

**Figure 4.** Hydrodynamic voltammogram for a mixture of 2.5 nmol of FMA and 2.5 nmol of FA<sup>+</sup>. The voltammogram was obtained from a cross section of Figure 3b at the peak time.

individual microband electrodes. Thus, the current responses at 80 different potentials were obtained in one cycle. The currents at the 16 microband electrodes were sampled at least 20 ms after each potential step to eliminate the influence of charging current. The collection and displaying of 80 current signals at different potentials were completed in 0.27 s.

The hydrodynamic voltammogram for this mixture can easily be obtained from a cross section at various times. Figure 4 shows the hydrodynamic voltammogram obtained from the cross section at the peak time of Figure 3b. The voltammogram has two stairs corresponding to the oxidation of two ferrocenes; the first for FMA and the second for FA<sup>+</sup>. The half-wave potentials for FMA and FA<sup>+</sup> were identical with those observed in cyclic voltammetry. The concentration of the ferrocenes can be determined from the height of the steady-state currents. Since each microband electrode has a different potential, cross talk between the electrodes may occur. However, the influence of the cross talk was negligible in this case. The steady-state currents for both ferrocenes linearly increased with concentration over the range 0.1 nmol ( $2 \times 10^{-6}$  M) to 200 nmol ( $4 \times 10^{-3}$  M). The detection limit ( $S/N = 2$ ) was 20 pmol ( $4 \times 10^{-7}$  M).

The results obtained in the present study are summarized in Table I, together with those in flow analyses with the potential scanning detections reported in the literature. The equivalent scan rates in the present method were calculated by dividing the potential range (750 mV) by data acquisition times. Table I also lists the time required to obtain a voltammogram over the potential range of 750 mV. The comparison demonstrates that the present system, especially with 16-channel detection, is superior to the potential scanning

methods in terms of the data acquisition time for voltammograms. Thus, the present system will be particularly suitable for three-dimensional detection by FIA with small injection volumes. Although the detection limit is not satisfactory at the present stage, it will be decreased by improving the flow cell construction and the circuits of the potentiostat. Various applications to biological samples in FIA and liquid chromatography as well as efforts to further refine the technique are now underway in our laboratory.

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## Lanthanum Hexaboride Electron Emitter for Electron Impact and Electron-Induced Dissociation Fourier Transform Ion Cyclotron Resonance Spectrometry

Sir: Ribbon filaments of either tungsten or rhenium have been used as electron sources for electron impact ionization studies by Fourier transform ion cyclotron resonance spectrometry (FT-ICR) for a number of years. Unfortunately, these filaments are also a major source of down time for these instruments. The primary reason for filament failure is me-

chanical instability resulting in twisting which, in turn, results in a loss of electron throughput due to breakage or misalignment. This twisting is a result of the torque imposed on the filament as a relatively high current (3-4 A) runs perpendicular to the strong magnetic fields employed in many of these instruments. These problems are intensified on in-

struments that use superconducting magnets. In addition, ribbon filaments require considerable power (work functions for W and Re on 4.55 and 4.96 eV, respectively) and operate at high temperatures (ca. 2500 °C) causing heating of the cell and concomitant outgassing. One solution to both of these problems is to mount the filament external to the field as in recent commercial systems.

LaB<sub>6</sub> cathodes (work function 3.5 eV) have been successfully used as thermionic electron emitters (1) in a number of devices including scanning electron and scanning tunneling microscopes and X-ray sources. These emitters have been successfully interfaced with both quadrupole and sector mass spectrometers operated in both chemical ionization (CI) and electron impact (EI) modes (2, 3). They offer several benefits over tungsten-rhenium filaments including (i) decreased power consumption (a few watts) (4), (ii) lower temperature operation (<2000 °C), (iii) increased thermal/mechanical stability, (iv) very tightly focused beams (0.5 mm to 2–3 μm (3)) with current densities of up to 100 A cm<sup>-2</sup> (5), and (v) low evaporation rate (operating at 10 A/cm<sup>2</sup>, the evaporation rate is about 10<sup>-8</sup> g cm<sup>-2</sup> s<sup>-1</sup> (4)) resulting in long emitter lifetime. A 10-fold increase in electron emitter lifetime was observed for a LaB<sub>6</sub> cathode over a rhenium filament operated at conditions generic to CI and EI ionization in quadrupole and sector mass spectrometers (2). In addition, LaB<sub>6</sub> emitters like tungsten and rhenium emitters are inert to repeated exposure to the atmosphere while cool.

