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VOLCANO-STYLE FIELD IONIZATION SOURCE AND  
FIELD EMITTING CATHODES FOR MASS  
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EVALUATION OF VOLCANO-STYLE FIELD IONIZATION  
SOURCE AND FIELD EMITTING CATHODES FOR MASS  
SPECTROMETRY AND APPLICATIONS

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## ABSTRACT

A novel volcano-style field ionization source developed by SRI International was tested with eight different gases: hydrogen, helium, ammonia, methane, argon, neon, water vapor, and hydrogen sulfide. For ammonia, hydrogen sulfide, and water, the ionization efficiency of the field ionization source was determined as a function of the electrical potential difference between the ionizer and its counterelectrode. The ionization efficiencies for the other gases were too low to be measured in the present apparatus. In a second part of the project, we studied the operating characteristics of a field emission cathode, another device developed by SRI, in the presence of the same eight gases at pressures up to  $10^{-5}$  torr. The presence of the gases caused little or no significant change in the electron emission from the cathodes. Our results indicate that the field emission cathode has advantages over electrically heated cathodes as a source of an electron beam in spacecraft mass spectrometers.

CONTENTS

ABSTRACT . . . . .	ii
LIST OF ILLUSTRATIONS . . . . .	iv
INTRODUCTION . . . . .	1
PART I: VOLCANO-STYLE FIELD IONIZER . . . . .	2
Description of Volcano Ion Source . . . . .	2
Results . . . . .	2
PART II: THIN FILM FIELD-EMITTING CATHODE (TFEC) . . . . .	9
Objective . . . . .	9
Experimental Setup and Procedure . . . . .	9
Experimental Results . . . . .	12
Discussion . . . . .	18
Recommendations . . . . .	18

## ILLUSTRATIONS

1.	Scanning Electron Micrograph of Volcano-Style Field Ionization Source . . . . .	3
2.	Field Ionization Efficiency Versus Ionizer Voltage for Ammonia, Hydrogen Sulfide, and Water . . . . .	6
3.	Field Ionization Efficiency Curve for Xylene . . . . .	7
4.	Thin Film Field Emission Cathode (TF FEC) . . . . .	10
5.	Experimental Setup . . . . .	11
6.	Emission Behavior as a Function of Time in Argon, Helium, and Neon . . . . .	13
7.	Emission Behavior as a Function of Time in Methane, Ammonia Vapor, and Hydrogen Sulfide . . . . .	14
8.	Emission Behavior as a Function of Time in Water Vapor and Hydrogen . . . . .	15

## INTRODUCTION

SRI International has developed a number of field emission cathodes and field ionizers that are produced by microfabrication techniques based on thin film deposition technology. The purpose of the work described in this report was to test two of these devices to determine the feasibility of applying them to the ionization of eight selected gases. The two devices studied were the volcano-style field ionization source, which produces positive ions directly from the gases, and the 5000-tip thin film field-emitting cathode, which produces high currents of electrons. The eight gases selected by JPL were hydrogen, helium, ammonia, methane, argon, neon, water, and hydrogen sulfide. Because the testing of these two very different devices proceeded as two separate tasks, this final report is divided into two separate, and essentially self-contained, parts. Part I describes the work done and the results obtained with the volcano-style field ionizer. Part II describes the work done and the results obtained for the thin film field-emitting cathode.

## PART I: VOLCANO-STYLE FIELD IONIZER

### Description of Volcano Ion Source

The SRI volcano-style field ionization source has been described in detail<sup>1</sup> in the open literature. Briefly, the ion source consists of a thin copper film in the shape of an inverted funnel or volcano. A scanning electron micrograph of a typical source is shown in Figure 1(a). Typical dimensions are: rim diameter, 20  $\mu\text{m}$ ; base diameter, 120  $\mu\text{m}$ ; throat length, 20  $\mu\text{m}$ ; height, 100  $\mu\text{m}$ . The rim of the volcano is covered with submicrometer-diameter needles, as shown in the scanning electron micrograph in Figure 1(b). When in use the volcano is mounted below one of the openings in a 100 lines/cm nickel grid counterelectrode. The distance between the grid and the volcano tip is usually 20  $\mu\text{m}$  or less. A potential difference of 1000V to 3500V between the counterelectrode and the volcano ionizes the neutral molecules passing through the volcano throat. At the present time, the volcano film structure is press-fitted onto a 3-mm diameter pedestal that has a 1-mm diameter hole to allow sample gas to pass through to the volcano base.

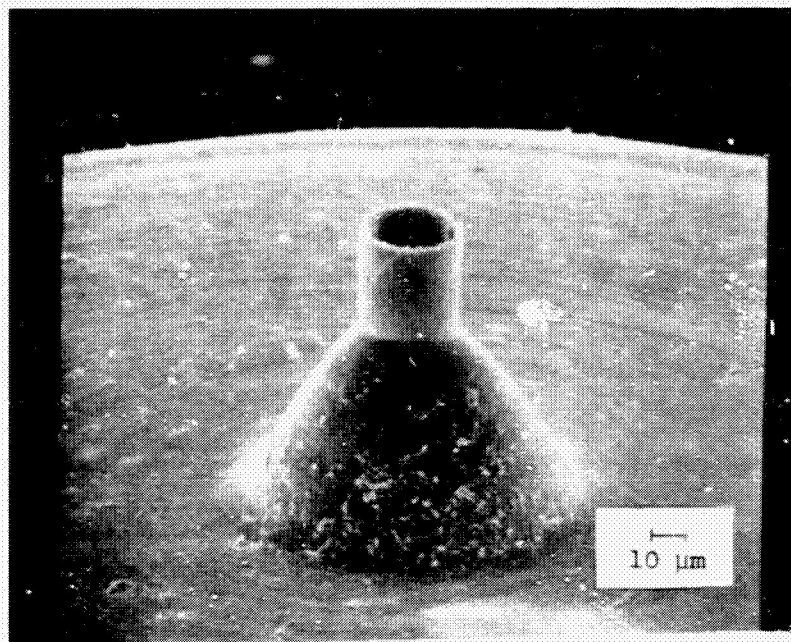
### Results

A volcano-style field ionizer and its counterelectrode and ion lense assembly were mounted in a glass bell jar vacuum station equipped with a 4-inch oil diffusion pump and refrigerated trap. A gas inlet system equipped with an MKS Baratron capacitance manometer was connected directly to the volcano source, so that the sample gas pressure inside the base of the source could be accurately measured. The total positive ion current produced by the ionizer was collected and measured using a shielded Faraday cup and electrometer.

