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## A Study of the CsI-TMAE Photocathode

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# A Study of the CsI-TMAE Photocathode

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## **Abstract**

The quantum efficiency of a CsI-TMAE photocathode has been found to increase by over a factor of 2 under bombardment of positive ions from the avalanche process. A quantum efficiency of about 40% has been achieved for wavelengths  $\leq 190$  nm. This "enhancement" can be removed by an electrical discharge or by a brief exposure to a vacuum. Results on photocathode ageing are also presented.

## 1. Introduction

Through the years there has been a continuous effort to develop photosensors with high quantum efficiencies and low energy thresholds to be coupled to wire chambers. The most noted applications for such a device are Ring Imaging Cherenkov counters (RICH) and the detection of the UV light produced by  $\text{BaF}_2$ . In operating experiments, the photosensitive gases TEA (triethylamine) and TMAE (tetrakis(dimethylamino)ethylene) have been used. TEA has a high vapor pressure, and it is insensitive to air, but its high ionization potential (7.5 eV) requires the use of  $\text{CaF}_2$  windows. TMAE has a low ionization potential (5.36 eV) allowing for the use of quartz windows, but it has a long absorption length at room temperature (on the order of 2 cm) [1-3] and is reactive with oxygen and many of the materials used in wire chamber construction.

There have been many ingenious techniques tried to develop non-gaseous photocathodes, usually involving TMAE. Some techniques have condensed TMAE on a surface or let it adhere to a metal to produce a photocathode[4-8]. TMAE has also been frozen or mixed with other liquids such as tetramethylsilane[6,7,9]. Other materials such as ethyl ferrocene have also been condensed on surfaces[10,11].

Recently, there has been an interest in using CsI as a photocathode coupled to a wire chamber. It has the advantages that a CsI photocathode is easy to make, can be handled for a short time in air, and has a quantum efficiency (QE) of about 10% at about 170 nm[8,12]. This photocathode, coupled to a wire chamber, was demonstrated by Charpak et al.[8], and shown to have good efficiency for the scintillation of Xe gas (peak  $\lambda \approx 170$  nm) by Dangendorf et al.[12,13]. Séguinot et al.[6] have reported a higher QE of 35% at 170 nm for a CsI photocathode after flushing it with pure methane.

The latest development in photosensors has been made by Séguinot et al.[6], who found that an adsorbed layer of TMAE on the CsI photocathode increases its QE, as it does for metal surfaces. They achieved a QE of 46% at 170 nm, about 30% higher than for an optically thick layer of TMAE gas. They also reported that the CsI-TMAE photocathode is less sensitive to exposure to air and can be restored with a flow of methane gas. This reduced sensitivity to air is unexpected since separately CsI reacts with the water in air and TMAE reacts vigorously with oxygen. They also demonstrated that the adsorbed TMAE effect did not diminish when the TMAE vapor was removed from the system nor when the photocathode was flushed for three weeks with clean methane.

Hoeneisen et al.[14] obtained a QE of 16% for the CsI-TMAE photocathode at 170 nm. Their major contribution was in achieving a single-step amplification of  $10^7$  (immediately above the photocathode) without photon feedback in a low-pressure chamber. This allows the photocathode to be deposited directly on a pad readout designed to handle

high multiplicity events. They also showed that a signal width of only 5 ns with less than 3 ns time jitter was achievable. Aging of the photocathode in the single-step amplification mode was studied and found to be a problem. The loss in QE is believed to be due to ion feedback.

In this work we report a confirmation of the high QE reported by Séguinot et al. Our studies show that a high QE does not depend upon the cleaning of the photocathode with a vigorous flow of pure methane for a long period of time. The high QE is a much more dynamic process which can be achieved with stagnant gas of many kinds in a matter of minutes. The key to achieving a high photocathode QE seems to be a controlled ion feedback. This process as well as further studies of ageing of the CsI-TMAE photocathodes are discussed in this work.

## 2. Experimental Procedures

The experimental chamber used is shown schematically in Fig. 1. (See ref. 14 for further details.) The cathode-anode and cathode-window distances were 1.59 mm and 20 mm, respectively. All gas fillings (with the exception of TMAE) of this chamber were at a pressure of 20 Torr, and the chamber was operated sealed.

The CsI was deposited to a thickness of 2.0  $\mu\text{m}$  on the cathode pads. In the studies involving the CsI-TMAE photocathode, immediately after depositing the CsI the evaporation chamber was filled with TMAE gas to a pressure of about 330 mTorr. This took approximately 10 minutes. The chamber was then evacuated to remove the TMAE gas, back filled with nitrogen, and the photocathode was removed. The photocathode was then installed in the chamber. The total time of exposure to air for the photocathode was between 10 to 15 minutes.

