EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

CERN-EP/88-166
25 November 1988

**ETHYL FERROCENE IN GAS, CONDENSED, OR ADSORBED PHASES:
THREE TYPES OF PHOTOSENSITIVE ELEMENTS
FOR USE IN GASEOUS DETECTORS**

G. Charpak, V. Peskov, F. Sauli and D. Scigocki

CERN, Geneva, Switzerland

ABSTRACT

We have investigated the properties of an organometallic compound, ethyl ferrocene (EF), which we propose to use as the photosensitive element in gaseous detectors, both in the gas (vapour) phase and, in condensed or adsorbed layers, as photocathodes. The big advantage of EF is that it is easy to handle, as it is not reactive to oxygen. The sensitivity for the detection of BaF_2 fast emission was measured with EF vapour and was found to be lower by a factor of close to 1.5 compared with TMAE vapour measured under the condition of full light absorption. Adsorbed or condensed layers of EF used as photocathodes in a gaseous detector achieved an efficiency that was lower by a factor of 4 to 10, depending on the experimental conditions.

(Submitted to Nuclear Instruments and Methods)

1. INTRODUCTION

The concept of using a photosensitive element in gaseous detectors has a long history [1]. The first idea for this type of device came from Séguinot and Ypsilantis [2], who proposed a ring-imaging Cherenkov detector. A wire chamber filled with photosensitive vapour was elaborated independently by Bogomolov et al. [3].

Further, and successful, developments made it possible to use triethylamine (TEA) vapour (ionization potential $E_i = 7.5$ eV) as the photosensitive element [4, 5]. The second idea, put forward by Peskov [6] and Policarpo [7], was for an imaging gas scintillation proportional chamber (GSPC); a realization of this idea was carried out by Charpak, Policarpo and Sauli [8]. The technique of using an organic vapour called tetrakis(dimethylamine)ethylene (TMAE), with $E_i = 5.36$ eV, as a photosensitive element in a GSPC was first employed by Anderson [9].

The proposal to couple a dense inorganic scintillator, BaF_2 , with a low-pressure multiwire proportional chamber (MWPC) came from Anderson et al. [10–12], who named the device the solid-scintillator proportional counter (SSPC). The properties of BaF_2 are: high density (4.9 g/cm^3); short radiation length (2.05 cm); a fast ultraviolet (UV) scintillation component with a decay-time of 600 ps [13]; a photon yield that is independent of temperature [14–15]; and resistance to radiation damage up to more than 10^7 rad [16, 17]. Adding these advantages to those of a low-pressure chamber (which resulted in a very good time-resolution [18] and low sensitivity to direct ionization) made the SSPC a most attractive device for many applications [19–21]. Until recently, the only photosensitive compound that had been used with MWPCs to detect, with good efficiency, the fast component emitted by BaF_2 , was TMAE. The major disadvantage of TMAE is that it is very reactive to oxygen. Furthermore, this compound has proved to be corrosive for many materials.

The aim of this work is to investigate the properties of an organometallic compound, ethyl ferrocene (EF), which we propose to use as the photosensitive element in gaseous detectors, either in the vapour phase or as a photocathode made with an adsorbed or a condensed layer of EF. We are carefully studying the possibility of using EF as the photosensitive element for the detection of BaF_2 fast emission in an SSPC.

2. GENERAL PROPERTIES OF ETHYL FERROCENE

Ethyl ferrocene [chemical formula $\text{Fe}(\text{C}_5\text{H}_4)_2\text{C}_2\text{H}_5$; $E_i = 6.2$ eV] is a brown liquid with a faint odour. It is relatively easy to produce, is not toxic, and is very stable. It does not interact chemically with oxygen, or with gases or materials commonly used in gaseous detectors [22], and can therefore be manipulated in air. On the other hand, the vapour pressure of EF, which is given in fig. 1 as a function of temperature [22], is very low compared with that of TMAE (0.1 Torr compared with 8.5 Torr, at 70°C [22]).

An important characteristic of photosensitive gases is the light emission generated during avalanches. On the one hand, this can produce photon feedback in the chamber [23]; on the other hand it can be used for the optical readout of wire chambers [24]. For these reasons, both the spectrum and the intensity of EF light emission were measured [25]. In the wavelength region between 200 and 800 nm, the main contribution to the emission shows a peak at 310 nm, the region belonging to OH^- . This emission, which is probably due to small traces of water in the EF or in the experimental set-up, is rather strong (see fig. 2), i.e. at the level of that of an argon + TMAE mixture. When we increased the proportion of water vapour in the gas mixture, the light emission increased and reached the level of that of an argon + TEA mixture, which is the maximum known at present [24]. But when the water traces were removed from the EF and from the whole system by heating at 90°C during a few days, this emission dropped by an order of magnitude (curve 4); with the elimination of water traces, the EF vapour becomes a very good quencher.