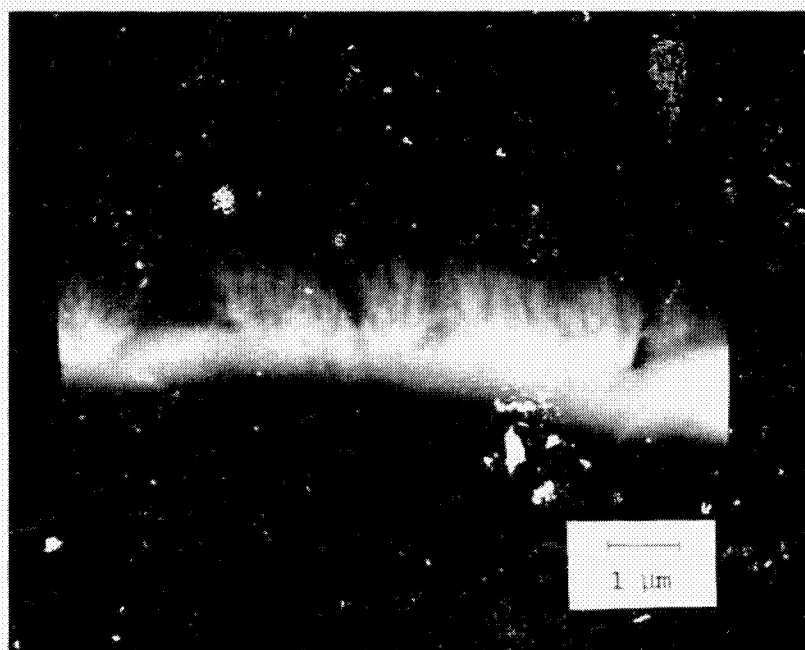
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<sup>1</sup>W. Aberth and C. A. Spindt, Int. J. Mass Spectrom. Ion Phys., 25, 183 (1977).

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(a. VOLCANO ION SOURCE



(b) SUBMICRON NEEDLES ON RIM OF VOLCANO ION SOURCE

FIGURE 1 SCANNING ELECTRON MICROGRAPH OF VOLCANO-STYLE FIELD IONIZATION SOURCE

In the absence of any sample gas, a large background signal was observed. It varied with ionizer potential in the same way as a true field ionization signal. Changing the ion lense potentials confirmed that the ion current originated from the volcano field ionizer and that it could be focused or defocused in the same manner as ions formed by field ionization of a sample gas. Because the background signal was so large ( $10^{-12}$  to  $10^{-10}$  A) and variable, it was impossible to obtain reproducible ionization efficiency curves for any of the gases with this arrangement.

A volcano-style field ionization source was adapted for mounting in SRI's  $60^\circ$  10-inch-radius magnetic sector mass spectrometer. The accelerating voltage used was 5 kV. The maximum voltage difference between the volcano and the counterelectrode was 3.8 kV. Sample gases were again introduced through a gas inlet system equipped with a capacitance manometer to ensure that the sample gas pressure behind the volcano was accurately known. Even without sample gas present, the source produced a large background current. The major background ions were  $H^+$  ( $m/z = 1$ ) and  $m/z = 19$ , presumably  $H_3O^+$ . The background signal apparently formed through field desorption of substances adsorbed onto the ionizer. Over a period of five days with the source at 500 K, the  $H^+$  signal gradually decreased while the  $H_3O^+$  fluctuated but did not show a consistent change. The background ionization varied with the ionizer voltage and was very unstable, changing by 20 to 50% within a few minutes. However, because the mass spectrometer separates the background ions from the ions formed by field ionization of the sample gases, it was possible to obtain ionization efficiency data.

Each of the eight gases was admitted into the ion source and the field ionization spectrum was recorded at several ionizer voltages. The intensity of the molecular ion signal was then measured as a function of ionizer voltage. The absolute ionization efficiency was calculated from the measured sample pressure and the conductance of the volcano throat. Ionization efficiencies are expressed in terms of the ratio of the number of ion detected to the number of sample molecules passing through the volcano source.



The ionization efficiency was found to depend very strongly on the ionization potential of the gas being tested. Compounds with lower ionization potentials ionize much more readily than do compounds of higher ionization potential. Table I lists the gases studied, shows their ionization potentials and indicates whether ionization was detectable.

