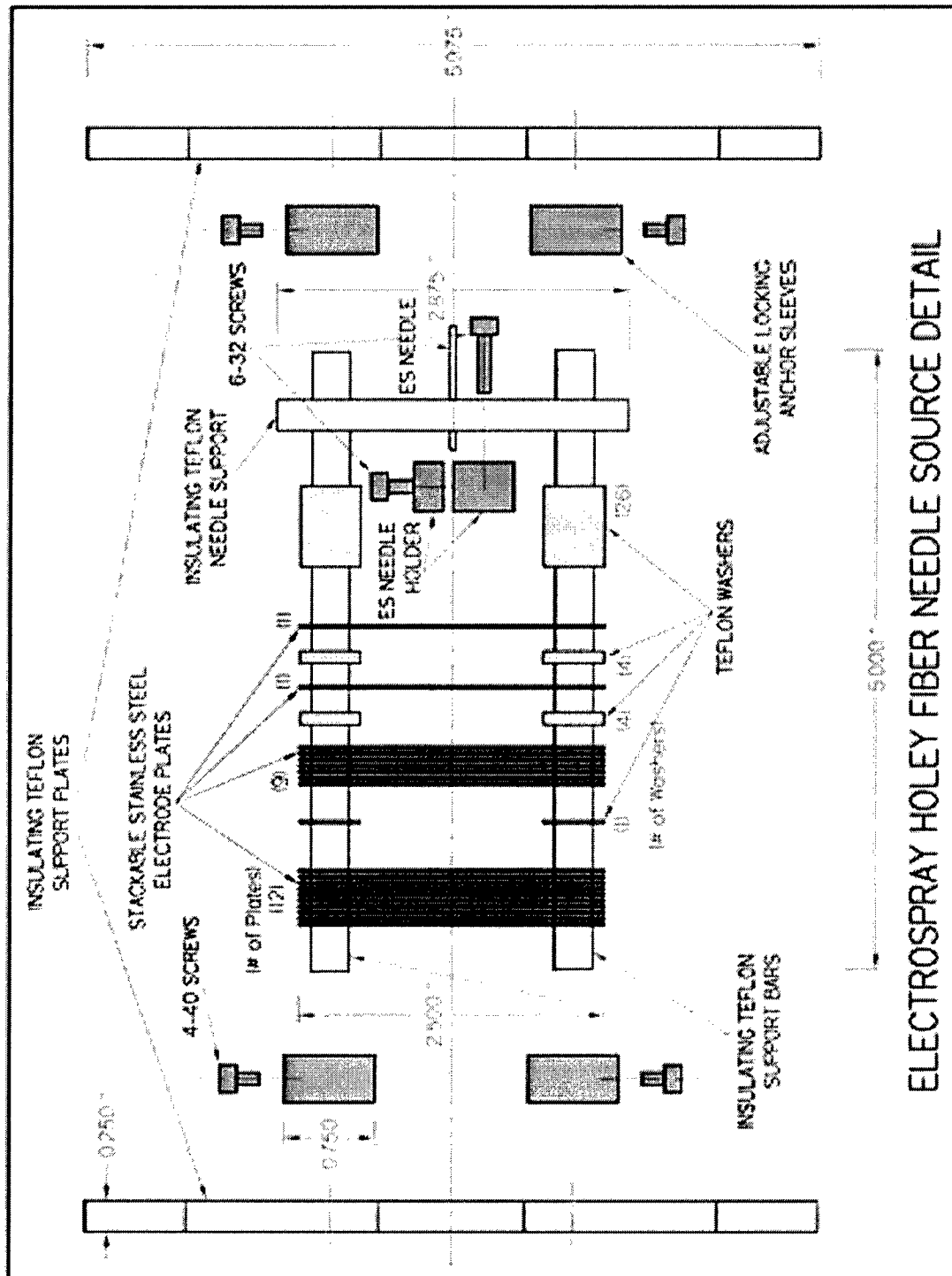
Lens configuration of Holey Fiber Test Fixture-Thruster Assembly

With the values shown below, this configuration achieves a 10x increase in current collection over a circular 3 cm² detector located at a distance of 15 cm from the extractor plate.



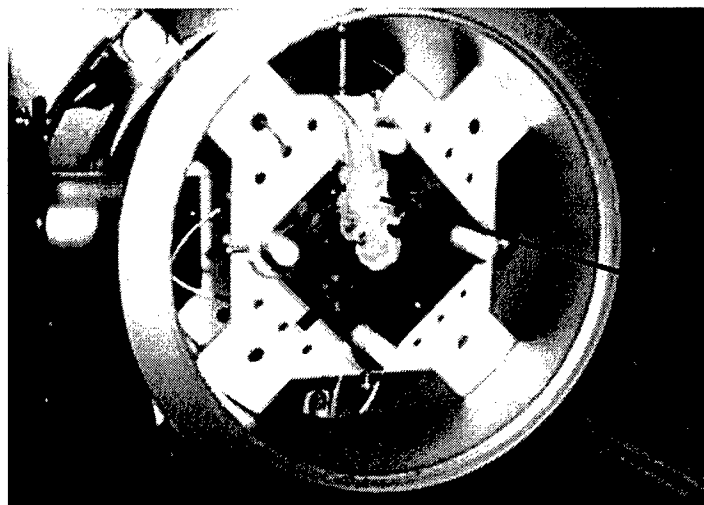
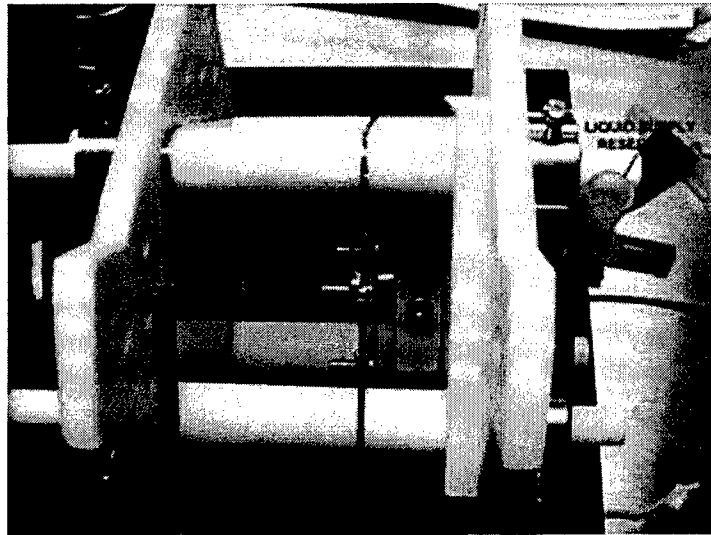
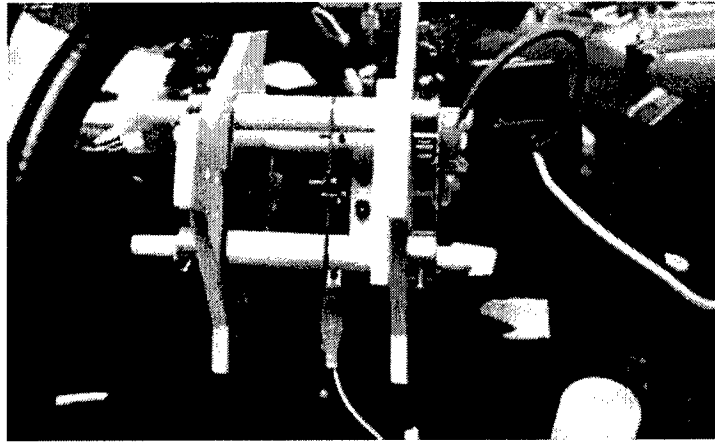
Thickness of the Extractor and Lens 1 plates is 0.025" = 0.635 mm