The QE of the photocathodes were compared to the QE of TMAE gas using the single photon technique. The cathode to anode voltage was adjusted so that the gain was sufficient to give a well defined single-photoelectron spectrum. A typical single-photoelectron spectrum is shown in fig. 2. The intensity of the pulsed UV light source was then reduced until the number of photoelectrons produced at the photocathode at wavelengths  $\leq 190$  nm averaged between 0.1 and 0.3 per pulse. The number of photoelectrons per pulse was then recorded as a function of wavelength.

The TMAE gas was then added to the counter along with 20 Torr of methane. The region between the quartz window and the "Anode" (fig.1) was operated as a conversion and drift region. For this measurement, the cathode pads were held at a higher positive potential than the mesh marked "Anode" in fig. 1 and used as the true anode. This second region was operated with sufficient gain to obtain a well resolved single-photoelectron

spectrum. This signal had no component from the photocathode. The number of photoelectrons detected per UV pulse was then recorded as a function of wavelength. The QE of the photocathode relative to the TMAE gas is simply the ratio of the number of photoelectrons per pulse for the two configurations. The QE of the TMAE gas was taken from the literature[1], corrected for transmission of the grids and for the finite absorption in the space between the quartz window and the "Anode". This yields the absolute QE of the photocathode.

### 3. Photocathode Enhancement

In our early work[14] we found we were not able to reproduce the high quantum efficiency of the CsI-TMAE reported by Séguinot et al. We were unable to achieve an enhancement of our photocathode by the flushing of clean methane gas as they proscribed. It was then discovered during ageing studies, that if the photocathode was exposed to a moderately intense UV source while the chamber was operated with gain, there was an increase in photocathode current with time. This increase in current was later determined to be due to an enhancement in QE and not a change in gain. This was determined by monitoring the peak channel of the single photoelectron, pulse-height spectrum.

The feedback of the positive ions proved to be the key to enhancing the photocathode QE. Fig. 3 shows the photocathode current as a function of collected charge for several values of initial current,  $I_0$ , which is the current measured immediately after applying the electric field. In fig. 3 the photocathode currents have been initially normalized to 1 for all values of  $I_0$  so that the change in current reflects the change in QE. Fig. 4 shows the initial enhancement of several of these curves in greater detail. The gas filling for these measurements was 20 torr of methane. It can be seen from these figures that there is a strong dependence on the level of enhancement with the rate of ion current. This is better seen in fig. 5 which shows the peak enhancement factor as a function of initial current. The higher the initial current, the smaller is the enhancement. At very low currents, such as detecting single photoelectrons, the process of enhancement of the photocathode is very slow. At the high currents used in the aging studies, the level of enhancement is much lower and a plateau is reached in a very short time. This correlation may have prevented this effect from being observed in earlier studies.

Figure 6 shows the QE as a function of wavelength for the non-enhanced CsI-TMAE photocathode, for optically thick TMAE gas, and for the photocathode enhanced with methane, ethane and pentane (not purified). These results are consistent with those of Séguinot et al[6]. The significant differences between curves will be considered in Section 5.

#### 4. Stability of Enhancement

The enhancement of the CsI-TMAE photocathode studied here is certainly due to the positive ions interacting with the photocathode. The important factor is the intensity of the ion current and not the intensity of the light source. When the intensity of the light source was reduced but the voltage increased to give the same current, the same rate in change of current (QE) with time was observed. Thus, it is not the energy of the positive ions that counts. Once the peak enhancement was achieved, the photocathode was stable for days. Two things were found to remove the QE enhancement: 1) evacuating the chamber and 2) a spark during the enhancement process.

Although the enhancement was stable, evacuating the chamber for even a minute would return it to its pre-enhanced condition. This is somewhat surprising when one considers that it proved to be stable for days with a gas pressure of only 20 Torr.

Sparking during enhancement would return the photocathode to its pre-enhanced condition immediately. This is dramatically demonstrated in Fig. 7 which shows current as a function of time. The initial current was set so the conditions were just below breakdown. As can be seen, the current (or QE) increases by about a factor of about 2.5, then there is a spark, and the enhancement begins again.

Once the photocathode had reached maximum enhancement, a spark does not seem to degrade the QE. Since sparking in a wire chamber is not a controlled phenomenon, we have no way of determining if the location of the sparking had moved after enhancement. It is still possible that a spark to the enhanced pad will destroy the enhancement.