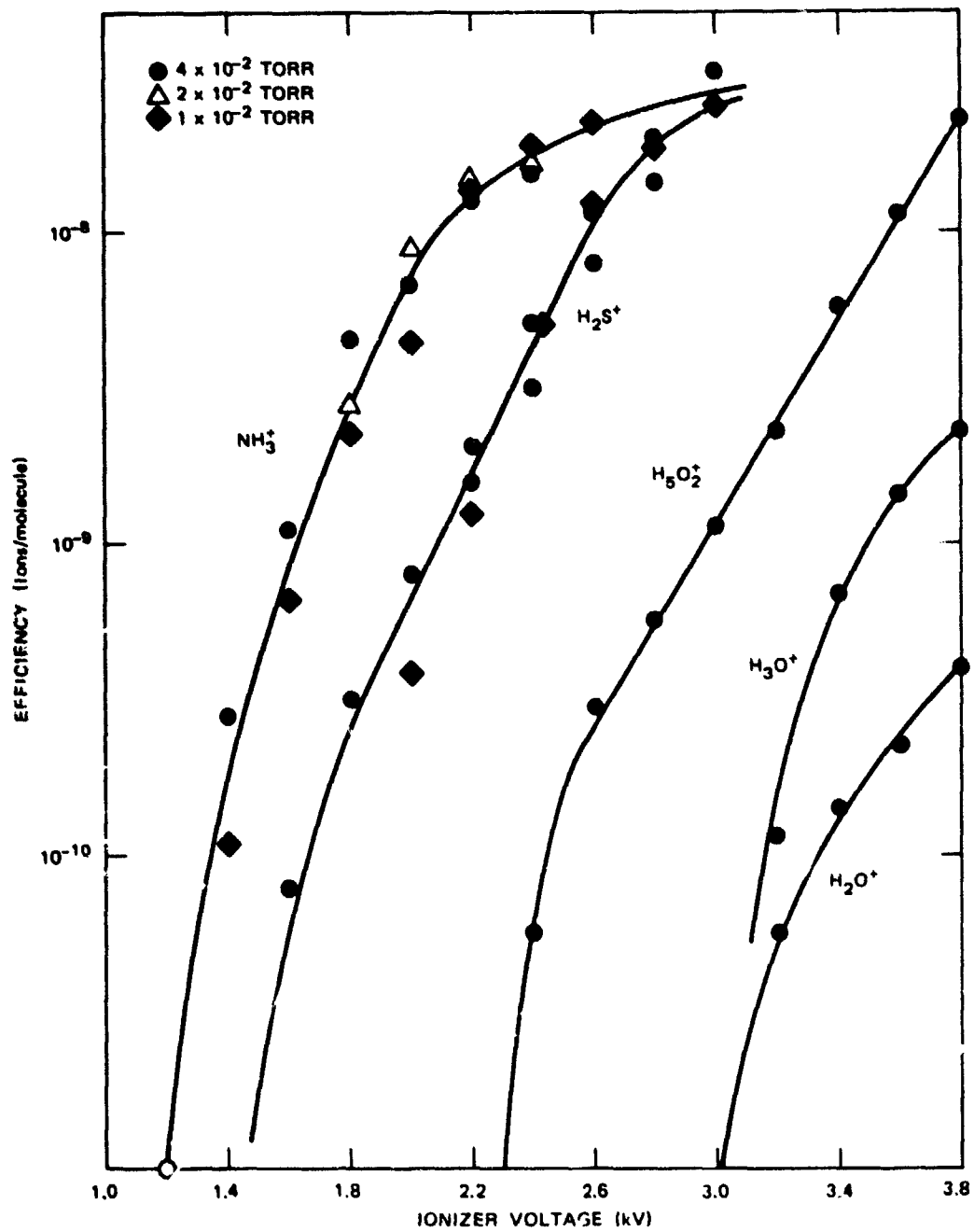
Table I  
Gases Studied

Gas Studied	Chemical Formula	Ionization Potential (eV)	Field Ionization Observed
Ammonia	NH <sub>3</sub>	10.17	Yes
Hydrogen sulfide	H <sub>2</sub> S	10.47	Yes
Water vapor	H <sub>2</sub> O	12.62	Yes
Methane	CH <sub>4</sub>	12.5	Weak
Hydrogen	H <sub>2</sub>	15.43	No
Argon	Ar	15.76	No
Neon	Ne	21.56	No
Helium	He	24.59	No

The field ionization spectrum of ammonia showed approximately 14% NH<sub>4</sub><sup>+</sup> at an ionizer potential of 2.7 kv. The percentage of NH<sub>4</sub><sup>+</sup> increases at decreasing ionizer potential, since lowering the potential favors the lower energy field desorption process. The field ionization efficiency for ammonia is plotted against ionizer voltage in Figure 2.

The field ionization spectrum of hydrogen sulfide was similar to that of ammonia, but the ionization efficiency was lower. At 3.0 kv there was approximately 5% H<sub>3</sub>S<sup>+</sup> and the percentage of this ion increased at lower voltages. No fragment ions were detectable. The ionization efficiency based on the molecular ion is shown in Figure 2.

For water, the largest peak in the field ionization mass spectrum was at m/z = 37, corresponding to H<sub>5</sub>O<sub>2</sub><sup>+</sup>. The dominant process is



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FIGURE 2 FIELD IONIZATION EFFICIENCY VERSUS IONIZER VOLTAGE FOR AMMONIA, HYDROGEN SULFIDE, AND WATER