There are two principal disadvantages to using LaB<sub>6</sub> electron emitters as electron sources for ionization in mass spectrometry. Namely, these cathodes (i) are expensive with respect to rhenium or tungsten counterparts, and (ii) show chemical sensitivity to electronegative species. It is thought that electronegative atoms (such as O and Cl) bind to the surface increasing the work function and reducing the electron emission. Poisoned cathodes can normally be cleaned by increasing the operating temperature for a short period of time to volatilize the oxidized LaX species (3). Surface oxidation reduces emitter lifetime in direct proportion to the amount of material that is poisoned, and exposure to high pressures (>10<sup>-6</sup> Torr) of oxidizing gases is, therefore, discouraged.

In this note, we discuss the use of a LaB<sub>6</sub> cathode as an electron source for electron impact Fourier transform ion cyclotron resonance spectrometry (FT-ICR). The feasibility of routine use of these emitters is considered in terms of projected lifetime and chemical sensitivity. Because the extremely high electron flux densities can be obtained by these emitters, we have also examined their use for electron induced ion dissociation.

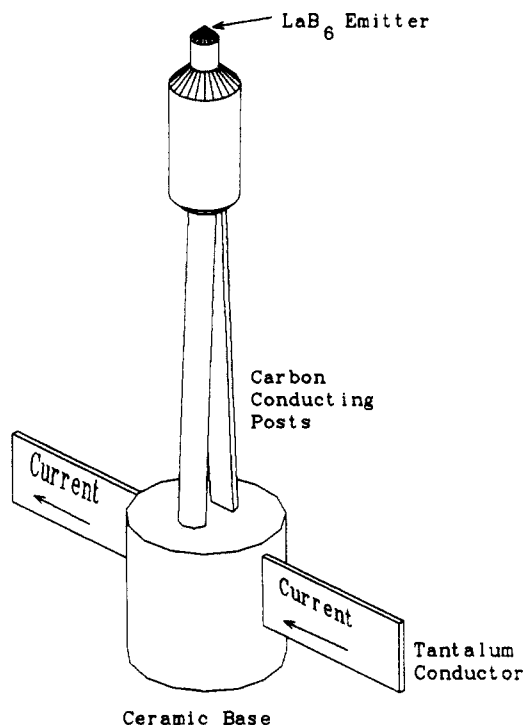
## EXPERIMENTAL SECTION

All experiments were performed on an ICR system built at TAMU and equipped with a Nicolet 1280 computer. The instrument is equipped with a 3-T superconducting magnet (Oxford). The instrument has been described in detail previously (6).

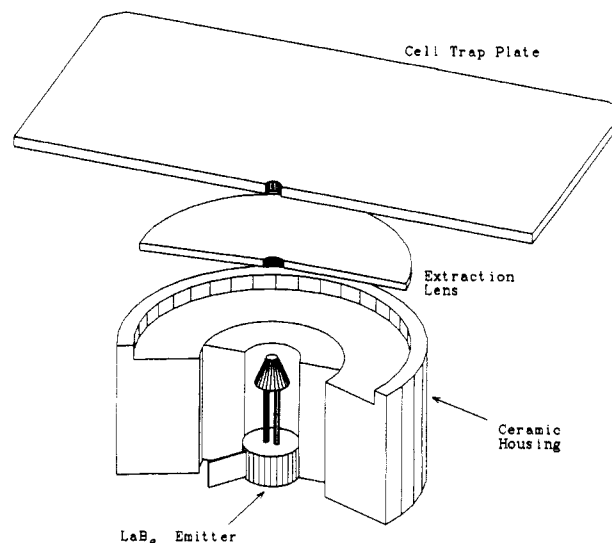
The LaB<sub>6</sub> cathode used for this work (Model ES-423-BF, Kimball Physics) has a circular single crystal plane emitting surface 0.33 mm in diameter (Figure 1). The emitter is mounted in a custom ceramic holder in order to support the cathode rigidly in the magnetic field and to protect it from damage (see Figure 2). The cathode support also holds an extraction lens. The LaB<sub>6</sub> emitter, lens, and holder are mounted as one unit to a trap plate of the ICR cell. The cathode is floated at the desired ionizing potential (10 to -70 V) and electrons are gated to the cell by pulsing the extraction plate from 5 V below to 5 V above this potential.