3. EXPERIMENTAL RESULTS

3.1 Experimental set-up

3.1.1 Single-wire counters

We have used two single-wire counters. The first counter consists of a cylindrical cathode, 40 mm in diameter, made from stainless steel and having a central anode wire of 50 μm diameter (fig. 3). Two transverse flanges were added in the middle of the cylinder. One of the flanges was equipped with a CaF_2 window; the other had joined to it a Cu cathode which could be independently cooled. In one set-up (fig. 3) a $15 \times 15 \times 40 \text{ mm}^3$ BaF_2 crystal was placed in contact with the CaF_2 window. This crystal was irradiated, through a lead collimator, by 59 keV gammas from a ^{241}Am source. In a second set-up (see ref. [26]), a Jobin-Yvon H20 UVL monochromator was joined to the flange that had the CaF_2 window. The counter was flushed with a gas mixture consisting of argon and EF or TMAE vapour at a total pressure of 1 atm. The counter and the gas system could be heated up to 90 $^\circ\text{C}$.

The second counter was mostly used for taking measurements of ageing. We assumed that the ageing characteristics can be largely dependent on the contamination of the gas and on the purity of the whole gas system. For this reason we tried to make these measurements under the cleanest conditions. A sealed counter was used, with a stainless-steel cathode, 16 mm in diameter, and a molybdenum anode having 0.1 mm diameter wires. The counter was equipped with an LiF_2 window of 2 mm diameter. Before sealing, the counter was pumped up to 5×10^{-6} Torr. It was then heated up to 200 $^\circ\text{C}$ over a period of a few days, after which the EF vapour was cryopumped into the counter and spectral clean argon, at 300 Torr, was added. The counter worked in the Geiger mode. During the measurements it was kept at 70 $^\circ\text{C}$ and was irradiated by vacuum ultraviolet (VUV) light in the spectral region between 105 and 200 nm.

3.1.2 The solid-scintillator proportional counter

The set-up of the SSPC used for these measurements is shown in fig. 4. It consists of an aluminium vessel containing a $5 \times 5 \times 5 \text{ cm}^3$ BaF_2 crystal that is in contact with a MWPC. The latter has an absorption gap ℓ that can be varied between 0.05 and 4 cm. The face of the crystal that is in contact with the chamber is covered by a stainless-steel mesh made of wires of 50 μm diameter, 500 μm apart. A negative voltage is applied to this mesh to repel the photoelectrons liberated on the crystal or in the conversion gap. The MWPC has two cathode planes made of 100 μm diameter wires, 1 mm apart, and orthogonal to each other, and an anode plane of 15 μm diameter wires. There is a gap of 3 mm between each of these three planes. Two types of anode planes were used: one with wires 1 mm apart at low pressure, and a second with wires 2 mm apart at atmospheric pressure. The anode is connected to a positive potential and the cathodes to ground. An aluminium plate is placed 3 mm after the last cathode plane and is grounded or connected to a positive voltage (+100 V).

The detector was assembled inside a thermostatic box, where the temperature could be varied between 5 and 80 $^\circ\text{C}$. We made two kinds of experimental tests: at low pressure (≤ 30 mbar), and at higher pressures (between 0.4 and 1 atm). For the low-pressure measurements a reservoir containing liquid EF was coupled to the detector and could be heated independently. Before these measurements, the detector was pumped up to 5×10^{-5} Torr and then EF vapour was introduced into it. The liquid EF was pumped for only a few minutes before each vapour filling and was not especially purified. In some cases, 30 mbar of CH_4 or a few millibars of isobutane, ethane, tetramethyl pentane (TMP), tetramethyl silane (TMS), or neopentane (NP), were added in order to allow higher gains in the detector. For comparison, some measurements were also performed with the chamber filled with TMAE vapour and with 30 mbar of CH_4 . At higher pressure, preliminary measurements were made under the same conditions of chamber operation but with the additive gas at different pressures. We used CH_4 at 0.5 atm or a gas mixture composed of $\text{He} + \text{CH}_4$ at 1 atm. In

a second phase, the set-up of the experiment was modified: instead of using a closed system, the He + CH₄ gas mixture, at atmospheric pressure, was continuously flushed through the detector after being bubbled in a bottle of liquid EF. For the measurements, the BaF₂ crystal was irradiated by collimated gamma sources [~ 1 MeV gammas from ⁶⁰Co (60 μ Ci) or 59 keV gammas from ²⁴¹Am (100 μ Ci)] placed 50 mm from the crystal. We measured the number of counts produced with the anode plane of the MWPC through an ORTEC 142 preamplifier followed by an ORTEC 450 research amplifier.