Longitudinal separations:	Cylinder lengths:	Aperture diameters:	Typical voltages
N = 0.3 mm	L2 = 5.59 mm	E = 5.08 mm	Vn = 606 V
A = 2.54 mm	L3 = 7.87 mm	LD1 = 11.4 mm	Ve = -751 V
B = 0.64 mm		LD3 = 16.25 mm	Vf = 678 V



ELECTROSPRAY HOLEY FIBER NEEDLE SOURCE DETAIL

Detail of Holey Fiber & Extractor Housing



Propellant Reservoir

Part III: Accomplishments / New Findings

Final Yale Phase I Propellant Report, AFOSR-MIT-Busek STTR

Prepared by Juan Fernandez de la Mora; 9/May/2005

1. Personnel: Graduate student C. Bueno was involved part time in this project until his recent departure in March/2005. A new graduate student, Mr. Sergio Castro has substituted him partially under this grant, though much of his activity is under a related AFOSR grant. He has been occupied with an effort to understand the ion evaporation mechanism in mixtures of propylene carbonate and the ionic liquid EMI-Im. His progress was reported at the recent colloidal workshop (MIT, 14/March/2005), but is still relatively preliminary. Much of the progress to be reported has been supported also in part by a separate AFOSR grant (CAC subcontract)

2. New ionic liquids suitable for purely ionic operation.

2.1 Acidification. Our previous report discussed the acidification of ionic liquids, by means of which EMIm was able to emit very close to the purely ionic regime. This route has been further pursued, with improvements reported at the recent MIT workshop

2.2 High surface tension ILs.

As also reported at the recent MIT workshop, we have noted that propellants with high surface tension γ favor attainment of the purely ionic regime. This point follows from known scaling laws for the electric field E on the meniscus tip, $E \sim \gamma^{1/2}$, from the fact that ion evaporation is activated by an intense electric field, and from the singularly large surface tension of EMIBF₄ with respect to other ionic liquids ($\gamma = 54$ dyn/cm, vs. $\gamma = 34.9$ dyn/cm for EMI-Im). We have confirmed the important role of γ by testing the ionic liquid with the highest γ value available in our lab, EMI-TfO (TfO = Trifluoromethane sulfonate, with $\gamma = 36$ dyn/cm) and verifying that it almost reaches also the purely ionic regime. This important finding has launched us into a more extensive search of ionic liquids with singularly high γ values. The literature on the surface tension of ionic liquids is scanty, so a systematic search will require a vast effort in terms of measuring physical properties. But there are a few important known facts that will facilitate this task.

1) Inorganic salts are known to have considerably higher γ values than ionic liquids.

This trend is indicated by the following examples, selected from G.J. Janz and R.P.T. Tomkins, J. Phys. and Chem. Ref. Data, Vol. 9 No 4, pp 831-1031, 1980). For instance, even the particularly modest γ value of NaBF₄: $\gamma(\text{dyn/cm}) = 140.68 - 75 \cdot 10^{-3} T (\text{K})$; ($\gamma = 88$ dyn/cm at $T = 700$ K), is much larger than that of EMIBF₄. As shown in Table 1, other materials have considerably higher surface tensions.

Table 1: illustrative values of surface tensions for molten inorganic salts.

Li ₂ MoO ₄ :	$\gamma = 233.9$ dyn/cm @ 1040 K
Zn(PO ₃) ₂ :	$\gamma = 199$ dyn/cm between 1250 and 1420 K
Mg(PO ₃) ₂ :	$\gamma = 227.6 - 225.0$ dyn/cm between 1430 and 1500 K
Cd(PO ₃) ₂ :	$\gamma = 205 - 206$ dyn/cm between 1170 and 1270 K
Rb ₂ CO ₃ :	$\gamma = 145 - 138$ dyn/cm between 1160 and 1230 K
Cs ₂ CO ₃ :	$\gamma = 133 - 124$ dyn/cm between 1100 and 1220 K

Notice that the advantage of inorganic salts is not a temperature effect, as surface tension decreases at increasing T .

2) The advantage of a more inorganic composition is also clear from the properties of EMI-BF₄, whose BF₄⁻ anion is the smallest known in a water and air stable ionic liquid with suitably small viscosity (or high electrical conductivity). This point is further confirmed by the data of George Law and Philip R. Watson (Surface Tension Measurements of *N*-Alkylimidazolium Ionic Liquids, *Langmuir* **2001**, *17*, 6138-6141), recently widened by Jonathan G. Huddleston, Ann E. Visser, W. Matthew Reichert, Heather D. Willauer, Grant A. Broker and Robin D. Rogers (Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, *Green Chemistry*, 2001, *3*, 156–164).