## RESULTS AND DISCUSSION

LaB<sub>6</sub> cathodes are superior to tungsten and rhenium filaments for most applications, but it was not known if such emitters could withstand the high magnetic fields used in



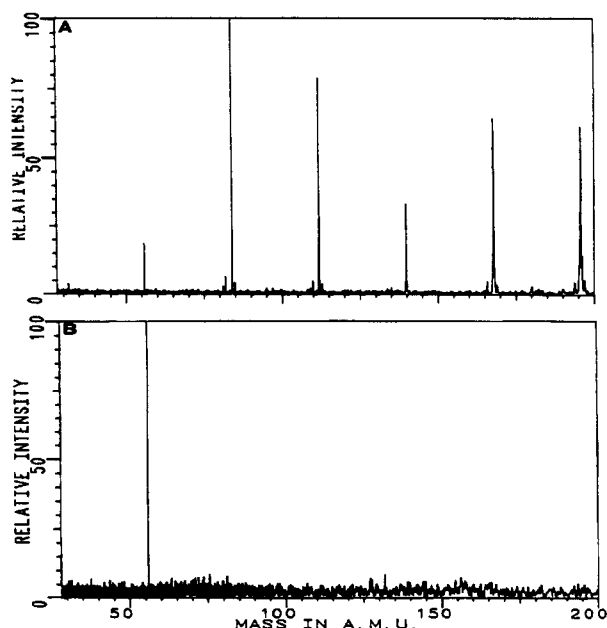
**Figure 1.** The Kimball Physics ES-423-BF LaB<sub>6</sub> electron emitter. Driving current flows in one tantalum conductor, up one of the conducting carbon posts, through the crystal mounting base, down the other carbon conductor post, and out of the other tantalum conductor.



**Figure 2.** Section view of the electron source used in the studies reported here. The LaB<sub>6</sub> emitter is held in place by a macor receiving cup placed in a macor terminal holder. The extraction lens also fits in the emitter holder assembly.

FT-ICR. It was feared that the current flowing through the cathode would break the carbon posts supporting the crystal emission surface due to the torque imposed by current flowing perpendicular to the high magnetic field at the emitter's tip. Experimentally, however, these concerns were found to have no basis. The cathode showed no sign of failure upon passing currents of up to 1.9 A while in the magnetic field. Emission currents of 25 nA to 200 μA were obtained on adjusting the driving current between 1.2 and 1.6 A. Outgassing of the cathode and the surrounding ceramic holder was not observed.

For these studies, the electron emitter is mounted at one end of a two-section FT-ICR cell described previously (6). Because the system is differentially pumped, the pressure in the region of the emitter could be maintained at  $2 \times 10^{-8}$  Torr



**Figure 3.** (A)  $\text{Fe(CO)}_5$  ionized by 20-eV electrons for 200  $\mu\text{s}$ , (B)  $\text{Fe(CO)}_5$  ionized by 9-eV electrons for 300 ms.

while the pressure in the ion cell (single cell mode) could be maintained at  $2 \times 10^{-6}$  or less.

The maximum current density for  $\text{LaB}_6$  emitters exceeds that for ribbon filaments by at least a factor of  $2 \times 10^5$  (5), allowing ionization periods to be very short ( $<60 \mu\text{s}$ ). Ionization periods of greater than 1 ms can easily result in Coulombic space charge effects between ionized sample molecules. Excellent signal-to-noise ratio spectra were obtained for benzene for ionization periods of 60  $\mu\text{s}$  at sample pressures of  $<10^{-7}$  Torr ( $S/N = 1000$ ; 1000 signal averaged scans). In addition, increase emission current density could have serious ramifications for chemical studies, because the possibility of multiple electron interactions is increased.