#### 5. Possible Mechanisms for Enhancement

It is fairly convincing that the enhancement of the the CsI-TMAE photocathode is due to the counter-gas ions becoming part of the photocathode. The effect grows with the accumulation of charge, is affected by the rate of ion bombardment, and it can be removed by evacuation of the chamber. If the positive ions are becoming part of the photocathode, it is reasonable to expect that there might be a small difference in the QE near the threshold for electron emission. A well established technique for measuring the work function ( $V_0$ ) of a liquid is to immerse a solid photocathode in the liquid and measure the shift in  $V_0$  is given by [15]:

$$\Phi_{liq} = \Phi_{vac} + V_0, \quad (1)$$

where  $\phi_{\text{liq}}$  and  $\phi_{\text{vac}}$  are the work functions of the solid photocathode in liquid and in vacuum, respectively. Thus, the threshold of the CsI-TMAE photocathode may be shifted, depending on the sign and magnitude of the  $V_0$  of the gas. One would not expect the effect to be as pronounced as implied by eq. (1) since the gas ions are very dilute in the photocathode and could not be considered a liquid.

An expansion of the long wavelength region of fig. 6 is shown in fig. 8. The values of  $V_0$  for methane, pentane, and ethane in the liquid phase are -0.25, 0, and +0.12 eV, respectively[16]. One can see that there is a suggestion of an effect, correlating with the sign of  $V_0$ , at least for the longer wavelengths. This is a region of the spectrum where the QE is very low and uncertainties high, and so one should not read too much into the data. One possibility of the effect of adsorbed gas ions on the photocathode is that they somehow increase the depth from which the photoelectrons can be extracted. There has been some work on the extraction of electrons from non-polar solvents[17,18] and it has been shown that the electrons can be extracted from such solvents with very high efficiency, certainly from a greater depth than photoelectrons are extracted from a solid. A possible explanation is that at the surface of a liquid there are dynamic processes going on which allow the electron to escape in an electric field without having to obtain an energy greater than the  $V_0$  of the bulk liquid. Certainly, the mechanism behind the enhancement phenomenon is still not clear.

## 6. Photocathode Ageing

One of the strengths of the single-step amplification scheme is that it allows for the use of pads, which is necessary for operation in a high-multiplicity of hits, RICH type environment. The weakness is that the positive ions, feeding back onto the photocathode, eventually reduces the QE. This has been studied for both the pure CsI[13,19] and CsI-TMAE[14] photocathodes.

Fig. 9 shows the relative QE as a function of collected charge for two CsI-TMAE photocathodes. Curve A of this figure was enhanced with a current of 2.5 pA/mm<sup>2</sup> (fig. 3, Curve A) until peak enhancement was achieved and then aged at a current of 2.7 nA/mm<sup>2</sup>. The enhancement of this curve occurs with such a small collected charge that it cannot be seen on this scale. The photocathode of Curve B in this figure was operated at 2.7 nA/mm<sup>2</sup> from the beginning (fig. 3, Curve G). A small amount of enhancement can be seen at the beginning of Curve B.

The relative QE of these two photocathodes degrades rapidly to a collected charge of about 10  $\mu\text{C}/\text{mm}$  and then levels off. These results are in agreement with the earlier work on the subject by Hoeneisen et al.[14]. Their photocathode degraded to about 30% of the

initial QE after a collected charge of about  $10 \mu\text{C}/\text{mm}$ . The major difference is that they did not see a reduction in the rate of ageing at this collected charge. This difference in results may be due to the difference in photocathode thickness. Their photocathode thickness was only  $0.3 \mu\text{m}$  thick while ours was  $2 \mu\text{m}$  thick.

As can be seen from fig. 9, the QE of the photocathode is substantially better for the pre-enhanced photocathode than for the non-enhanced photocathode. This can also be seen in fig. 10 where the QE as a function of wavelength is shown for the two aged photocathodes of fig. 9. The QE of a pre-enhanced and a non-enhanced photocathode are included as a comparison. It can be seen from the figure that, below  $210 \text{ nm}$ , the aged, pre-enhanced photocathode has a 50% higher QE than the aged, non-enhanced photocathode. Above  $210 \text{ nm}$  the QE of the aged photocathodes are essentially the same.

## 7. Discussion

The enhancement of the photocathode QE is certainly a complicated phenomenon. Séguinot et al. obtained a similar QE to what we have reported without the feedback of positive ions. It is possible that we are both obtaining the same final condition, but by different paths. An examination of fig. 5 shows the peak enhancement factor as a function of initial current and one possible conclusion is that the enhancement will be maximum when the current is zero. A test that we are achieving the same final state as Séguinot et al. would be to produce an enhanced photocathode by their procedure and see if it survives a few minutes in a vacuum. This will be tested in the near future.