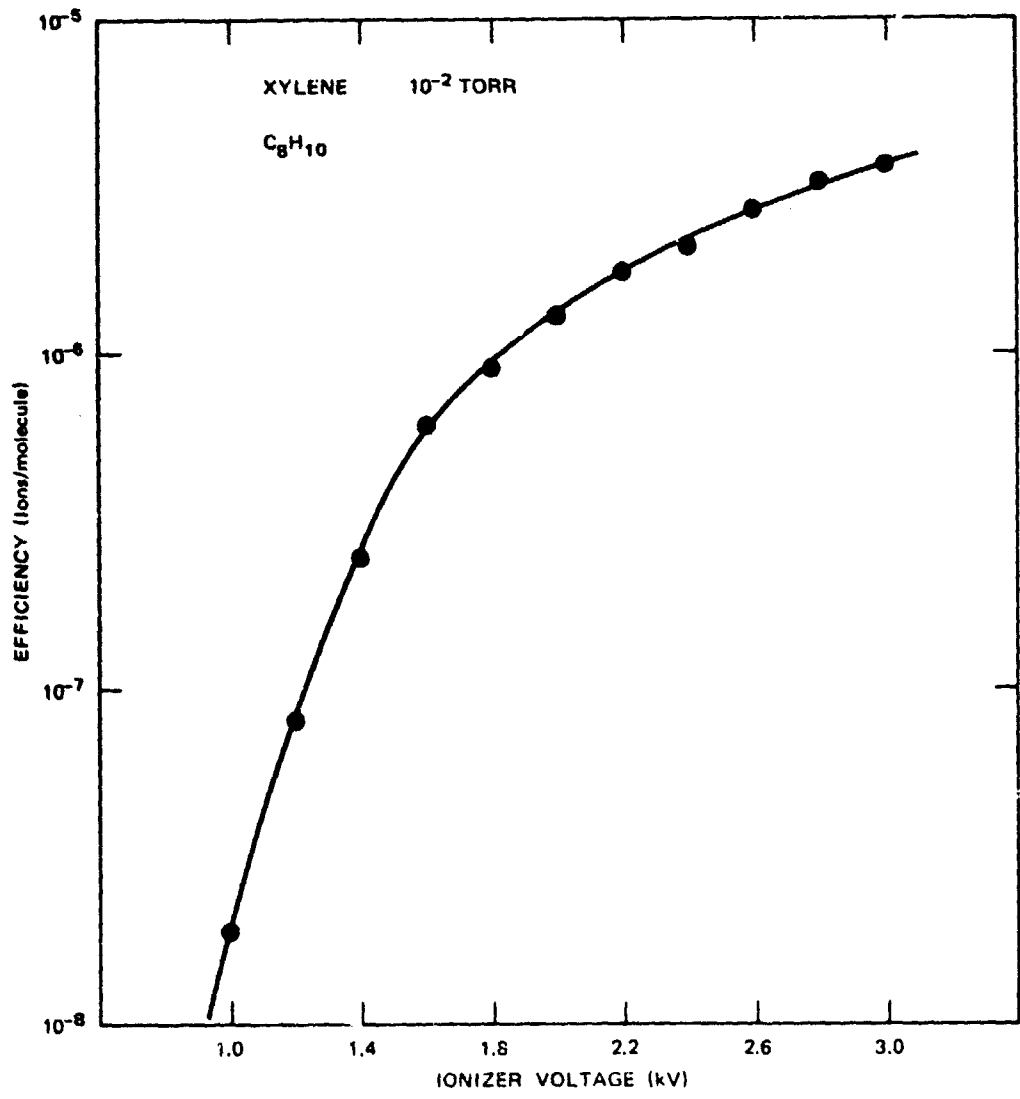


FIGURE 3 FIELD IONIZATION EFFICIENCY CURVE FOR XYLENE

therefore field desorption of ions formed in water adsorbed to the ionizer. The true field ionization of gas-phase water molecules forms ions at  $m/z$  18 with a low, but measurable efficiency. The apparent ionization efficiencies for  $m/z$  18, 19, and 37 are plotted in Figure 2.

A spectrum of methane containing primarily  $\text{CH}_4^+$  could be recorded, but the signal was so weak and unsteady that a reproducible ionization efficiency curve could not be obtained. The ionization efficiency of methane would be less than that for  $\text{H}_2\text{O}^+$ , shown in Figure 2 at all ionizer voltages. Hydrogen, argon, neon, and helium showed no detectable field ionization. The ionization potentials of these compounds are apparently too high for them to be field ionized at the field strengths attainable with our present volcano source and counterelectrode configuration. The dependence of ionization efficiency on the ionization potential of the sample is illustrated by the ionization efficiency curve of xylene,  $\text{C}_8\text{H}_{10}$ , shown in Figure 3. Xylene has an ionization potential of 8.5 eV.

## PART II: THIN FILM FIELD-EMITTING CATHODE (TFEFC)

### Objective

The purpose of this part of the project was to determine the feasibility of applying the SRI-developed 5000-tip thin film field emission cathode<sup>2</sup> (TFEFC), shown in figure 4, to the ionization of selected gases. The immediate interest is in a planetary probe mass spectrometer to be flown into the Jovian atmosphere. Thus, the gases investigated were those expected to be found in Jupiter's environment, i.e., argon, neon, helium, hydrogen, ammonia (NH<sub>3</sub>), methane (CH<sub>4</sub>), water vapor, and hydrogen sulfide (H<sub>2</sub>S).

Conventional field emitters would not be expected to be useful for this purpose because they typically operate in the kilovolt range, and sputtering of the tip becomes excessive as the pressure increases much above the 10<sup>-9</sup> torr level. The TFEFC has been shown to produce useful currents (mA range) at relatively low voltages (100V to 200V), with relatively negligible ion sputtering of the emitter tip. In addition, the TFEFC tips are well shielded by a closely spaced (<1μm) anode structure. Thus, it could be assumed that the TFEFC might have useful lifetimes even when operating at relatively high pressures, e.g., 10<sup>-6</sup> to 10<sup>-5</sup> torr. The objective of our work was to determine if such an assumption is valid.

### Experimental Setup and Procedure

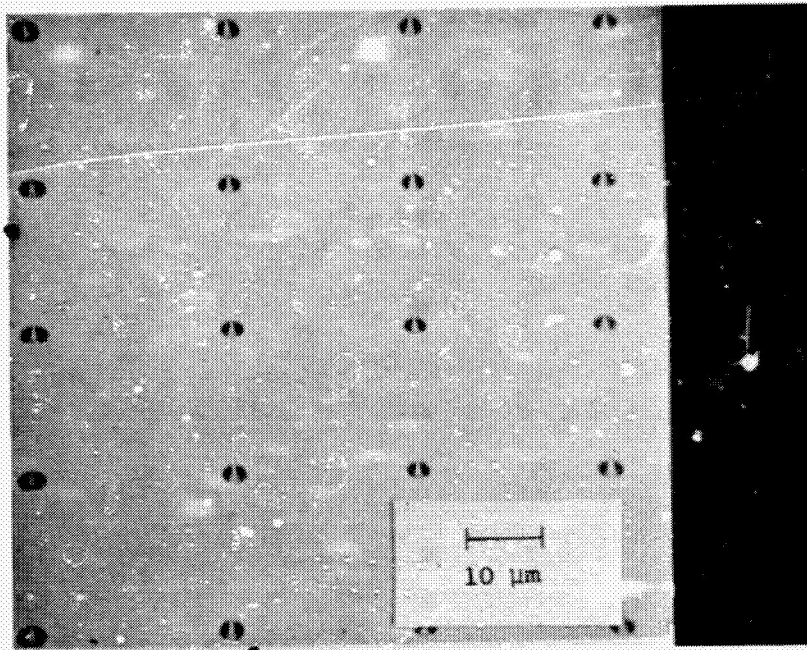
The experiment was setup as shown in Figure 5, and the following measurements were made:

- A TFEFC was examined and mounted in the UHV chamber about 1 cm from a collector electrode. The UHV chamber was then pumped down to about 2 x 10<sup>-8</sup> torr and baked out at 350°C.

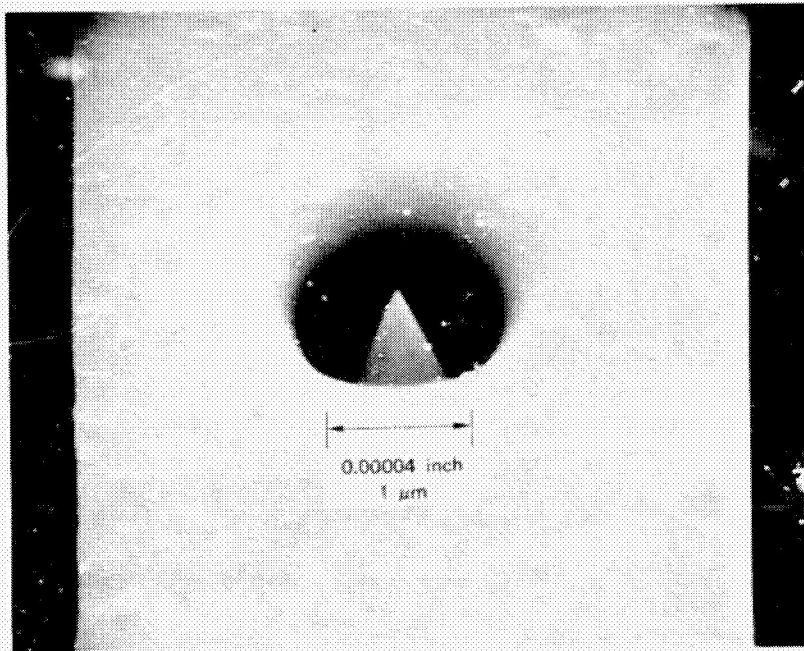
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<sup>2</sup>C. A. Spindt, I. Brodie, L. Humphrey, and E. R. Westerberg, J. App. Phys., 47, 5248 (1976).