3.2 Results

3.2.1 EF vapour

a) Measurements with the single-wire counters. Figure 5a shows our rough estimate of the behaviour of the efficiency of EF vapour obtained from our measurements at $T_{EF} \approx 70$ °C, for an absorption gap $\ell_{EF} = 16$ mm in the spectral region 105 to 200 nm, measured with the first single-wire counter described in subsection 3.1.1. For the case of full absorption, we expected an efficiency of more than 25%.

For comparison, fig. 5b gives the quantum efficiency of TMAE vapour ($E_i = 5.36$ eV) measured between 150 and 250 nm [27] (curve 3), the BaF₂ fast emission spectrum [10] (curve 1), and the estimated quantum efficiency of EF (curve 2). In the region of the first peak at shorter wavelengths (180 to 200 nm), which according to calculations gives the largest contribution to the SSPC's response, the integral quantum yield of EF is estimated to be about one half the one of TMAE.

To verify this estimate experimentally, we measured the count rate N_{EF} using the single-wire counter in the configuration shown in fig. 3, in the Geiger regime. The advantage of the Geiger mode is that the pulse-height spectrum has a sharp peak and so its efficiency for single-electron detection is close to 100%. This allows a very precise comparison to be made between TMAE (in conditions of full light absorption) and EF vapour efficiencies for BaF₂ emission. Table 1 shows the results of this comparison. The BaF₂ crystal was irradiated with 59 keV gammas from a ²⁴¹Am source. Because of the small amount of energy deposited in the BaF₂, the average number of photoelectrons n_{pe} produced in the chamber is < 1 . Therefore, the ratio N_{TMAE}/N_{EF} gives the relative quantum efficiency of TMAE and EF. The result is slightly better than our preliminary estimate based on figs. 5.

In other measurements we used the sealed counter described in subsection 3.1.1 to estimate the effect of ageing on the properties of EF vapour under clean conditions in the gas system. The single-wire counter worked in the Geiger mode, and information on the ageing was obtained by measuring the gas gain versus the applied voltage. The total charge collected in our experiment is estimated to be $\sim 10^{-3}$ C, without any change observed in the gas gain. Therefore the ageing characteristics of EF vapour are at least not worse than those of TMAE (see ref. [28]).

b) Measurements with the SSPC. All the measurements using the SSPC with EF vapour were made at low pressure, using the detector shown in fig. 4. To avoid condensation, the detector was kept at a temperature higher (~ 10 °C more) than that of the bottle of EF liquid.

With this wire chamber we can operate in the proportional mode only. Since, as above, $n_{pe} < 1$, the pulse-height spectrum was exponential-like. In this case, owing to the discrimination level in the recording electronics, the measured number of counts can be less than in the Geiger mode. To verify this, we made two experimental checks: first, we checked whether we had a counting plateau; secondly, we measured N_{TMAE}/N_{EF} in conditions of gain large enough to detect single photoelectrons. Table 1 gives the results.

The highest efficiency with the SSPC confirmed our result obtained with the single-wire counter under similar conditions, and indicates that, even in the proportional mode, the efficiency of the

SSPC filled with EF vapour is close to that of TMAE. Figure 6 shows N_{EF} as a function of the temperature and for different ℓ_{EF} . The points show clearly the increase of efficiency with the vapour pressure. The best result is $\sim (67 \pm 5)\%$ of the efficiency obtained with TMAE vapour in conditions of full light absorption; it was measured with $T_{EF} = 80^\circ\text{C}$ and $\ell_{EF} = 35\text{ mm}$.

To check once more that, for $T_{EF} \approx 70\text{--}80^\circ\text{C}$, we worked close to full absorption, we inverted the polarity in the drift region and made measurements for different ℓ_{EF} . Photoelectrons produced in the drift region cannot reach the wire chamber, and only those created inside the chamber gave a signal. From this measurement we have inferred that at an EF vapour pressure corresponding to a temperature of 70°C , the mean free path of VUV BaF_2 photons is about 1 cm. We do not know if this is due to real absorption in the EF vapour or to electronegative impurities in it.