It has been suggested that we are observing the charging up of the photocathode and that this effect would not be seen with a thinner layer. Our photocathodes were  $2 \mu\text{m}$  thick and the one of Séguinot et al. was  $0.5 \mu\text{m}$ . Breskin et al.[19] have found a constant QE for pure CsI photocathodes over a thickness range of  $0.2\text{-}1.5 \mu\text{m}$ . Also, charging up of the photocathode would reduce the electric field and thus reduce the QE. Also, such ions are not easily removed by evacuation. Ions on an insulator tend to be preserved in a vacuum.

We have seen that simply flushing the photocathode with pure methane does not change the quantum efficiency of the photocathode. Dangendorf et.al., working with a pure CsI photocathode, also observed no change in quantum efficiency by flushing with methane. This could simply be our inability to reproduce the excellent conditions of Séguinot et al. The dependence of the quantum efficiency and the enhancement process on the thickness of the CsI layer has not been studied systematically. Using a  $0.3 \mu\text{m}$  pure CsI photocathode, we observed that its QE is about 70% of the  $2.0 \mu\text{m}$  thick CsI photocathode. We also observed a difference in the radiation tolerance between

photocathode of different thickness of CsI. This will be carefully studied in the future to determine if there is an optimum thickness for the CsI layer.

The enhancement can be achieved with different gases. However, we have not tried the effect of different gas pressures on the enhancement process and on the ageing. Dangendorf et.al.[13] have found that for the same total gain in the pre-amplification stage, a slower decay of the photocathode occurs at higher pressure. This is interpreted to be due to the lower velocity of molecular radicals in the gas. Gas pressure and composition are just two of many parameters that must be studied in future tests. There is a great deal of work left to be done in understanding the CsI-TMAE photocathode.

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## Figure Captions

- Figure 1: Schematic of experimental chamber (ref.14).
- Figure 2: A typical single-photoelectron, pulse-height spectrum.
- Figure 3: Normalized photocathode current as a function of collected charge for different initial currents.
- Figure 4: Initial enhancement of normalized photocathode current as a function of collected charge. (Detail of fig. 3)
- Figure 5: Peak enhancement factor as a function of initial current.
- Figure 6: Quantum efficiency as a function of wavelength for the non-enhanced CsI-TMAE photocathode and for the photocathode enhanced separately with methane, ethane and pentane. The quantum efficiency of an optically thick layer of TMAE gas is also shown.
- Figure 7: Current as a function of time.
- Figure 8: Quantum efficiency as a function of wavelength above 200 nm for the photocathode enhanced with gases of different  $V_0$ . (Detail of fig. 6)
- Figure 9: Relative quantum efficiency as a function of collected charge for a pre-enhanced CsI-TMAE and for a non-enhanced CsI-TMAE photocathode.
- Figure 10: Quantum efficiency as a function of wavelength for a pre-enhanced and a non-enhanced CsI-TMAE photocathode after ageing. The quantum efficiency of an enhanced photocathode is included as a comparison.