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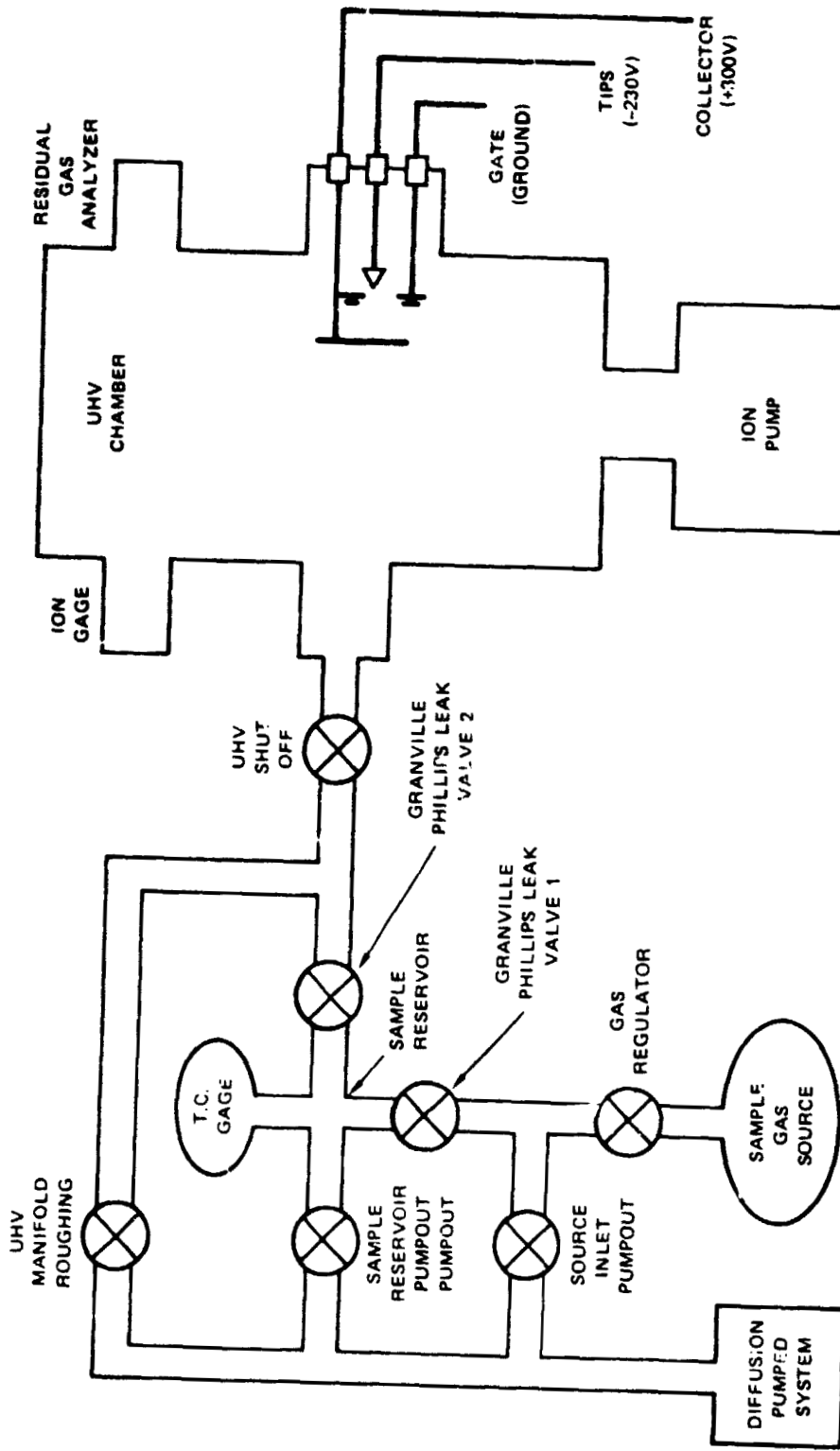
(a) REGULAR ARRAY OF CATHODE TIPS



(b) MAGNIFIED VIEW OF FIELD EMISSION TIP

FIGURE 4 THIN FILM FIELD EMISSION CATHODE (TF FEC)