As a test of multiple electron interactions, a study of electron impact ionization of  $\text{Fe(CO)}_5$  was performed.  $\text{Fe(CO)}_5$  was admitted to the vacuum system at a static pressure of  $2 \times 10^{-7}$  Torr. Two different ionization conditions were probed. In the first, the electron energy was set to 20 eV for a period of 200  $\mu\text{s}$  at an emission current of ca. 10  $\mu\text{A}$ . The resulting spectrum for these ionization conditions is found in Figure 3A. Note that all the  $\text{Fe(CO)}_x$  ( $x = 0-5$ ) species are present in the spectrum as expected due to the fact that the appearance potentials for all members of this series are less than 20 eV (7). In the second test, the electron energy was set at 9 eV and the ionization period was set to 300 ms. Again, the emission current was maintained at ca. 10  $\mu\text{A}$ . The spectrum for these conditions (Figure 3B) shows that only  $\text{Fe}^+$  is in the cell (appearance energy (AE) ca. 15 eV). On the basis of the appearance energies for the fragment ions, only  $\text{Fe(CO)}_4^+$  (AE = 9 eV) and  $\text{Fe(CO)}_5^+$  (AE = 8 eV) (7) should appear in the spectrum if single electron interactions are occurring. Clearly, multiple electron interactions with  $\text{Fe(CO)}_x^+$  are occurring under the latter conditions. The electron beam flux density for the spectrum in Figure 3A was approximately  $1.5 \times 10^{-3}$  electron/ $\text{\AA}$  and approximately 2 electrons/ $\text{\AA}$  for the spectrum

in Figure 3B. Multiple electron interactions have been observed to cause ion dissociation in FT-ICR studies using conventional ribbon filaments (8, 9).

The potential use of  $\text{LaB}_6$  emitters as high flux density electron sources for electron impact induced dissociation is very promising. Potential studies in this laboratory indicate that polyatomic species can be readily fragmented by using the electron beam produced by these cathodes. Significant fragmentation of benzene was observed by using ionizing electrons with nominal energies between 10 and 12 eV under high flux conditions (i.e. emission current  $>100 \mu\text{A}$ ). Under these conditions, ionization periods of  $<100 \mu\text{s}$  produced  $\text{C}_3$  and  $\text{C}_4$  fragment ions in abundance.

The lifetime of  $\text{LaB}_6$  emitters for operation at a given emission current with reference to a different emission current is given approximately by  $n^{2.45}$  (4). That is, if the emission current is decreased by a factor of 4300, then emitter lifetime increases by  $4300^{2.45}$  or  $8 \times 10^8$ . For our system, operating the emitter at  $0.023 \text{ A cm}^{-2}$  (20  $\mu\text{A}$  emission) should increase its lifetime by  $8 \times 10^8$  times over operating at  $100 \text{ A cm}^{-2}$ . On the basis of an estimated lifetime of 400 h at  $100 \text{ A cm}^{-2}$ , the projected lifetime of the  $\text{LaB}_6$  emitter in the TAMU system is approximately  $3.2 \times 10^{11}$  h without considering chemical degradation.

As mentioned above,  $\text{LaX}$  species formed by the reaction of electronegative atoms with  $\text{LaB}_6$  increase the work function, thereby poisoning the emissive properties of the cathode. To circumvent this problem, the cathode must be operated at temperatures such that the various oxidized  $\text{LaX}$  species evaporate at a rate greater than the formation rate of  $\text{LaX}$  species itself (4) decreasing the expected lifetime by orders of magnitude. Actual performance will depend strongly on the chemical environments to which the emitter is exposed; higher pressures of oxidizing species will dramatically attenuate the lifetime. We anticipate that functional lifetimes will probably not exceed 5000 h under the conditions of the FT-ICR experiment.

**Registry No.**  $\text{LaB}_6$ , 12008-21-8.

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