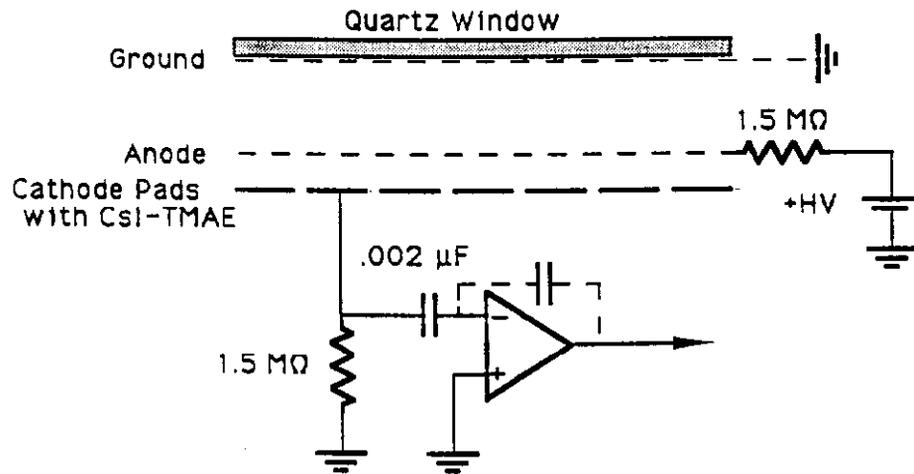


Figure 1

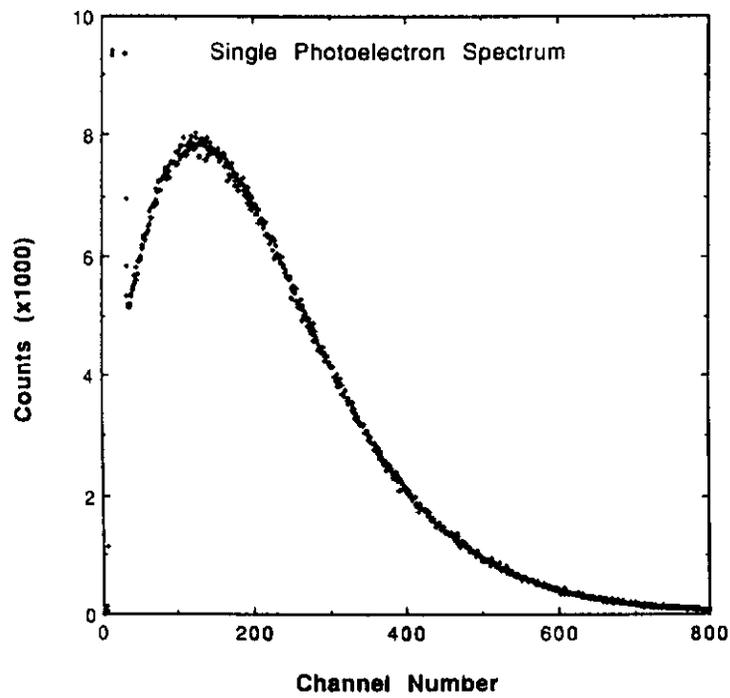


Figure 2

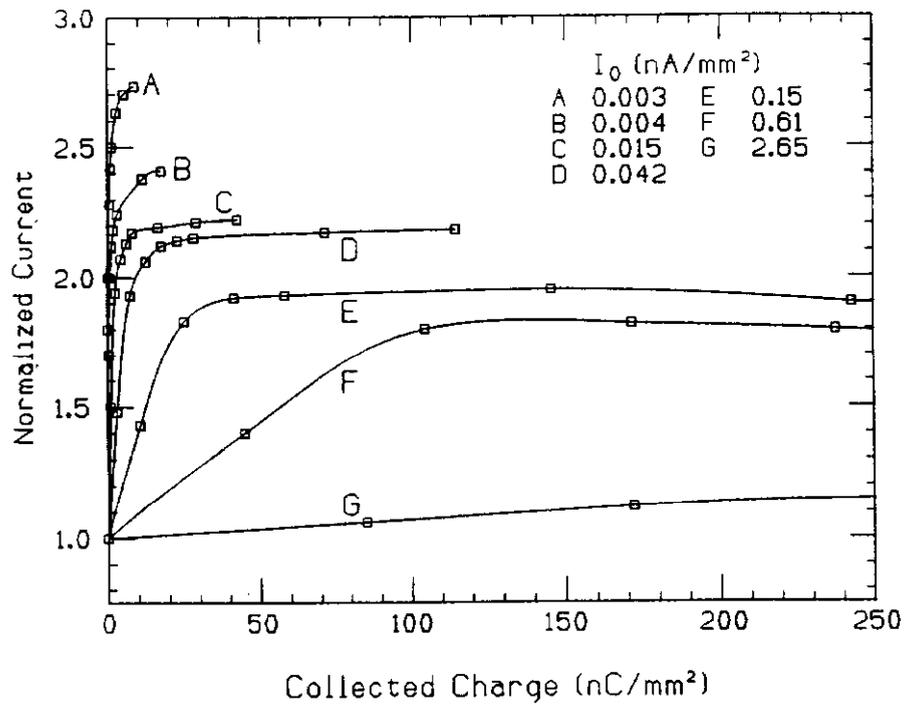