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FIGURE 5 EXPERIMENTAL SETUP

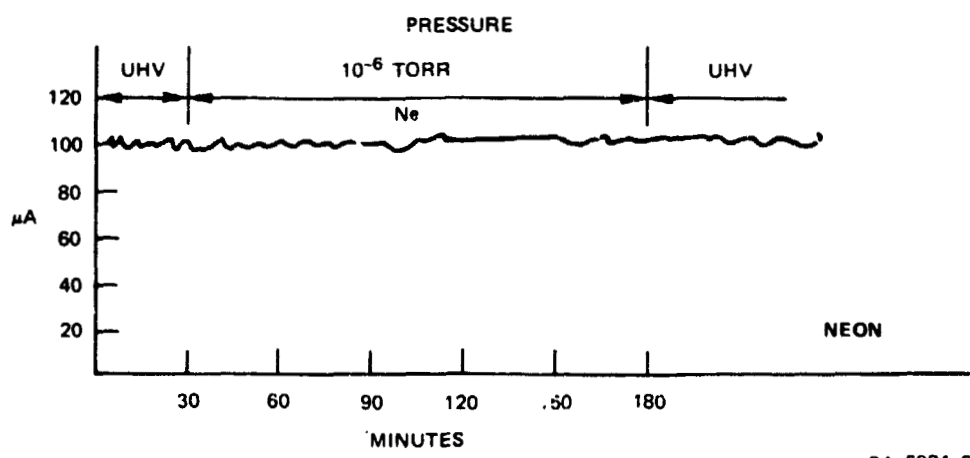
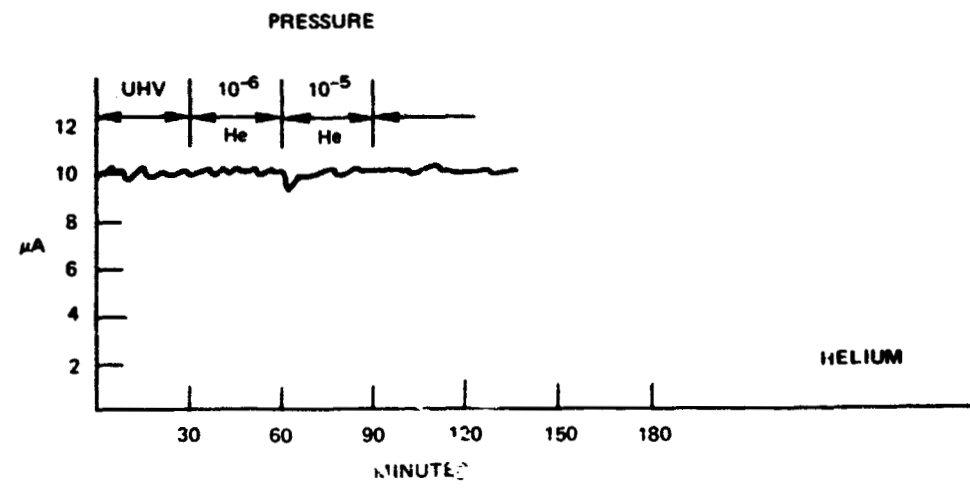
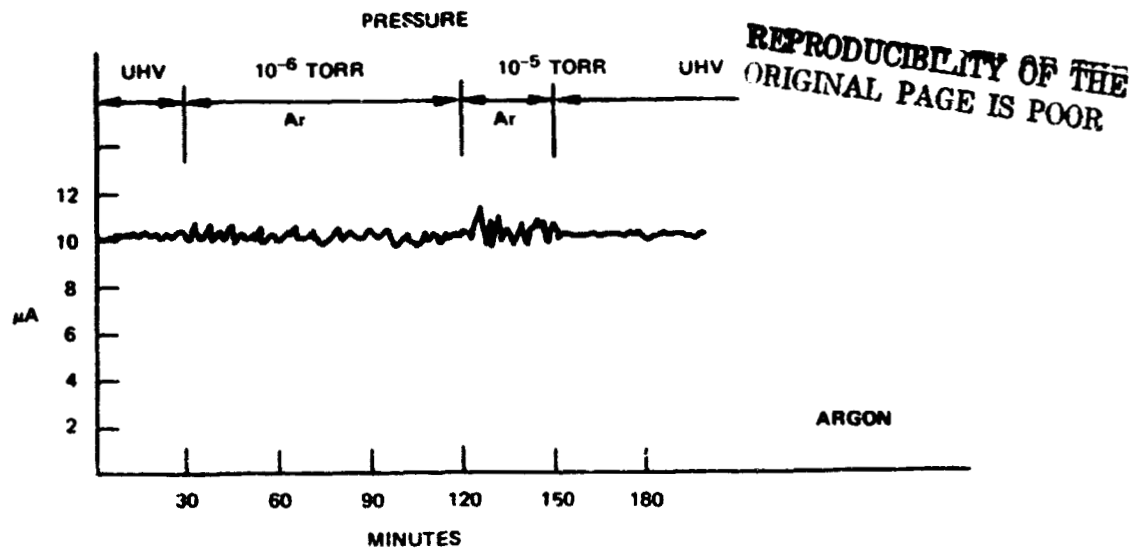
- The UHV manifold was evacuated and the UHV shut-off valve opened.
- The TFFEC was cooled to room temperature and voltage was applied to produce emission. (For the first tests 10  $\mu$ A of electron emission was used while we checked out the setup. Later tests were done with up to 2 mA emissions.)
- The sample reservoir was evacuated.
- The source inlet was evacuated, purged with sample gas, evacuated, and finally filled with sample gas at a positive pressure relative to atmosphere.
- Sample gas was admitted into the sample reservoir with leak valve 1, while the reservoir was pumped with the diffusion pump system. Pressure in the reservoir was adjusted to about 500  $\mu$ m as indicated on the thermocouple gage.
- Leak valve 2 was opened slowly to increase the pressure in the UHV system to between  $10^{-5}$  and  $10^{-6}$  torr as measured on the ion gage and residual gas analyzer.
- Emission to the collector was observed and recorded on a chart recorder while the voltage applied to the cathode was held constant.
- When the emission was stabilized or a trend definitely identified, leak valve 2 was closed and the chamber pumped back down to ultra vacuum.
- Emission was recorded on the chart recorder continuously during these tests to register changes at any time during the experiment.

The order in which the gases were tested was; Ar, N<sub>3</sub>, He, H<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub>S, H<sub>2</sub>O.