3.2.2 Condensed layer of EF

a) Measurements with the single-wire counters. Recently, the possibility of using liquid or solid organic photocathodes for gaseous detectors with a good sensitivity in the spectral region between 105 and 300 nm was successfully investigated [26]. We tried to perform the same measurement for condensed EF, using the set-up described in ref. [26]. In the present experiment, the single-wire counter was heated to 40°C and the external part of the Cu cathode was cooled to 0°C (for details, see ref. [26]). The measurements were made in the Geiger mode, at atmospheric pressure. In this case we can be sure that the detection efficiency for single photoelectrons is about $\sim 100\%$ (see above).

Figure 7 (curve 2) shows the quantum efficiency measured between 180 and 250 nm for a thin condensed layer of EF deposited on the copper cathode. For comparison, the curve of EF vapour at $T_{EF} = 40^\circ\text{C}$ for $\ell_{EF} = 15\text{ mm}$ (curve 1) and that of a clean copper cathode (curve 3) were added. As can be seen, the condensed layer of EF is sensitive to radiation at wavelengths longer than the photoionization threshold in the gas phase. The efficiency of this layer, measured with a monochromator at $\lambda = 240\text{ nm}$ is shown, as a function of cooling duration, in fig. 8. In this case, to condense on the cathode, we kept its temperature at a few degrees less than that of the whole counter. These results indicate that above a certain thickness of the condensed layer, the efficiency stays unchanged. The simplest explanation is that after a delay of five hours we reached a thickness that was sufficient to achieve full absorption for the UV light. In this case, the efficiency of photoelectrons creation in a liquid layer would be constant. This opens up the possibility of interesting applications, e.g. EF could be used as a liquid photocathode.

b) Measurements with the SSPC. All the measurements done to study a condensed layer of EF in the SSPC described in subsection 3.1.2 (fig. 4), were made at low pressure.

To test liquid EF as the photosensitive element in the SSPC, we began by filling the detector, kept at 65°C , with EF at a vapour pressure corresponding to a liquid temperature of 55°C and adding 30 mbar of CH_4 or a few millibars of other additive gases. We then cooled the detector slowly until it reached room temperature. We expected the EF to be condensed uniformly in the detector, thus producing a photocathode deposited on the BaF_2 crystals. Under these conditions the detector worked successfully and we measured the count rate produced by the gamma irradiation from a ^{60}Co or ^{241}Am source. Using methane as the additive gas, and with a gap $\ell = 5\text{ mm}$, we then found that at room temperature the count rate was only 1.5 lower than the rate measured when the EF was in the vapour phase and at a pressure corresponding to a liquid temperature of 55°C . To verify that this efficiency came from the condensed liquid layer and not from the vapour, we brought the temperature down to $\sim 10^\circ\text{C}$: the signal was the same as before (see fig. 9) whereas, according to our estimate based on calculations taking into account the EF vapour pressure, it should have dropped by a factor of more than 5.

To check this by other means, we measured the count rate produced by scintillation of BaF₂ irradiated by the ⁶⁰Co source as a function of T_{EF}. For these measurements, the chamber and the whole gas system were kept at the same temperature, and the temperature of the EF container was a few degrees lower. Then we introduced the EF vapour and 30 mbar of CH₄ into the chamber, as described earlier. The measured count rates, as a function of T_{EF}, are given in fig. 9. As can be seen, when T_{EF} goes from 55 °C to 10 °C, the count rate drops by about a factor of 6, which is in good agreement with our estimate. But when T_{EF} goes from 20 °C to 5 °C, the count rate drops by about a factor of 2.5. This is less than we expected from calculations (about a factor of 10). We suggest that this discrepancy is due to a contribution to photoelectron creation in a thin layer of EF adsorbed everywhere, including on the BaF₂ crystal (see subsection 3.2.3).

We also compared the efficiency when different gases were added in the chamber: 30 mbar of CH₄, or a few millibars of TMP, TMS, or NP. After cooling from 65 °C to room temperature, we measured an equivalent efficiency for the EF layer with all these gases, and found that it was lower by a factor of 2 compared with that obtained with the EF vapour corresponding to T_{EF} = 65 °C with $\ell_{EF} = 5$ mm. These results differ from those obtained with a condensed liquid layer of TMAE [26], where the quantum efficiency of the photocathode increased when the additives TMP, TMS, or NP were used.