Figure 3

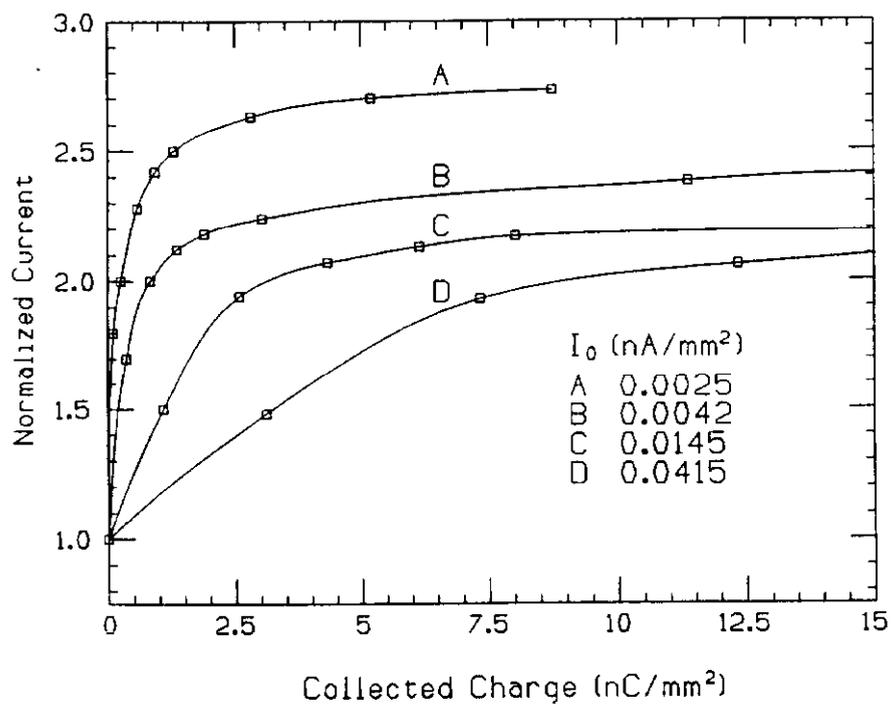


Figure 4

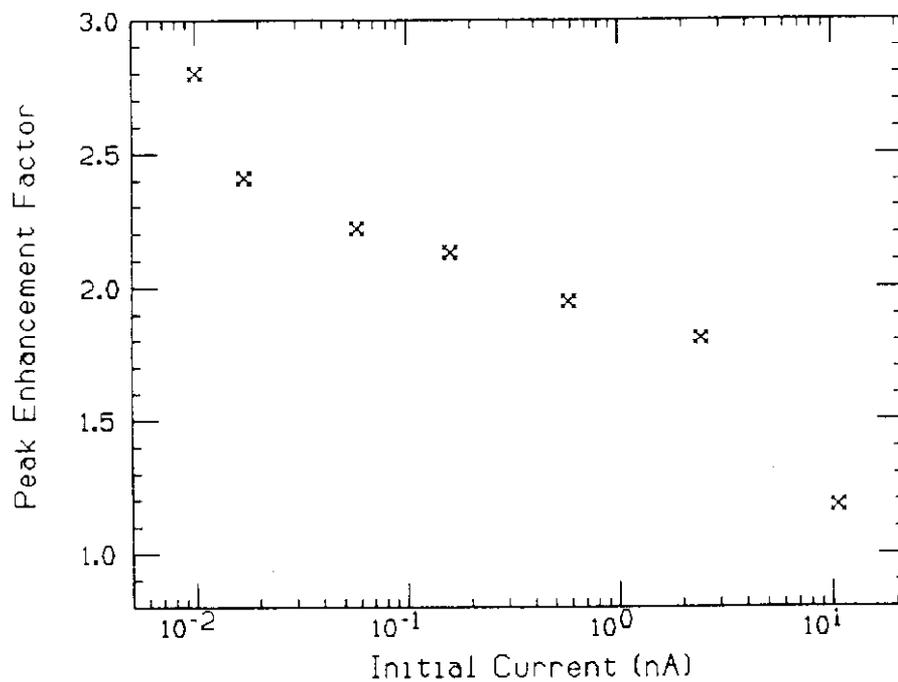


Figure 5