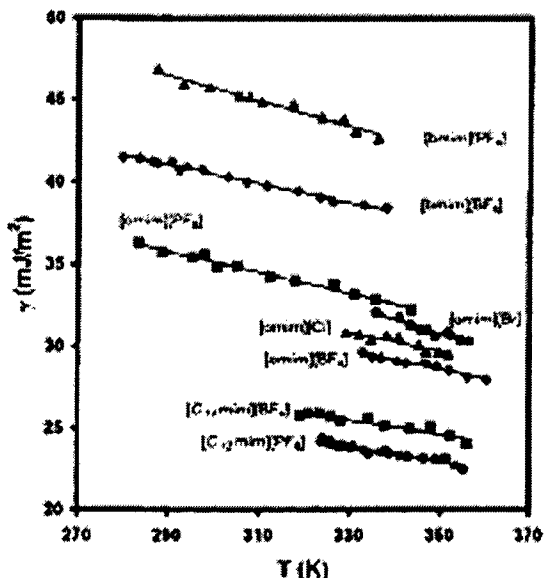


Figure 1 on the left is from Law and Watson (2001). It shows temperature dependence of surface tension for several salts (b=Butyl, o=Octyl, C₁₂=dodecyl), for the two anions BF₄ and PF₆. It is evident that the longer the carbon chain in the imidazolium group the lower the surface tension, a point further confirmed by the datum of EMIBF₄ not included in the figure (E = ethyl; g(297 K) = 54 dyn/cm). An interesting and clear advantage of the PF₆ over the BF₄ cation is also clear. An advantage of Br over Cl and over BF₄ (but not over PF₆) is also seen for the OMI salts. Note that the temperature dependence is almost linear

The propellant optimization task would then consist of finding a material with a high inorganic component yet a low melting point and a modest viscosity coefficient. Many ionic liquids from which to pick exist commercially, as indicated by the following list from Merck, including only salts with the cation EMI⁺.

Table 2. Properties of several ionic liquids based on the EMI⁺ cation.

Substance	T _m (°C)	ν(mm ² /s)	γ(dyn/cm)	K
EMI-Cl	83			
EMI-Br				
EMI-BF ₄	-50	30.6	52	1.4
EMI-TfO	-12	32.6	36(22C)	0.86
EMI-PF ₆	60			
EMI-SbF ₆				
EMI-Im		22.4	34.9	0.88
EMI-Im-dicyanamide (C ₂ N ₃)	-21	20(25 C) ⁺		

⁺Douglas R. MacFarlane, * Jake Golding, Stewart Forsyth, Maria Forsyth and Glen B. Deacon, *Chem. Commun.*, 2001, 1430–1431

But the scarcity of information on the two key physical properties, electrical conductivity K and surface tension γ makes the selection process rather effort intensive. For instance, it would seem from the figure included of Law and Watson (2001) that EMI-PF₆ would be a better candidate than EMI-BF₄. Unfortunately its melting point (60 °C) is well above room temperature.

It follows from these observation that a more inorganic ionic liquid will tend to have a higher surface tension than a more organic one. Similarly, it appears that a shift into the even smaller anions Br and Cl would be advantageous surface tension wise, but EMICl melts at 83 °C, and both EMICl and EMIBr are too viscous to have the desired range of electrical conductivity. The dicyanamide cation included last in **Table 2** was originally presented as the least viscous ionic liquid known. Although its electrical conductivity and surface tension remain unreported, the compactness of the cation makes it a promising candidate for an elevated surface tension, and its small viscosity makes a high electrical conductivity also likely. This substance therefore deserves a full evaluation as an electrical propulsion fuel. Another peculiarity of the dicyanamide ion is its small molecular weight (66 amu), which singles it out for high specific impulse missions.

2.3 Mixtures of ionic liquids among themselves and with solid salts

This approach has been so far very useful to understand the transition between the mixed and the purely ionic regime. As reported at the recent MIT workshop, and as illustrated in **Table 3** below, the mixtures of EMIBF₄ with Ethyl₃N-Im have served to demonstrate that this transition occurs abruptly when a certain combination of surface tension and electrical conductivity reaches a critical value. But such mixtures have so far not revealed any combination of propellants with properties superior of those of EMIBF₄.

The alternative of mixing ionic liquids with solid inorganic salts with anions or cations of high mobility (other than acids) is unlikely to be useful to increase electrical conductivity. In a recent study (Kikuko Hayamizu, Yuichi Aihara, Hiroe Nakagawa, Toshiyuki Nukuda, William S. Price (*J. Phys. Chem. B* 2004, 108, 19527-19532) on the "Ionic Conduction and Ion Diffusion in Binary Room-Temperature Ionic Liquids Composed of [emim][BF₄] and LiBF₄), they conclude that the electrical conductivity of the mixtures decreases at all temperatures and compositions with respect to that of the neat ionic liquid. Similarly negative have been the tests announced in our recent report on mixtures of amine + ImH salts with acids or EMIBF₄. None of them has shown exceptional properties. But these negative results do not necessarily imply that the mixture approach will not be fruitful in other cases. For instance, a potentially interesting option includes mixtures of EMIBF₄ and EMIPF₆, where the later would presumably increase the surface tension, hopefully without an excessively negative impact on viscosity, electrical conductivity and melting point.

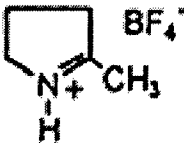
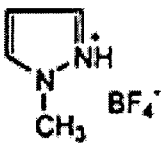
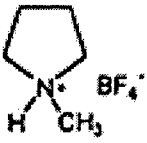
Table 3: Characteristics of Et₃NHIm + EMIBF₄ mixtures vs. EMIBF₄ concentration. M = mixed regime; I = purely ionic regime.

Vol %	0	10	30	50	60	65	70	80	100
K(S/m)	0.39	0.53	0.65	0.66	0.74	0.72	0.82	0.99	1.3
Regime	M	M	M	M	M	M&I	I	I	I

2.4 Other ionic liquids based on reactions of amines with acids

We have been involved in the search of ionic liquids based on neutralization of amines, and synthesized quite a few ourselves. Recently we have discovered a Japanese study combining numerous amines with BF_4H , with the discovery of these liquids with considerably higher electrical conductivity than EMIBF_4 (see **Table 4**). These promising ionic liquids are not commercially available, but we have already obtained the reactants and plan on synthesizing and testing them soon.

Table 4: Names and structures of several starting amines, and electrical conductivities of their corresponding tetrafluoroborate salts at 25 and 50° C. From Michiko Hirao, Hiromi Sugimoto, and Hiroyuki Ohno, Preparation of Novel Room-Temperature Molten Salts by Neutralization of Amines, *Journal of The Electrochemical Society*, 147 (11) 4168-4172 (2000)

Amine	2-Methyl-1pyrroline	1-Methylpyrrazole	1-Methylpyrrolidine
			
K(50° C)	2.7 S/m	3.5 S/m	2.5 S/m
K(25° C)	1.6 S/m	1.9 S/m	1.6 S/m

2.5 new low-viscosity ionic liquids based on reactions of amines with diketones

A new class of easily synthesized ionic liquids has been recently introduced by Om D. Gupta, Brendan Twamley and Jean M. Shreeve (Low melting and slightly viscous ionic liquids via protonation of trialkylamines by perfluoroalkyl β -diketones, *Tetrahedron Letters* 45 (2004) 1733–1736). They note that diketones such as hexafluoroacetylacetone (see scheme below) are capable of transferring a proton from the central CH_2 group into an amine, similarly as an acid. The result is a salt with a wide thermal stability range and a very small or null volatility.