#### Experimental Results

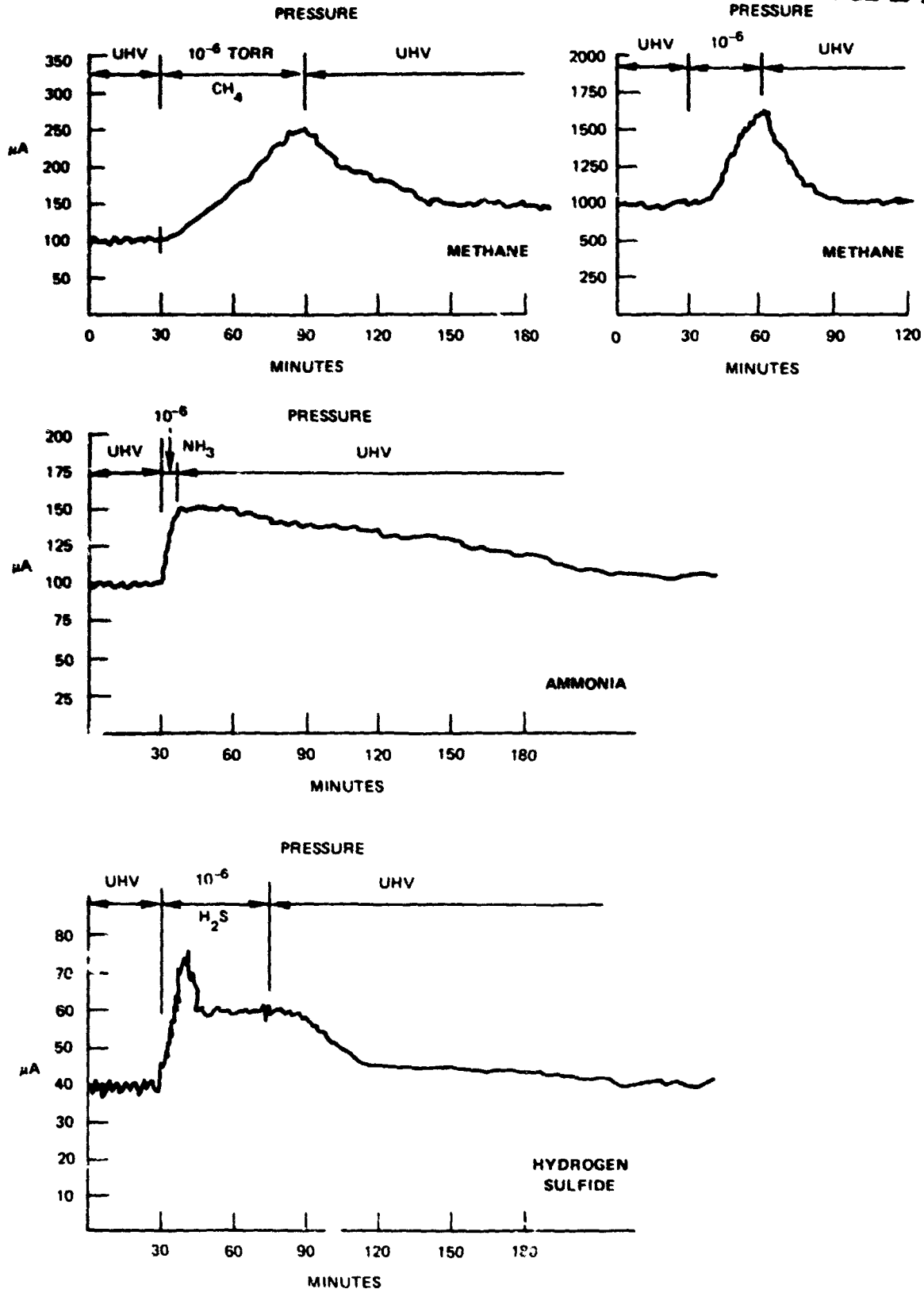
The results are shown in Figures 6, 7, and 8. The curves shown were all taken at room temperature and are representative of several tests for each gas except in the case of ammonia and hydrogen sulfide. These two were tested only once each because of the very limited quantities remaining in the cylinders. Since the effect in each case was very positive, the expense of procuring new cylinders to repeat these results seems unnecessary. The noble gases (Ar, He, and Ne) had virtually no effect on the emission. Argon did increase the fluctuation amplitude





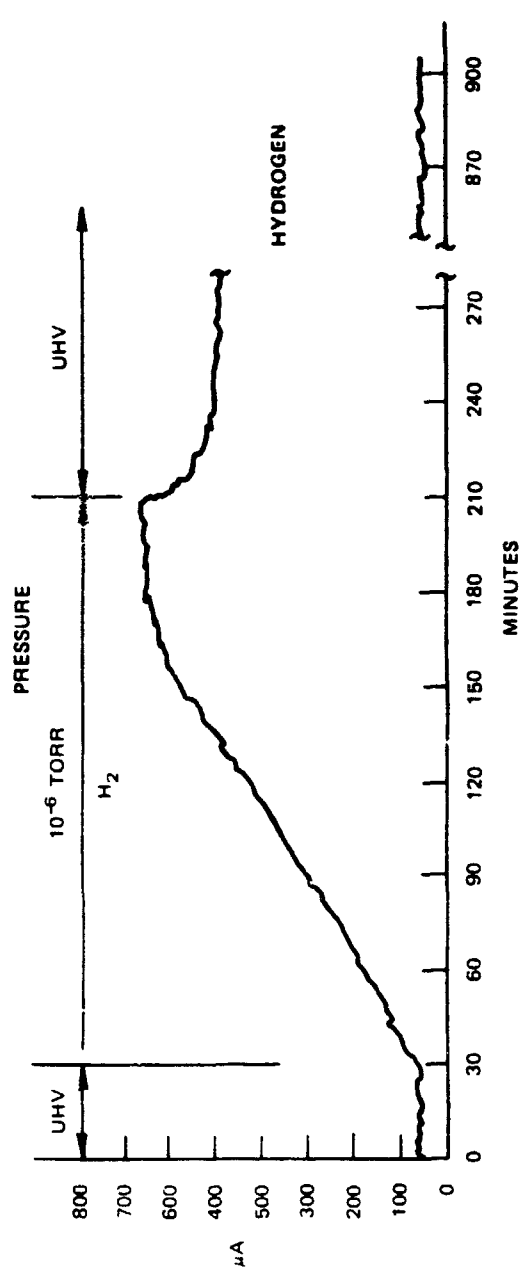
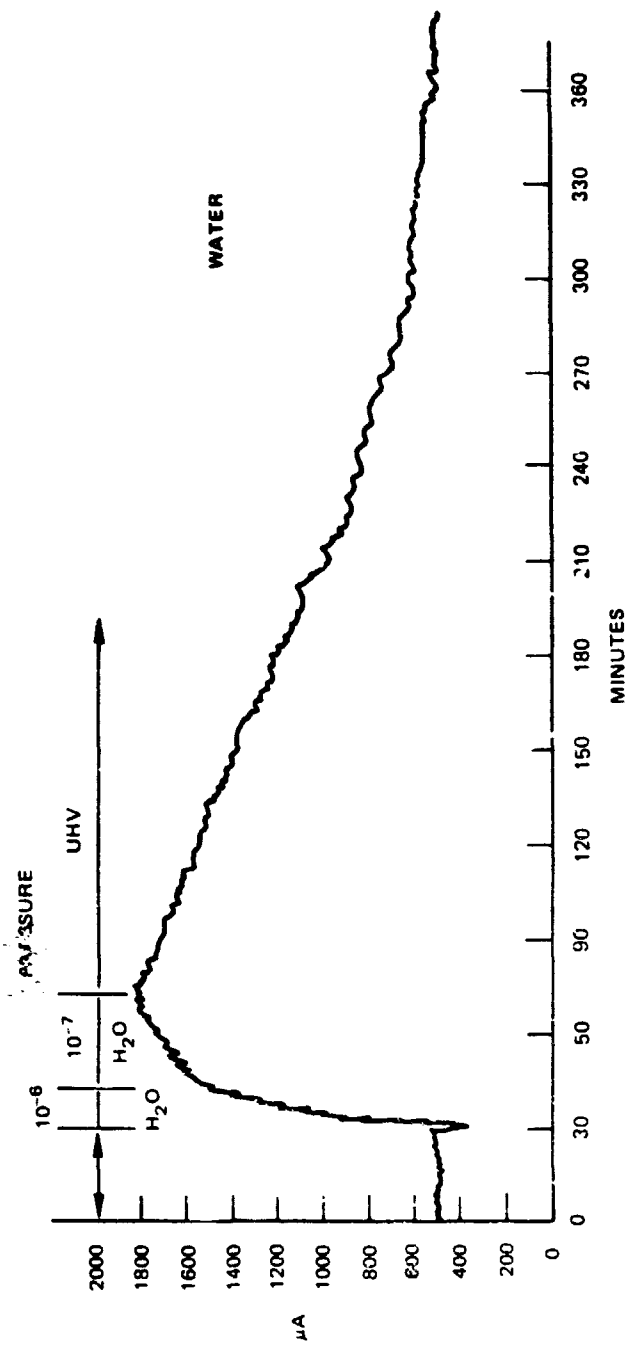
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FIGURE 6 EMISSION BEHAVIOR AS A FUNCTION OF TIME IN ARGON, HELIUM, AND NEON



