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**ORGANOMETALLIC PHOTOCATHODES FOR
PARALLEL-PLATE AND WIRE CHAMBERS**

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ABSTRACT

We have investigated the possibility of using organometallic photocathodes (ferrocene, diethyl ferrocene, ethyl ferrocene, and cyclopentadienyl-iron-hexamethyl-benzene) in gaseous detectors. We found that condensed layers of these substances could increase the sensitivity of metallic cathodes to VUV radiation by several orders of magnitude. The best choice seems to be ethyl ferrocene, which can be used as the photosensitive element in the vapour phase as well as in condensed and absorbed layers. A parallel-plate chamber with this photocathode, operated at atmospheric pressure, combines rather good time resolution (~ 10 ns or better) with sensitivity better than 1% for wavelengths shorter than 230 nm.

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1. INTRODUCTION

The molecular structure of organometallic compounds enables them to combine the desirable properties of low ionization potential and little chemical activity [1]. For this reason these compounds seem to be very attractive for use as photocathodes in gaseous detectors. We have tested four substances as candidates: ferrocene [2], diethyl ferrocene [2], ethyl ferrocene (EF) [3], and cyclopentadienyl-iron-hexamethyl-benzene (CPIHMB) [4]. The highest sensitivities in the spectral range 200–300 nm were achieved with the last two substances, on which we have therefore concentrated our investigations. In this article we give a review of our last results obtained using CPIHMB and EF as photocathodes for gaseous detectors.

This work has been done in the framework of the LAA Project on Detector Research and Development [5].

2. THE CPIHMB PHOTOCATHODE

2.1 Experiment

CPIHMB [chemical formula: $\text{Fe}(\eta\text{-C}_5\text{H}_5)\eta\text{-(C}_6\text{Me}_6\text{)}^*$] is a brown powder with a vapour pressure of $\sim 10^{-6}$ Torr at room temperature, and a photoionization potential in the gas phase, $E_{\text{i}} = 4.5$ eV (275 nm) [1].

For this investigation, the set-up was the same as that described in ref. [2]. A single-wire counter associated with a cooled metallic cathode was used. This detector and the method of depositing these substances on the cooled cathode are also described in detail in ref. [2]. Different gas mixtures— CH_4 , argon (90%) + CH_4 (10%), and CH_4 + tetramethyl pentane (TMP) or tetramethyl silane (TMS) vapour—were flushed at a total pressure of 1 atm through a bubbler containing CPIHMB powder, and through the counter. The bubbler, the single-wire counter, and the whole gas system were maintained at 70°C , and the temperature of the metallic cathode was kept at only a few degrees. The gas flow carried the CPIHMB vapour from the bubbler to the counter volume, where it was cryopumped onto the cooled metallic cathode. After deposition of more than a few monolayers of CPIHMB, all the measurements were made at room temperature.

2.2 Results

The quantum efficiency of the CPIHMB photocathode was measured in the range 200 to 300 nm. The results are presented in fig. 1 [4]: curve 1 is the sensitivity of a clean copper cathode; curve 2 is the efficiency of the cathode with a layer of CPIHMB; curve 3 gives the sensitivity obtained with the layer of CPIHMB when TMS vapour was present in the gas mixture. It can be seen that after deposition of the CPIHMB layer, the efficiency of the metallic cathode increases by 1 to 2 orders of magnitude in the wavelength region $\lambda < 260$ nm. As we expected (see ref. [2]), the measured photoionization threshold of CPIHMB in the condensed form $E_{\text{i,cond}} = 4.2$ eV (295 nm) was smaller than $E_{\text{i,gas}}$ in the gas phase.

The formation time and the stability of the CPIHMB photocathode are shown in fig. 2. In these measurements the single-wire counter was flushed with CH_4 + CPIHMB vapour, as described in ref. [2]. Cooling of the metallic cathode was started at time $t = 0$ and stopped at t_{stop} . It was then kept at room temperature, as were the counter and the whole gas system. The photocathode remained stable during a few days, even after the cooling was stopped—a property that is favourable for practical applications.