Of particular interest is the fact that the electron cloud in the deprotonated diketone is widely distributed over the anion, apparently suppressing hydrogen bonding and leading to remarkably small viscosity coefficients. In the particular case of the reaction between trioctylamine (C_8H_{17})₃NH and hexafluoroacetylacetone (scheme above), the resulting salt has a viscosity coefficient of 3.44 cP at 25 °C ($\eta = 4.3 \text{ mm}^2/\text{s}$). This is about five times less than the previous record held by EMI-dicyanamide. No data are yet available on the electrical conductivity of this substance, whose surface tension will probably be rather modest. We have already ordered the chemicals for this synthesis. Carrying the reaction is as easy as the neutralization of amines with acids. But purifying the final product is less straightforward. If we are successful at both tasks we plan on measuring such key physical properties. We will also test the promise of this material for electrical propulsion. Even if the electrical conductivity is insufficient, the singularly low viscosity of this new salt makes it also ideal as a solvent for other salts or ionic liquids. For instance, its viscosity coefficient drops to 1.6 cP at 40 °C. This is considerably lower than the room temperature values for the neutral solvents propylene carbonate (PC) and formamide, with the additional advantage that the new medium is essentially involatile at these and even higher temperatures.

NASA-CAC-AFOSR Final Propellant Development at Yale, Preparation for Phase II

J. Fernandez de la Mora

On an AFOSR Phase II, Yale will continue its research into new propellants suitable for Holey Fiber thrusters. These will include the traditional ionic liquids, Formamide, acidified mixtures, and possibly propellant suitable for coaxial jets. For the purposes of this proposal illustrating the direction of our studies thus far, we condense here the main highlights on propellant development from earlier reports, as well as new developments on conductivity enhancement by acidification and propulsion characteristics of irradiated propellants.

1. Considerations leading to the selection of ionic liquids as the appropriate fuel

Yale's function in this program was to select a suitable liquid as propellant. The choice made at CAC of a capillary-based fuel-feeding scheme was originally based on a wicking surface with a relatively large surface area exposure of the liquid to the vacuum environment (until the discovery of Holey fibers), and this forced the use of involatile propellants. Accordingly, most of the effort to date has used involatile ionic liquid propellants, many of which have the properties of being liquid at room temperature and having electrical conductivities in the range of $K = 1 \text{ S/m}$. A limited amount of exploration with electrolytes of the organic solvent propylene carbonate has also undertaken. When the Holey fiber concept was discovered during the Phase II JPL effort and continued under AFOSR support, volatile propellants again became candidates, although much work needs to be done in this area and will be the focus of a possible Phase II effort. An AFOSR Phase II study will encompass both ionic liquids, volatile fluids such as Formamide, and suitable propellant mixtures.

2 Ionic liquids: Ionic vs. Colloidal Regime of Operation

Very little was known at the start of this project on the suitability of ionic liquids as fuels for colloidal propulsion. Much has been learned since then. Two rather different regimes of Taylor cone operation with ionic liquids are known: One where they produce mostly drops (colloidal regime), and another where they produce primarily ions (ionic regime). Although NASA's DRS program at Busek has opted for the mixed colloidal-ionic regime of EMI-Im (EMI = Ethylmethyl imidazolium; Imidazolium is a pentagonal ring with two non-contiguous nitrogen atoms; Im⁺ = TFSI⁻ = (bis trifluoromethyl sulfonyl imide = $(\text{CF}_3\text{SO}_2)_2\text{N}^-$), the purely ionic regime offers more promise, particularly for missions requiring thrust levels above 1 mN. Most of our work has therefore been directed at the identification of ionic liquids capable of operating in the purely ionic regime.

3 Purely ionic propulsion with ionic liquids

3.1 Room temperature operation

EMI-BF₄. To date the only pure material (other than liquid metals) able to reach the purely ionic regime at ambient conditions is EMI-BF₄. The first study to report this finding [1] indicated currents of only a few hundred nA, with minute thrust levels ($< 0.1 \text{ mN}$) per Taylor cone. A subsequent study with a wider capillary emitter [2] showed current levels of several mA, and revealed also high quality ion beams with narrow energy distributions. These findings have been confirmed both at MIT as well as in Dr. Dressler's Air Force lab. However, it became apparent that this high current purely ionic regime had also operating regions of poor performance, particularly at currents of tens of mA, where the ion energy broadens and the energy loss associated to beam formation becomes substantial. In particular, we have seen that the range of conditions of stable operation depends strongly on electrode geometry, with larger emitting tips ($\sim 150 \text{ mm}$) yielding substantially more current than smaller tips ($\sim 20\text{-}40 \text{ mm}$). Another finding was that the energy-efficient regime is fragile, in the sense that it cannot always be reached. For instance, when we pulse the Taylor cone in order to perform time of flight mass spectrometric (TOF-MS) characterization of the ion beam, the efficient ionic regime is lost.

This has forced us to keep the Taylor cone steady and pulse the ion beam itself by means of gates. The investigation of EMI-BF₄ is by no means complete, and is still proceeding at CAC, Yale and MIT under AFOSR support.

Acidified Ionic Liquids

All known water and air stable non-volatile ionic liquids have room temperature electrical conductivities typically below 0.8 S/m, considerably below that for EMI-BF₄ ($K = 1.3$ S/m). Until very recently, it was believed that the inability of these other materials to match the purely ionic regime of EMI-BF₄ was due to their insufficient electrical conductivity. Recently, however, we have discovered a method to enhance the conductivity of a number of ionic liquids to reach K values well above 1.3 S/m. This has led to the discovery that the superiority of EMI-BF₄ over other materials is not just a matter of electrical conductivity.