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FIGURE 7 EMISSION BEHAVIOR AS A FUNCTION OF TIME IN METHANE, AMMONIA VAPOR, AND HYDROGEN SULFIDE



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FIGURE 8 EMISSION BEHAVIOR AS A FUNCTION OF TIME IN WATER VAPOR AND HYDROGEN

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to some extent; however, we suspect that this increase might be due to contamination introduced from the new manifold apparatus, since argon was the first gas tested.

Argon and helium were the only two gases tested up to  $10^{-5}$  torr, since in both cases the ion pump seemed to operate with difficulty at this level, whereas in the  $10^{-6}$  range it seemed to work comfortably. As seen in Figure 6, helium and neon had no effect at all on the emission behavior.

Figure 7 shows the results of two experiments with methane. Methane produced a definite increase in emission. In the first, the cathode initially operated at 100  $\mu$ A. Within an hour after methane was introduced to raise the pressure to  $10^{-6}$  torr electron emission increased to 250  $\mu$ A. When the methane was pumped away, the emission decreased and finally returned to the original value after several hours. In the second experiment, the initial emission was set at 1 mA and increased to about 1.6 mA after 30 minutes of exposure to methane (see Figure 7). This percentage change is consistent with the result obtained in the 100  $\mu$ A case. Again the emission returned to the original value when the methane was removed.

As shown in Figure 7, ammonia and hydrogen sulfide produced relatively rapid increases in emission, e.g., 50% in about 10 minutes for ammonia compared with approximately 30 minutes for a similar rise with methane. The decay time with ammonia, however, was much longer.

The reason for the unique double hump in the hydrogen sulfide curve is most likely that the gas cylinder was very nearly exhausted and the partial pressure of  $H_2S$  could have been varying even though the total pressure was held constant. The RGA was intended to help in instances of this kind, but it turned out to be too insensitive to provide any more than qualitative information.

The result obtained with water vapor (shown in Figure 8) was one of the most surprising and dramatic of the entire set of experiments. We suspect that the initial drop in emission when the water leak was opened

stemmed from the method used to prepare the water sample; that is, a small vial of pure water was frozen with liquid nitrogen and then pumped out as is normally done with liquid mass spectrographic samples having high vapor pressures. Thus, some of the constituents in the surrounding air were very possibly also dissolved in or adsorbed onto the water (ice) surface and, therefore, not completely pumped away before the leak valve to the UHV system was opened. The assumption is that this "air" in the sample depressed the emission. When these "air" impurities were pumped away, the effects of the pure water vapor could be seen. As a quick check of this hypothesis, air was used as sample gas in a later test. The emission did go down (and stabilize) but recovered when the air was pumped out again. Air was the only gas tested that decreased the emission, however, and this aspect of the experiment needs more study than was possible within the limited scope of the work reported here. Two other observations on the water curve are that the rate of increase showed a not unexpected dependence on the pressure, and that the emission returned to the original value about 300 hours after the water leak was shut off. It is very likely that heating the cathode would be shorten the time required to return to the original value.

Figure 8 shows that hydrogen behaved very much like the pure water but with a much longer time factor. Hydrogen was the only case where the high pressure was maintained until a saturation or equilibrium effect was noted. After 150 minutes the emission leveled off and remained constant for 30 minutes before the leak was shut off. Again, the emission returned to its original value many hours after the hydrogen was pumped away.

The emitter was left on continuously during the tests for a total emission time of 1200 hours. At the end of this time the cathode was removed from the system and examined. Approximately 9% of the tips appeared to have failed.

## Discussion

This work was a first look into the feasibility of using the TFFEC as a source for an electron impact ionizer. Thus, several interesting aspects of the work were not pursued further. For example, it would be interesting to know what it is in air that causes the emission to go down, what would be the effects of temperature changes, what is the importance of the order in which the gases were used, what are the effects of a number of other gases, how might different emitter materials alter the results, etc.

From the results obtained in this study, we concluded that

- The TFFEC is capable of operating at pressure of up to  $10^{-5}$  torr in a variety of gases.
- When the TFFEC is operated at room temperature, its emission seems to depend greatly on the makeup of the background gas in its environment.
- The effective work function of the tips appears to change by exposure to some gases but to reach some equilibrium with the cathode's environment at a given operating condition.
- The change in effective work function by exposure to the gases tested is completely reversible and nondamaging to the cathode (within the pressure range investigated).
- The TFFEC would probably perform very well as a cathode in an ion source for the gases tested.
- The emission at a given voltage varies over wide ranges that depend on the vacuum environment. However, due to the exponential voltage-current relationship  $[I = AV \exp(-\frac{B}{V})]$  for a given cathode it would be simple to devise a feedback circuit to maintain a constant current with moderate voltage changes.

## Recommendations

Based on the results obtained in this study of the TFFEC, we recommend extending the work to include other gases especially those found in air, to determine which gases cause a decrease in emission. The effects of long off-times also need to be studied with respect to the possibilities of local gas bursts due to desorption when the cathode is turned on again. Cleanup by a quick local heating may be desirable, for example.

Another worthwhile study would be to incorporate the cathode into an ionizer system and check the cathode's performance in an actual ionizer design. This could be done by modifying the ionizer of a commercial RGA or other conveniently available mass analyzer.