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*) Me = methyl

3. EF PHOTOCATHODE

Our results from the previous investigation of EF as a photosensitive element were presented in ref. [3]. The efficiency of EF photocathodes is shown as curve 4 in fig. 1. Although the efficiency of EF as a photocathode is slightly lower than that of CPIHMB, the fact that EF is easy to handle because it does not react with air makes it rather attractive. We therefore tried to use it as the photosensitive element in a BaF₂ scintillator proportional counter [3]. The efficiency achieved at 1 atm (in He + 10% CH₄) for BaF₂ fast scintillation light ($\lambda = 193$ nm) was about 10% compared with TMAE gas under the condition of full absorption. The efficiency curve showed a peak at 193 nm. Previously published information [5] on vapour pressure led us to estimate that this efficiency is due to the photosensitive layer, and that the contribution from the gas can be neglected since the vapour pressure at room temperature is $\sim 10^{-4}$ Torr. However, during the course of an experiment with an ionization chamber, we found that this pressure was higher (see fig. 1 in ref. [3]). This meant that although the absolute efficiency measured in ref. [3] was correct, it was likely that the gas contribution could not be neglected. For this reason, we made some additional investigations; their results are presented below.

3.1 Measurements of EF vapour pressure

In order to check on qualitative observations made with the above-mentioned ionization chamber, we performed our own measurements of EF vapour pressure (see fig. 3). Two methods were used: i) In the temperature interval 80–200°C, we used the standard method of determining the boiling point of EF at a given pressure (points $\blacklozenge$ in fig. 3). ii) In the interval 25–55°C, where the standard method is not applicable, we used a pressure transducer (Baratron MKS type 221A) (points $\times$ in fig. 3). The results of these measurements are in good agreement (fig. 3). However, our results give a much higher vapour pressure than was previously quoted (dashed line) [3, 6]. We attribute this discrepancy to the fact that our earlier measurements were made in a temperature range where the accuracy of the method is poor.

Since our new results indicated that at room temperature the EF vapour contribution to the full ionization signal could not, as we had thought [3], be neglected, we started to do another set of measurements to separate clearly, in the signal, the contributions coming from the photocathode and from the vapour.

3.2 Detailed investigation of the wire chamber with an EF photocathode

3.2.1 Experiments with a pulsed VUV lamp

The wire chamber construction was described in refs. [2] and [3]. But in this latest experiment the aluminium container of the chamber had a CaF₂ window placed just near the BaF₂ crystal (see fig. 4). The wire chamber was irradiated through the BaF₂ crystal by a hydrogen flash lamp [7]. The output window of the lamp was covered by an interference filter 193-N-ID (Acton Research Co.), with a maximum transmission at 193 nm and a FWHM of 18 nm. In this way, we can imitate the BaF₂ fast-component scintillation. A typical light-pulse measured by a photomultiplier (PM XP2020Q) was seen to be rather short, with a FWHM of 25 ns. In principle, the light-flash can liberate the photoelectrons from the cathode and from the EF gas. The number of photoelectrons created inside the wire chamber was about 100. Because of the short pulse duration, measuring the drift-time enabled us to recognize in which part of the wire chamber the electrons were created. By applying a positive voltage on the Al plate or on the mesh on the BaF₂ crystal, it was possible to exclude the contributions from the cathode and from the adjoining drift regions.

Typical signals from the fast charge-sensitive amplifier (rise-time ≈ 10 ns) are sketched in figs. 5. In each figure the solid line corresponds to average results obtained with hot EF vapour ($T_{\text{EF}} \approx 60^\circ\text{C}$), the dashed line to EF vapour at room temperature (an absorbed layer of EF was also

found [3]), whereas the dash-dotted line shows the results obtained with a condensed layer of EF; in the last case the chamber, at a temperature of 60°C, was filled with EF vapour at the same temperature, then cooled down to 20°C or 0°C. In all cases, 100 Torr of CH₄ was added to the EF vapour filling, and the pressure was then brought to 1 atm.

Within a division of 200 ns per division on the time scale, most of the signal is from photoelectrons collected on the anode wire, and the influence of ions can be neglected.

Figure 5a corresponds to the case where a positive voltage was applied to the anode wire while the potential of the Al plate on the mesh placed against the BaF₂ crystal was kept at 0 V. Since the electric field penetrated the drift region, we collected not only the electrons created in the wire chamber, but also some that came from the drift gap. Figure 5b shows the case of a negative voltage applied to the Al plate. Here, in addition to the electrons created inside the wire chamber, we collected those from the drift space between the Al plate and the wire chamber, and also those liberated by the plate itself. The results shown in fig. 5c were obtained when a negative voltage was applied to the mesh on the BaF₂ crystal. In this case, the electrons were collected in the wire chamber itself, in the gap between the chamber and the BaF₂, and in the photosensitive layer on the surface of the crystal. When a positive voltage was applied to the mesh and to the Al plate (fig. 5d), the only electrons collected were those from the wire chamber.