It is known that addition of moderate quantities of acids to electrolytes greatly enhances their electrical conductivity due to the introduction of highly mobile protons in the solution. We have found that a number of ionic liquids bind strongly to certain acids. For instance, the volatile acid TFSIH (bis trifluoromethyl sulfonyl imide acid) is miscible with numerous ionic liquids, including its salts formed with a number of amines (see Table 2 below), as well as EMI-Im, EMI-BF₄, etc. These mixtures exhibit a substantially larger electrical conductivity than the neat ionic liquid, and, in many cases, exceed the value of 1.3 S/m of pure EMIBF₄. For instance, in measurements made by Mr. Carlos Bueno, 1% addition of TFSIH to EMI-Im and EMI-BF₄ results in K values well above 2 S/m. Most notably, in spite of the volatility of the pure acid, the acidity of its dilute mixtures in these ionic liquids remains unchanged after long periods exposed to a vacuum. This interesting property has been reported in the literature for certain materials related to ionic liquids [3, 4], even at temperatures well above 100 °C. We have encountered it ourselves, first in the synthesis of salts combining a variety of amines with TFSIH. We recently confirmed further this general trend, when an acidified sample received from colleagues at Covalent (Dr. Victor Koch PI) retained its acidity even after hours of evacuation at elevated temperature. Seeding various ionic liquids with TFSIH has provided us for the first time with the freedom to control the key variable K while keeping all other ionic liquid variables (density, viscosity, surface tension, ...) essentially constant. Mr. Bueno has therefore been able to study the emissions from Taylor cones of EMI-Im with K varying in the range from 0.8 to 2.2 S/m. Of considerable interest is the fact that the pure ionic regime does not set in at $K = 1.3$ S/m, nor at $K = 2$ S/m. One sees a gradual conversion of the drop emissions into ion emission, but it is not complete, not even at $K = 2.2$ S/m.

Two interesting conclusions follow. First, one can approach the purely ionic regime with acidified forms of a number of ionic liquids. Second, the electrical conductivity K is an important parameter towards reaching the purely ionic regime, but it is evidently not the only one. The other significant variables are expected to be the liquid surface tension γ (which is singularly high for EMIBF₄), and its viscosity coefficient η (which is singularly low for EMI-Im).

Now that we have managed to control K in liquids having different g and m values, we are on our way to establish which are the key properties besides K enabling the purely ionic regime. In very recent preliminary experiments, Mr. Bueno has acidified two relatively viscous materials with 2% TFSIH [1-Methyl-3-pentyl-imidazolium(C_2F_5)₃PF₆ and EMI-Beti; see Tables 1 and 4 for their physical properties], to attain electrical conductivities in excess of 1.8 S/m. Neither of these substances has approached the purely ionic regime, indicating that viscosity is not the key parameter facilitating ion evaporation. Our provisional conclusion is that the key parameter must therefore be the surface tension g . This hypothesis remains to be proven (perhaps by adding a surfactant to EMI-BF₄ and observing the suppression of the purely ionic regime), but it is made reasonable from the knowledge that the electric field at the tip of the Taylor cone scales as $g^{1/2}$, and is therefore a factor $(52/34.9)^{1/2} = 1.22$ for EMI-BF₄ than for EMI-Im. With the exception of EMI-CF₃SO₂, DMP-Beti and EMI-BF₄, EMI-Im has the highest surface tension among the ionic liquids shown in table 4, and this is congruent with the observation that it is the one among those tested that gets closer to the purely ionic regime ionic liquids. This finding suggests the study of acidified EMI-CF₃SO₂ and DMPI-Methide.

3.2 Purely Ionic Regime under Heated Conditions

Because the purely ionic regime is not attainable at room temperature in most unseeded ionic liquids, we have investigated heated Taylor cone sources. All this work has been carried out by Mr. I. Romero, sponsored primarily by AFOSR (90%), with final contributions from Busek and NASA-CAC.

A large number of ionic liquids have been examined under heated conditions. They are marked in red in the compilation of ionic liquid properties shown below as Table 2. Among those tested (EMI-BF₄, EMI-Im, EMI-Beti, EMI-Methide, BMI-Beti, DMPI-Beti, DMPI-Methide, Cyphos-Im, Cyphos-(CN)₂N, MPI-(C₂F₅)₃PF₆), those indicated in blue yield the ionic regime when heated, most often with ion currents in excess of 10 mA. The most interesting one from the point of view of reaching high ion mass and attaining the purely ionic regime at modest temperatures is MPI-(C₂F₅)₃PF₆, which is commercially available from Merck. All members examined of the large family of Cyphos ionic liquids (some produced commercially by Cytec, Canada, and sold as a useful kit by Strem Chemicals, others kindly synthesized for us by Prof. John Wilkes of the Air Force Academy at Colorado Springs) are unfortunately highly viscous and of insufficient conductivity. Even the least viscous in this group, Cyphos-TfO₂N, Cyphos-(CN)₂N fail to reach the purely ionic regime, and produce at most a few mA of ions at the highest temperature before they began to bubble. DMPI-Methide behaves similarly as these cyphos salts.

This work includes a large number of figures and Tables, some of which were included in our earlier report. A first manuscript discussing the case of EMI-Beti is in press [5], all other data will be soon sent for publication. Some additional remarks based on findings following earlier reports (and following [5]) are in order here.

i) All TOF-MS characterization of emissions from Taylor cones of heated ionic liquids was based on pulsing the Taylor cone rather than the ion beam. We have already noted that this system precludes reaching some of the most favorable regions of the stability range of the Taylor cone. This work needs therefore to be repeated with our new gating system

ii) The most viscous liquids which did bubble before attaining the purely ionic regime were not degassed under heated conditions. Due to their high viscosity, room temperature degassing would likely be unable to eliminate all small bubbles. This work needs therefore to be extended.

iii) No acidified samples were tried. Acidification is, however, a promising option, since it is known that the acid does generally not evaporate from ionic liquid solution, not even at temperatures well above 100 C.

The main message from the three limitations just noted is that, once they are corrected, the list of suitable purely ionic emitter ionic liquids will surely expand greatly.

4. Research on Drop Emission (Colloidal Regime)

Some earlier results on formamide solutions (mostly under Busek and AFOSR sponsorship) have been reported by Bocanegra et al [7]. The most interesting later results relate to mixtures of the low volatility solvent propylene carbonate with the ionic liquid EMI-Im. At 10-15% (vol) addition of EMI-Im, these mixtures can span the purely ionic regime as well as the purely colloidal (drops) regime. The transition from one to the other is achieved by just controlling the flow rate of liquid injected into each Taylor cone. An article describing these results is in preparation [8].

5. Sources of some promising Ionic Liquids

The source of ionic liquids obtained is included below.