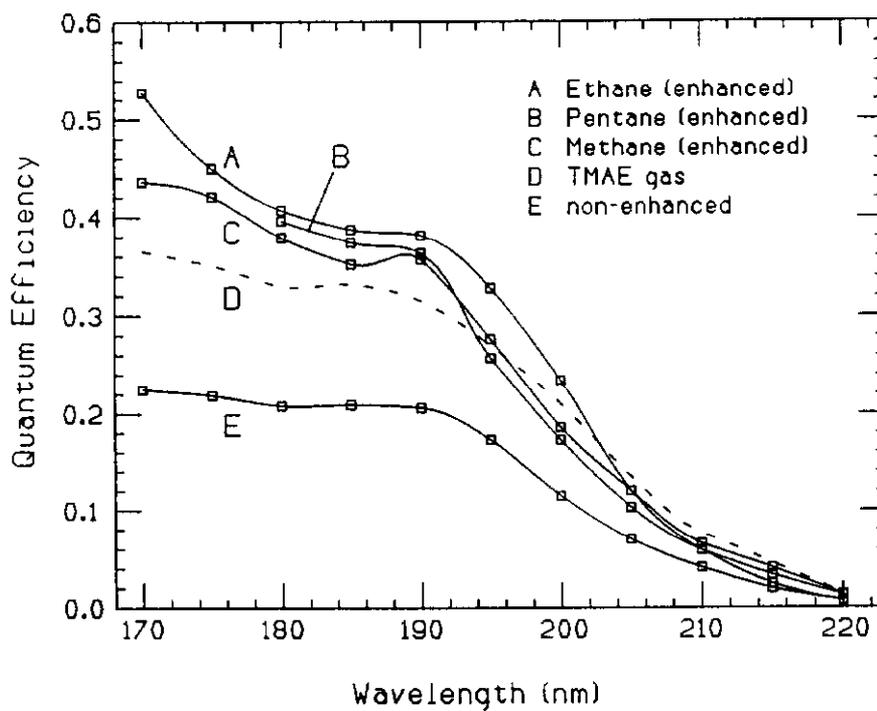


Figure 6

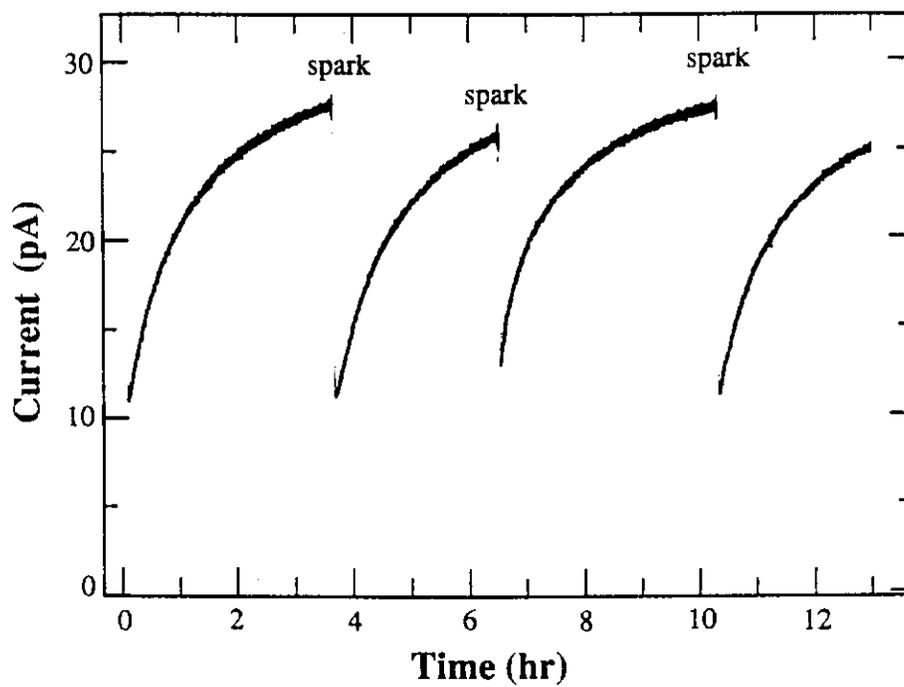


Figure 7

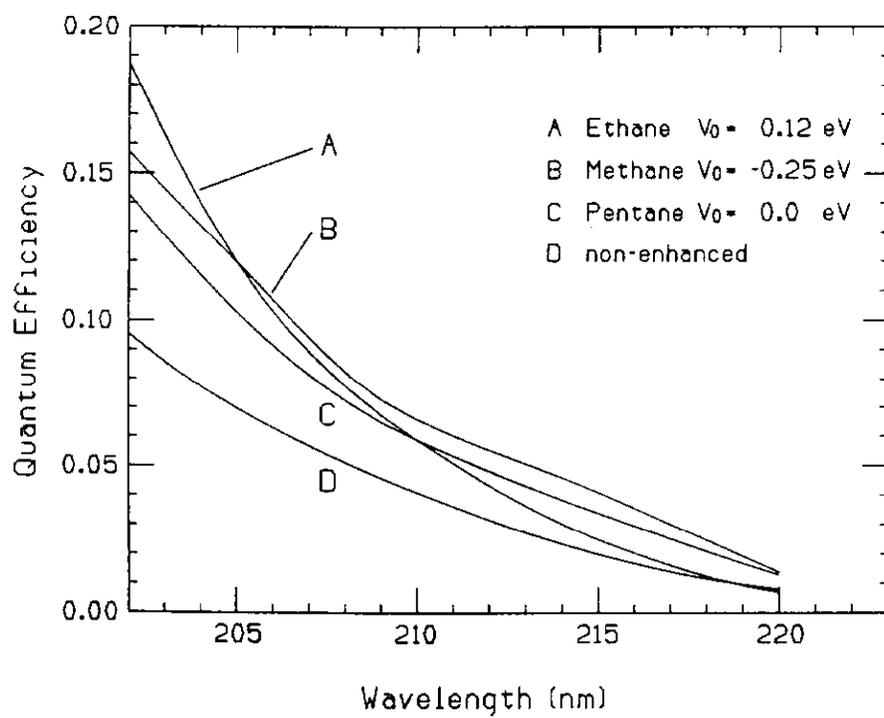