Let us now analyse the shape of the pulses. In the case of a hot EF vapour, the signal grows monotonically, i.e. for several hundred nanoseconds the collection of photoelectrons, which are due to photoionization of the gas, is continuous.

When the signals were obtained at room temperature, their shape was completely different. Then the partial pressure of EF was much less, but a photosensitive layer of it was formed (adsorbed or condensed) on the BaF₂ crystal and on the Al plate. These signals clearly start off by growing sharply: this corresponds to the collection of photoelectrons from the wire chamber (including those created on the surface of the wire). They then show a slightly rising plateau, indicating that we collect a relatively small number of photoelectrons from the drift space, followed by another sharp rise corresponding to the collection of electrons liberated from the surfaces. The duration of the plateau corresponds to the drift-time of the electrons in the gap; the rise-time of the sharp growth that follows this plateau corresponds to the duration of the VUV pulse produced by the lamp. We can thus conclude that although we obtain a big signal from the surfaces, there exists a contribution from ionization of the EF vapour, even at room temperature.

Measurements done in a mixture of He + CH₄, without EF vapour, and with cleaned surfaces of the wire chamber, including the Al and BaF₂, did not exhibit any signal from either the gas or the surfaces, even though the high voltage was pushed to the breakdown limit. This proves that the sharp rise in the signals shown in figs. 5b and 5c come from the electrons liberated by the photocathode.

If we know the vapour pressure of EF as a function of temperature, it is possible, from the shape of the pulses shown in fig. 5, to estimate the absolute quantum efficiency of the EF photosensitive layer. Using the data for the absolute quantum efficiency of the detector at T_{EF} = 70°C (see fig. 5 of ref. [3]), we can recalculate the efficiency of our wire chamber at room temperature. The efficiency due only to gas ionization, under the condition of full photoelectron collection (wire chamber and two drift spaces), is $\approx 0.7\%$ for $\lambda = 193$ nm. The amplitude of the signal from the cathode was approximately twice that of the signal from the vapour (see fig. 5). Therefore the efficiency of the adsorbed layer is in the range between 0.7% and 1.5%, increasing with the electric field. In the case of the condensed layer, the efficiency is between 1.5% and 2%. The full efficiency of the chamber (i.e. gas and surfaces) would be about 3%, which is about 10% of that of TMAE vapour under the condition of full absorption. This is in very good agreement with the data presented in ref. [3] for the same gas mixture. It should be noted that the efficiency of the EF layer increases with the electric field E and the concentration of the quencher gas. For example, in pure CH₄ at $p = 0.5$ atm and

$E \sim 6 \text{ kV/cm}$, the quantum efficiency of the layer for $\lambda = 193 \text{ nm}$ was about 6.5%, which is $\approx 22\%$ of that of TMAE.

3.2.2 Measurements with radioactive sources

All these measurements were done under the same conditions: the chamber was filled with EF vapour at room temperature, and then 100 Torr of $\text{CH}_4 + \text{He}$, up to 1 atm, were added.

a) Investigation based on the shape of the pulses

It was expected that the wire chamber with the EF photocathode would have a high photon feedback, and that it would be impossible to achieve a high gas gain. To understand this, we studied the shape of the pulses produced by VUV emission of BaF_2 excited by radioactive sources of ^{241}Am and ^{60}Co .

In the case of the ^{241}Am source of γ -rays (59 keV), which produced single photoelectrons in the wire chamber with very small efficiency, we could not observe any photon feedback (double pulses) up to a rather high gain ($\sim 10^5$). Inverting the polarity in the drift region hardly changed the shape of the pulses at all: only their rise-time became a little shorter.

The ^{60}Co source of γ -rays (of 1.17 and 1.33 MeV) produced mostly single photoelectrons, with an efficiency 20 times larger (per incident photon). In this case, when the polarity on the mesh or the crystal was negative, we could sometimes observe double pulses, even at gains of 10^5 . The second pulse was delayed by a time corresponding to the electron drift from the surface. Since the gain was 10^5 , where we know that there is no feedback, the second pulse was an indication that, in the case of the ^{60}Co , two photoelectrons per photon were sometimes detected from the scintillation light of the BaF_2 , the second one coming from the photocathode itself. It was thus shown that the largest contribution to the chamber sensitivity came from the photocathode.

b) Measurements of the absolute efficiency of the wire chamber

Using the radioactive sources and the experimental set-up shown in fig. 4, we made two independent measurements of the absolute efficiency of the wire chamber. In the first one, a PM (C31000M) was placed directly against the CaF_2 window of the wire chamber. We found that the BaF_2 was slightly radioactive. This contamination created bursts of VUV light. It has been shown earlier [8] that approximately half of these pulses come from the fast component ($\lambda = 193 \text{ nm}$) of the light. By comparing the count rate of pulses from the PM with that from the wire chamber [the latter being delayed by the time the electrons drifted from the Al plate to the wire chamber ($\sim 200 \text{ ns}$)], it was possible to estimate the absolute efficiency of the EF adsorbed layer. In our case this ratio of count rates was about 100, increasing with the electric field. Taking into account the solid angle of the PM, it can be concluded that the absolute efficiency of the adsorbed layer was between 0.7% and 1%, which is consistent with previous measurements.