Fluka: EMI-BF₄; EMI-TfO (TfO = Trifluoromethyl sulfonyl); BMI-BF₄

Covalent Associates inc. (Woburn Massachusetts): EMI-Im; EMI-Beti; DBM-Beti; & DBM-Me

Cytec, Strem: We have already discussed the large molecular weight but very viscous Cyphos materials. Many more including molecular masses of several thousand amu have been synthesized by Prof. John Wilkes. These materials, however, appear to be too viscous to attain the purely ionic regime, even when heated (see however final remarks in section 3.2). Strem's catalog contains an ample number of ionic liquids, including Cyphos materials, as well as Covalents products

Merck: Merck's home page contains a vast collection of commercial ionic liquids, including many useful physical properties (though quite a few are in error). From it we have identified several relatively heavy substances, included in Table 1 below along with some physical properties. Substances 1, 2, 3 and 5 are of the Cyphos family and are all far too viscous. We have only tested 4, whose promising behavior under heated conditions has been discussed in section 3.2. This substance is under current evaluation in acidified form. We have been unable to obtain substance 6 from Merck, in spite of our numerous attempts.

Table 1: Characteristics of several heavy ionic liquids available from Merck

#	Melting(C)	m ⁺ (amu)	m ⁻ (amu)	ρ(g/cc)	ν(cP)	Merck #	Euro/5g
1	-71(131 dec)	483.86	289.41	0.89	5549	490007	145,50□□
2	-50	483.86	280.15	1.07	401.4	490008	193,95□□
3	-71	483.86	445.01	0.89	5549	490002	242,50□□
4	-50	153.24	445.01	1.59	88.4	490000	266,70□□
5	-9	483.86	171.26	0.88		490006	145,50□□
6		153.24	745.05			490083	303,00□□
7	-50	142.26	445.01	1.59	184		
8	-50	144.24	445.01	1.6	108.8		
9	-50	483.86	445.01	1.18	393.5		
10	-50	445.01	1.56	74.3			

- 1) Trihexyl-tetradecyl-phosphonium; bis(2,4,4-trimethylpentyl)phosphinate
- 2) Trihexyl-tetradecyl-phosphonium; bis(trifluoromethylsulfonyl)imide
- 3) Trihexyl-tetradecyl-phosphonium; tris(pentafluoroethyl)trifluorophosphate
- 4) 1-Methyl-3-pentyl-3H-imidazolium; tris(pentafluoroethyl)trifluorophosphate
- 5) Decanoatetrihexyl-tetradecyl-phosphonium;
- 6) 3-Methyl-1-pentyl-3H-imidazol-1-ium; tris(nonafluorobutyl)trifluorophosphate
- 7) 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate
- 8) N,N,N',N'-Tetramethyl-N''-ethylguanidinium tris(pentafluoroethyl)trifluorophosphate
- 9) Trihexyltetradecylphosphonium tris(pentafluoroethyl)trifluorophosphate
- 10) 1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate

6. New ionic liquids synthesized at Yale.

Some of the most easily prepared ionic liquids are formed by combination of acids and amines. We did synthesize a number of these, following the interesting findings by Angel et al. on the exceptional electrical conductivities of those based on formic acid and small amines such as ethyl amine. We include some of their properties in Table 2. This work was all carried at Yale by Mr. David Garoz. Unfortunately, all these materials are relatively volatile and therefore unsuitable as space propellants.

Note the singular electrical conductivity of dimethyl amine formate

Amine Formates

Table 2: Properties of ionic liquids synthesized from reactions of amines with formic acid

Ionic Liquid	Molecular Mass (amu)	Density (g/cm ³)	Surface tension (dyn/cm)	Conductivity (S/m)	Volatility
MethNH ₃ COOH	77.086	1.12±0.01		2.9±0.3	low
Meth ₂ NH ₂ COOH	91.11	1.06±0.02		6.7±0.9	med
Meth ₃ NHCOOH	105.136	1.092±0.002		3.8±0.8	high
EthylNH ₃ COOH	91.11	1.1±0.02	43.8±0.5	1.4±0.1	low
Ethyl ₂ NH ₂ COOH	119.166	1.02±0.02		0.96±0.09	low
Ethyl ₃ NHCOOH	147.226	1.061±0.005		1.04±0.09	high
Octyl ₃ NHCOOH	399.706	0.84±0.01		0.014±0.001	-
Ethyl ₃ NHCF ₃ O ₃ S	251.3	1.19±0.01		0.46±0.06	no

Table 3: properties of ionic liquids synthesized from reactions of amines with TFSIH

Substance	K (S/m)	ρ (g/cc)	Author	ΔV(Volt)	Remarks
MethylNH ₃ Im					Solid
Methyl ₂ NH ₂ Im	0.61	1.48	David		
Methyl ₃ NHIm	0.703		Carlos		
EthylNH ₃ Im	2.44/0.45		Jacob	5.59/124	Wet/dry
Ethyl ₂ NH ₂ Im					Solid
Ethyl ₃ NHIm	0.455		Jacob	11.35	
Ethyl ₃ NHIm	0.52	1.4	David		

The work with amine formates was extended by Mr. Garoz by substitution of formic acid by BF₄H and TFSIH, with corresponding properties included also in Table 3. The tetrafluoroborates were either solid at room temperature or had properties inferior to those of EMI-BF₄. They are however far less volatile (perhaps completely involatile) than the formates. The TFSI salts were all liquid at room temperature, with no clear indications of being volatile. Their electrical conductivities, however, are in the range of 0.5-0.7 S/m, inferior even to EMI-Im (Table 3). The viscosities of these liquids have not yet been measured, but they appear to be exceptionally small. They are all completely miscible with water, and also with hydrophobic ionic liquids (such as EMI-Im) as well as hydrophilic ones (EMI-BF₄). They have also the interesting property of being miscible with the acid TFSIH, and holding on to it even after extended exposure to vacuum. We have not yet investigated whether or not these mixtures attain the purely ionic regime.