Figure 8

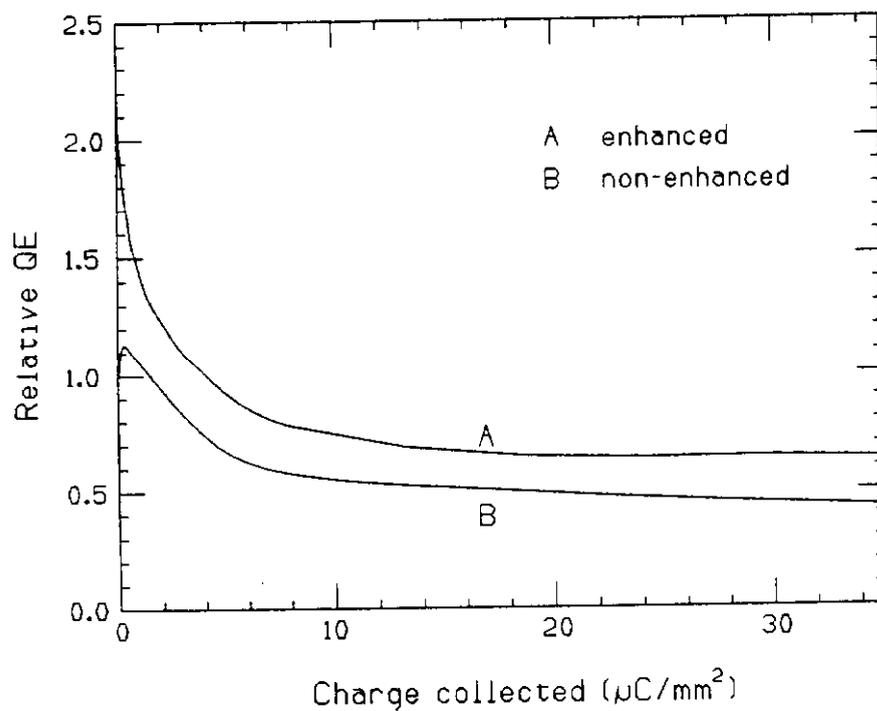


Figure 9

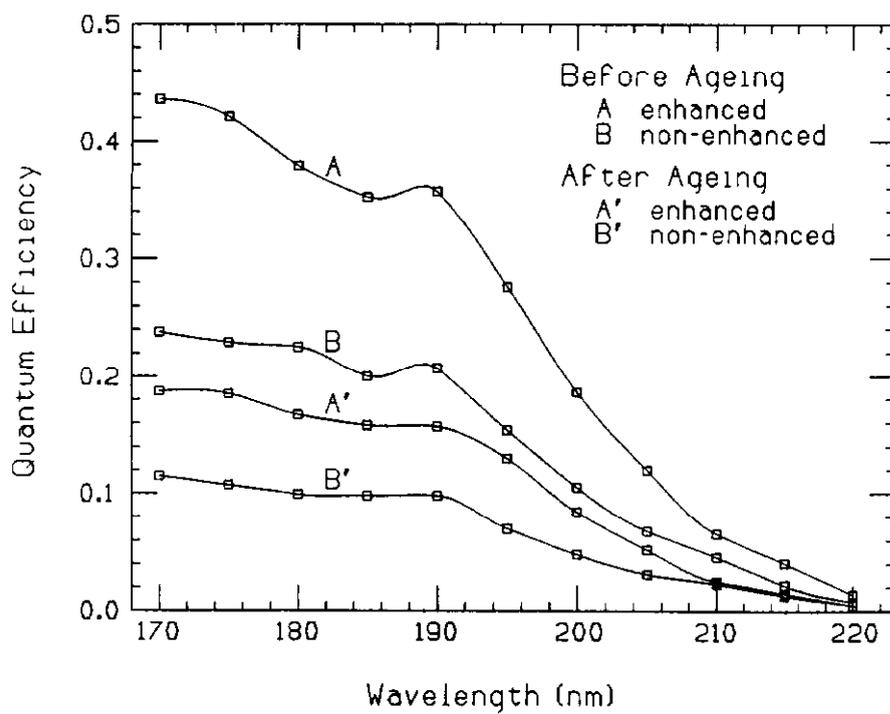


Figure 10