The number of wire chamber pulses delayed by at most $1 \mu\text{s}$ increase with decreasing temperature and also with the drift voltage. Observations made at different temperatures showed that:

- at 9.1°C , 50% of the coincidence pulses were delayed by 200 ns,
- at 2°C , 70% of the coincidence pulses were delayed by 200 ns.

So at 2°C , at least 70% of all photoelectrons come from the photocathode.

In the second measurement, the PM, with the other BaF_2 scintillator, was placed 10 cm away from the CaF_2 window of the wire chamber. The BaF_2 crystal in the wire chamber and the one on the PM were irradiated by a ^{22}Na source, placed between them on the common axis. They were thus irradiated simultaneously, giving two photons of $\sim 0.5 \text{ MeV}$ energy, propagating in opposite directions and producing scintillation pulses in both crystals. The pulse-amplitude spectrum of BaF_2

VUV emission consists in the peak produced by 0.5 MeV photons, the background being produced by ^{22}Na itself and by the internal radioactivity of the BaF_2 . After subtraction of this background, the numbers N of coincidences (with 200 ns delay) measured at different electric fields E were the following: at $E = 200 \text{ V/cm}$, $N \approx 1/200$; at $E = 400 \text{ V/cm}$, $N \approx 1/130$; at $E = 2 \text{ kV/cm}$, $N \approx 1/100$. Since the PM records the bursts of scintillation light from the BaF_2 with 100% efficiency, the value of the absolute efficiency of the EF layer, for $\lambda = 193 \text{ nm}$, can be estimated to be between 0.5% and 1%, depending on the electric field. This is again in good agreement with the above-mentioned data.

3.3 Parallel-plate avalanche chamber with the BaF_2 scintillation

As was shown above, the BaF_2 scintillation emission in the wire chamber, containing EF vapour at room temperature, produced photoelectrons due both to photoionization of EF vapour and to extraction of the electrons from the photocathode. In order to investigate the EF photocathode under ‘clean’ experimental conditions, i.e. without any contribution from EF vapour, we constructed a parallel-plate avalanche chamber (PPAC) containing a BaF_2 crystal, $2.5 \times 2.5 \times 7 \text{ cm}^3$. The transparency of the crystal along the axis for $\lambda = 193 \text{ nm}$ was about 50%. The chamber construction is presented in fig. 6. The distance between the two electrodes was 4 mm. It was filled with EF vapour at room temperature, and then 100 Torr of TMS mixed with He up to 1 atm were added. As in the case of the wire chamber, the EF vapour formed a photosensitive layer, which was deposited everywhere, including on the surface of the BaF_2 crystal and of the Cu cathode. The photoelectrons extracted from the surfaces produced avalanches, so that the number of electrons reaching the anode was larger by a factor N , corresponding to the gas gain. In principle, the photons emitted by the BaF_2 crystal can also ionize the EF vapour; but the photoelectrons that are created at a distance from the cathode larger than λ_i , the mean free path before ionization, will produce avalanches with a much smaller gas gain. For $N = 10^5$, $\lambda_i \approx 0.3 \text{ mm}$; therefore only 1/10 of the gap can in principle contribute to the creation of photoelectrons due to photoionization. Under these conditions and at room temperature, we can really neglect the contribution of the gas photoionization.

3.3.1 Investigation of the BaF_2 PPAC with a VUV lamp and with radioactive sources

Measurements with the VUV flash lamp give efficiencies that are of the same order of magnitude for a layer of EF adsorbed on the BaF_2 crystal and on the Cu cathode. The chamber was stable during operation and the gas gain ($\geq 10^5$) was sufficient to detect single photoelectrons.

Measurements made with an ^{241}Am source, as described in ref. [3], show that the BaF_2 fast emission detection efficiency of a PPAC, with an adsorbed layer of EF, is four times less than that of a wire chamber [3]. For a radiation of $\lambda \approx 193 \text{ nm}$, the absolute efficiency of an EF layer for the given gas mixture is thus $\approx 0.7\%$. The rise-time of the signals from the PPAC was $\approx 10 \text{ ns}$.