Table 4: Compilation of physical constants of Ionic Liquids

Liquid	γ (dyn/cm)	ρ (g/cm ³)	μ (cP)	K (S/m)	T_{melt} (C)	m^+ (amu)	m^- (amu)	Added Reference
PMP-Im		1.44 ^d				100.23	280.1	
EMI-BF ₄	52(24C) ^a	1.24	38	1.4	15	111.2	86.8	Hagiwara
EMI-TfO	36(22C) ^a	1.38	45	0.86		111.2	149	Hagiwara
EMI-Im	34.9 ^a	1.52	34 ^b	0.88		111.2	280.1	Hagiwara
EMI-Beti	31.2 ^a	1.6 ^a	61	0.34		111.2	380.15	Ohno
EMI-Methide	32.4 ^a	1.496 ^a	195 ^c	0.13		111.2	411.2	Hagiwara
EMI-HB		1.45	105	0.27	liq	111.2	213	Bonhote
EMI-C ₄ F ₉ SO ₃					28	111.2	299	Hagiwara
BMI-Im			52	0.39		139.27	280.1	Hagiwara
BMI-C ₄ F ₉ SO ₃		1.473	373	0.045	20	139.27	299	Hagiwara
BMI-Beti	27.6 ^a	1.425 ^a				139.27	380.15	
DMPI-Im		1.47 ^d	60	0.252		139.27	280.1	Hagiwara
DMPI-Beti	29.7 ^a	1.506 ^a				139.27	380.15	Ohno
DMPI-Methide	37.8 ^a	1.55 ^a	726 ^c	0.046		139.27	411.2	Hagiwara
BMP-Im		1.4 ^d				162.3	280.1	
MeCF ₃ CH ₂ I-Im		1.656	248	0.098	<-30		280.1	Bonhote
(C ₂ H ₄ CF ₃) ₂ I-Im		1.85			-62		280.1	Singh R.P.
Cyphos Im	27.4 ^a	1.021 ^a	401		-76	483	280	Merck
Cyphos (CN) ₂ N	29.2 ^a	0.987 ^a	597			483		Merck
Cyphos [Co(NCS) ₄] ²⁻					-72	483	350	
MPI ⁺ (C ₂ F ₅) ₃ PF ₃ ⁻	33.3 ^a	1.59	88.4		-50	153.2	445.01	Merck

^a Rough in-house measurements

^b Often quoted value published by Bonhote. The alternative value of 28 cP at 26 C published by McEwen et al. (1999) is also reliable for the higher temperature used.

^c EMIME possesses a room temp viscosity of 195 cP, whereas DMPIMe jumps to 726 cP at RT.□ Private communication, V. Koch, Covalent (2/Sept/2003)

^d Covalent webpage.

Cations:

EMI = 1-ethyl-3-methylimidazolium
 DMPI = 1,2-dimethyl-3-propylimidazolium
 BMI = 1-butyl-3-methylimidazolium
 PMP = 1-N-propyl-3-methylpyridinium
 BMP = 1-N-butyl-3-methylpyridinium
 MPI = 1-Methyl-3-pentylimidazolium
 Cyphos = trihexyl tetradecylphosphonium

Anions:

Im=(CF₃SO₂)₂N⁻: bis(trifluoromethylsulfonyl)imide
 Beti=(C₂F₅SO₂)₂N⁻: bis(perfluoroethylsulfonyl)imide
 Methide=(CF₃SO₂)₃C⁻
 : (trifluoromethylsulfonyl)₃methide
 HB=heptafluorobutanoate
 TfO= CF₃SO₂⁻
 (C₂F₅)₃PF₃⁻

After investigating a considerable number of families of ionic liquids we have not yet been able to identify one with propulsive characteristics superior to EMI-BF₄ under room temperature conditions, though quite a few are as interesting or more under heated conditions.

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Studies on irradiated ionic liquids under JPL Support

Several selected ionic liquids and their mixtures with propylene carbonate or TFSIH have been tested at various radiation doses for determination of their ability to operate in the purely ionic regime after irradiation. EMI-BF₄ and 1% TFSIH in EMI-Im did not show any apparent difference in their propulsion characteristics after receiving very large radiation doses. (Under possible AFOSR Phase II, additional radiation degradation tests will be undertaken with propellants developed for Holey Fibers.)

Materials

The following is a list of the samples irradiated with remarks on their state of dryness & purity:

- 1) EMI-Methide (Covalent associates Inc.), electronic grade: 0.5cc in small dark glass vial. Not dried, but dry from origin, rapidly opened and introduced from Covalent's virgin bottle. Since this material is additionally highly hydrophobic, the water content is surely very small
- 2) EMI-Beti: Covalent, electronic grade: 0.5cc in small dark glass vial; not dried, but dry from origin, rapidly opened and introduced from Covalent's virgin bottle. Since this material is additionally highly hydrophobic, the water content is surely very small.
- 3) EMI-Im, Covalent, electronic grade: 0.5cc in small dark glass vial; not dried. From a bottle 1 year old, perhaps saturated with water, but also highly hydrophobic. Water content small
- 4) EMIBF₄: From Solvent-Innovations Inc.; 0.5 cc in polypropylene vial with teflon protected leak tight cap. Sample is not of high purity, as obvious from slight coloration. It does nonetheless run correctly in the pure ionic regime prior to irradiation. It was not dried, and may have fair water content as it is hydrophilic and came from a bottle first opened about one year before.
- 5) 90-10 (vol) Propylene carbonate (PC)+ EMI-Im; 0.5 cc. Polypropylene vial with teflon protected leak tight cap. PC is HPLC grade, from new bottle just opened (with tight metallic cork bottle cap), rapidly poured and closed, hence very little water content.
- 6) 1% (vol) TFSI acid in EMI-Im. (TFSI acid is just H-Im). 0.5 cc in polypropylene vial with teflon protected leak-tight cap. This sample has been carefully dried by pumping overnight at room temperature.

Radioactive Source:

The gamma radiation source used in this investigation is a circular Co-60 irradiator at Neutron Products in Dickerson, MD, designed by that firm. The samples were suspended on a metal rotor above water pool, and the source raised to yield the requisite exposure. The emitted photons produce secondary electrons via Compton scattering, which then produce ionization within the vials containing the subject propellants.