3.3.2 Measurements in a test beam

To check once more the efficiency of an EF layer, we also made preliminary tests in an unseparated charged-particle beam, of about 7 GeV energy, that contained also electrons. By inserting a thick absorber, we could also work only with muons. We estimated that the energy deposited by the muons in our BaF_2 crystal was approximately 49 MeV, and the maximum energy deposited by the electrons was about 0.7 GeV. The stainless-steel container of the BaF_2 PPAC was closed with a CaF_2 window, on which the PM (C31000M) was directly mounted (see fig. 6) as was done for the measurement of the absolute efficiency of the EF layer in a wire chamber (see subsection 3.2.2b). This BaF_2 crystal was without Al reflector. Calculations and measurements show that this reduces by $\approx 30\%$ the intensity of the BaF_2 light entering the PPAC. When we worked with the muon beam, the efficiency of the PPAC in coincidence with the PM was about 100%. The amplitude

of the signal from the PM for the fast component was 50 photoelectrons (the absolute efficiency of the PM to this radiation was about 25%). This means that in the case of the PPAC, with an efficiency of $\approx 0.7\%$ for the EF layer adsorbed on Cu, we should expect about 2 photoelectrons for 49 MeV deposited energy and about 50 photoelectrons for 0.7 GeV. Therefore, in the case of the muon beam, we expect the pulse-height distribution to have a broad maximum. For the 0.7 GeV electrons, we expect an energy resolution [9] of $\approx \sqrt{2/50} \approx 20\%$, since the trigger is a signal from the PM, corresponding to the maximum energy loss in the BaF₂. Qualitative results from the beam tests confirm these data, and we can say that the efficiency of an EF adsorbed layer was really about 1%. This means that in the case of a crystal with 90% transparency and with an Al reflector we can expect the energy resolution at 1 GeV to be about 10%. The gap between the plates is thin, only 4 mm, which makes it possible to collect light on the front and the back surface of the crystal (or on all six surfaces), thus increasing the signal and partly compensating the loss of efficiency with respect to TMAE. We are now also preparing for another test in a beam, with a PPAC working with a condensed layer of EF. There we may expect the efficiency to be better.

We remind the reader that, in the case of TMAE under the condition of full absorption of the scintillation light from the BaF₂ crystal (with a transparency of the crystal of 75% and with an Al reflector), the energy resolution for 1 GeV was 6%, improving to $3.9\%/\sqrt{E}$ at high energies [10]. With EF, we may also expect such an improvement, which would make the calorimetry with an adsorbed layer attractive, even at the present level of sensitivity.

4. CONCLUSION

All the experiments described above show that the absolute efficiency of an adsorbed layer of EF is about 1% for $\lambda = 193$ nm. When the EF layer is condensed, this efficiency increases by a factor of 3 to 4, which makes such a calorimeter very useful at very high energies.

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Figure captions

- Fig. 1 Quantum yield as a function of wavelength for different photocathodes. 1 Clean Cu; 2 Cu + condensed CPIHMB; 3 Cu + condensed CPIHMB + TMS; 4 Cu + condensed EF.
- Fig. 2 Quantum efficiency of a CPIHMB photocathode as a function of the deposition time (up to t_{stop}) and of the stability of the sensitivity (as from t_{stop}).
- Fig. 3 EF vapour pressure as a function of temperature: $\circ$ old measurements [6]; $\blacklozenge$ and $\times$ our measurements (see text).
- Fig. 4 Experimental set-up for the investigation of the EF photocathode: 1 shows the position of the H_2 flash lamp (or of the ^{22}Na source, for the measurements with the PM). 2 is the position of the PM for the measurement using the internal radioactivity of BaF_2 .
- Fig. 5 Shape of pulses from the wire chamber. a) Potential of the mesh on the BaF_2 crystal (V_{BaF_2}) and potential of the Al plate (V_{Al}) are kept at 0 V; b) $V_{\text{BaF}_2} = 0$ V, $V_{\text{Al}} = -200$ V; c) $V_{\text{BaF}_2} = -200$ V, $V_{\text{Al}} = 0$ V; d) $V_{\text{BaF}_2} = +100$ V, $V_{\text{Al}} = +100$ V. Solid lines: EF vapour at 60°C ; dashed lines: EF at 20°C ; dash-dotted lines: condensed EF (i.e. the vapour was cooled from 60°C to 20°C).
- Fig. 6 Construction of the PPAC. The thick arrow shows the direction of the beam.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6