Exposed Dose:

Minimum 10.0 kGy

Maximum was not specified

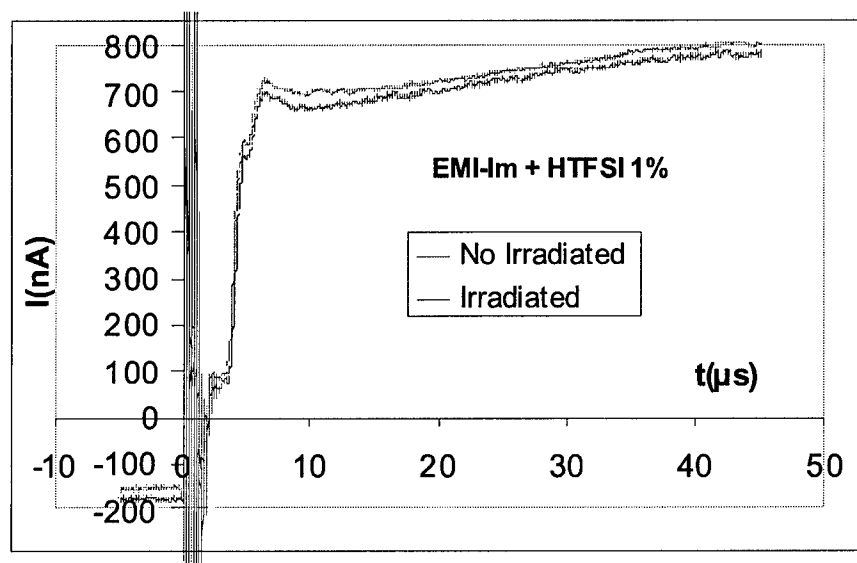
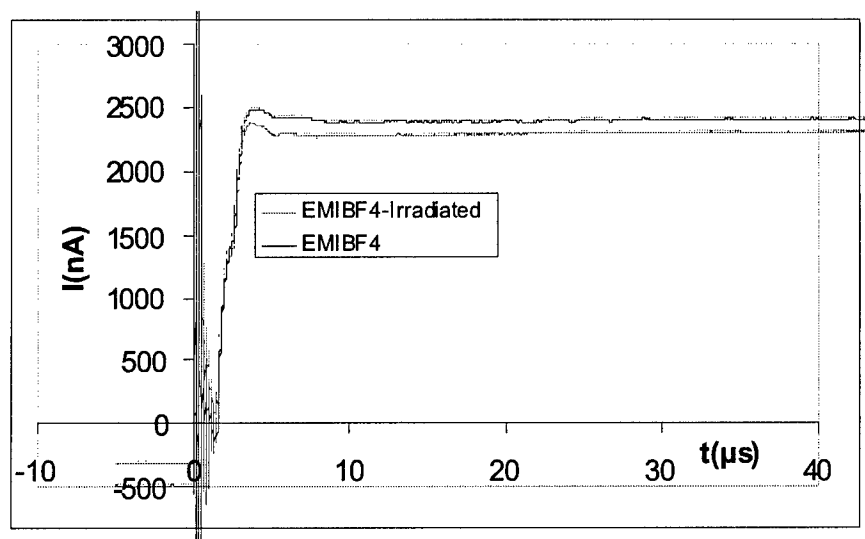
Absorbed Dose Measured:

Min 9.2 kGy

Max 11.2 kGy

Dose delivered based on confirmation that the correct exposure time has been received. The exposure time was computed by isotopically decaying the minimum dose rate measured on exterior surface of 6 vials by FTW-60-00 dosimeters. The maximum dose is based on the maximum ratio of 1.22 to 1.0 measured on set samples. Uncertainty of measurement +/-3.2% at a 95% confidence level.

Figure 1 TOF: Comparison of the time of flight curves from Taylor cone emissions in vacuum of irradiated vs. non irradiated samples of EMI-BF₄ and lightly acidified EMI-Im



Results for Irradiated Samples under NASA Support

The samples were examined for their electrical propulsion characteristics before and after irradiation. The only tests carried out involved electrospraying the liquids from a Taylor cone held in a vacuum, in one of Yale's time of flight mass spectrometry (TOF-MS) systems. Conditions of liquid flow rate and voltages were approximately identical for the irradiated and non irradiated samples. We will compare only the native liquids with those irradiated with the highest doses, since the effects to be seen are imperceptible, and would be even smaller at the smaller dose. The TOF curves are shown in figure TOF below for samples 4 and 6. One sees in both cases that the ionic composition (height of first, second and subsequent steps) is unchanged. The EMI-BF₄ samples were both essentially drop free (purely ionic regime). The EMI-lm + 1%TFSI acid samples show also identical behaviors, with a modest component of drops

A prior study at JPL has investigated with a much better control of purity and dryness a number of physical and chemical characteristics of the ionic liquid EMI-lm. The present is the first study on liquids capable of reaching the purely ionic regime. Accordingly, the crucial matter to be established was whether or not radiation would affect the poorly understood characteristics leading to this highly favorable regime. That this regime persists in spite of the rather high dose of radiation imparted to both ionic liquids is truly excellent news for the future of ionic liquid based ionic propulsion. Worth of note is that the two materials tested are the only ones known at present to be able to reach or closely approach this regime at room temperature.

Unfortunately the TOF systems available for this project at CAC and Yale are not presently operational at elevated temperature, while samples, 1, 2, 3 are of interest only well above room temperature. We have therefore been unable to perform the necessary test to determine if the corresponding heated samples do still operate in the purely ionic regime after being irradiated.

We hope to complete this investigation under possible AFOSR Phase II funding in 2005-6

Part IV. Difficulties / Problems

Our primary challenge was the extractor fabrication. A guaranteed fabrication method is employing the outer ring of emitters of a Holey Fiber Cane and coupling this to an annular ring. Degradation of a grid extractor limits this approach to only very short operation, i.e., a few hours at best. The annular ring has no operational time constraints. While very effective, and with more emitters per unit area than a comparably sized chip thruster, the full 5,500 emitter capacity of a Holey Fiber Cane is not utilized. After meeting with the Yale team, it was decided that a conformal insulator and sputter coated extractor conductor may be the solution. This extractor design is being investigated.

Part V. Work Planned For Next Period

Submitted Phase II plan in March. Contract currently under negotiation.

Part VI. Personnel Supported

Joseph Bango, PI at CAC

Michael Dziekan, Research Engineer at CAC

Juan Fernandez de la Mora, PI at Yale, Propellant Development

David LaVan, PI at Yale, Extractor Microfabrication

Part VII. Publications

None this period

Part VIII. Interactions / Transitions

None this period

Part IX. New Discoveries, Inventions

None this period

Work Plan Detail: Performance Schedule

The Phase I tasks are summarized in the following Chart outlined in Red:

Task / Month	0	1	2	3	4	5	6	7	8	9
Task 1: Research Review Meeting	X									
Task 2: Order Supplies, Chemicals	<----->									
Task 3: Begin Propellant R & D (Yale)	<----->									
Task 4: Begin Extractor Fabrication(Yale)	<----->									
Task 5: Test Holey Fibers in Vacuum			<----->							
Task 6: Begin Time-Of-Flight			<----->							
Task 7: Fabricate and test Fiber Bundle					<----->					
Task 8: Test Bundle in Vacuum						<----->				
Task 9: Prepare Final Report									<----->	
Task 10: Prepare Phase II Proposal									<----->X	