Other results were obtained with isobutane or ethane (at a pressure of a few Torr) as the additive gases in the SSPC. With ethane, the efficiency of the condensed layer of EF was 2.5 times lower and with isobutane ~ 3 times lower than what was achieved with the other gases. Therefore, isobutane and ethane would seem to deteriorate the efficiency of the condensed liquid layer of EF. Similar results were obtained with a liquid layer of TMAE [26].

We next increased T_{EF} from 65 °C to 80 °C before filling the detector and then cooled it to room temperature. With 30 mbar of methane as the additive gas we did not observe any improvement in the efficiency of the condensed layer. This is in good agreement with the results obtained with the single-wire counter (see 3.2.2a).

The maximum efficiency reached by the condensed layer of EF for the BaF₂ fast component was estimated to be ~ (10 ± 3)% of that obtained with TMAE vapour under the condition of full light absorption.

3.2.3 Adsorbed layer of EF

We have discovered that when EF vapour, at a pressure corresponding to room temperature, is introduced into an SSPC kept at the same temperature, an efficient and stable layer of EF is adsorbed on the BaF₂ crystal. This adsorbed layer of EF can be used as a photocathode to detect the fast component of the BaF₂ scintillation.

The measurements with an adsorbed layer of EF deposited on a BaF₂ crystal were made, with the same SSPC, at low and up to atmospheric pressure.

a) Experiments at low pressure. At a temperature of 26 °C, with a gap of 5 mm, and with 30 mbar of methane as the additive gas, we measured an efficiency equivalent to that obtained with the condensed layer of EF, i.e. (10 ± 3)%, under similar conditions (see above). In principle, the total efficiency can be divided into two parts: one part coming from the adsorbed layer itself, and the other being due to the influence of EF vapour at room temperature with a gap $\ell_{EF} = 5$ mm. We estimated the latter by heating the detector to 78 °C, which strongly reduces the effect of the adsorption, and adding EF vapour corresponding to a liquid temperature of 27 °C. The efficiency measured was lower, by a factor of ~ 3, than with the detector at room temperature. This means that not more than 30% of the signal comes from the vapour. But even this residual efficiency is probably still due to the electron extraction from the surface, because the EF vapour pressure at

room temperature is so low ($\sim 10^{-4}$ Torr, see fig. 1) that the EF gas efficiency in a gap of 5 mm would be much lower than the efficiency measured under these conditions.

b) Experiments up to atmospheric pressure

The gain of gaseous detectors depends essentially on the reduced electric field per unit of pressure E/P . At low pressures it is possible to achieve a very high value of E/P and, as a consequence, a good gain with low electric fields, typically about a few hundred volts per centimetre. Higher fields are needed (approximately a few kilovolts per centimetre) at atmospheric pressure in order to reach similar multiplication. The efficiency of extraction of photoelectrons produced in a liquid photocathode placed in a gaseous detector increases with the electric field [29], and it has been observed in ref. [28], for quencher gases, that it is not strongly dependent on the pressure. This means that low pressure is not favourable for liquid photocathode efficiency because it is not possible to apply a very high electric field without discharges. To test whether the comportment of an adsorbed layer of EF is equivalent to that of a condensed layer, we tried to improve the efficiency of the EF layer adsorbed at room temperature on BaF_2 by increasing the pressure in the SSPC.

As a first step we ensured that the experimental conditions were similar to those at low pressure with a closed system. After vacuum pumping and the introduction of EF vapour at room temperature, ~ 0.5 atm of pure CH_4 or a gas mixture composed of $\text{He} + \text{CH}_4$ at atmospheric pressure were added in the SSPC. We found that the sensitivity of the layer was not disturbed and continued to be very stable. In comparison with TMAE vapour in the condition of full light absorption, the efficiency of the EF layer measured with $\ell_{\text{EF}} = 5$ mm was

- (25 ± 2)% with CH_4 at 0.5 atm,
- (20 ± 2)% with CH_4 at 0.4 atm,
- (10 ± 3)% with $\text{He} + 10\% \text{CH}_4$ at 1 atm.

The difference in sensitivity observed when the gas and the pressure were changed is correlated with the electric field applied. As we expected, the efficiency seems to increase with the electric field, which indicates that it comes essentially from the layer adsorbed on the BaF_2 crystal and not from the vapour. Some tests were made to verify this. First, we varied ℓ between 5 and 40 mm; the number of counts remained unchanged. If the EF vapour contributed strongly to the signal, the number of counts should increase linearly with ℓ . Another indication was given by reversing the field applied in the gap $\ell = 5$ mm. Under these conditions the number of counts decreased by a factor of close to 5. If the vapour gives a large contribution, the signal should drop by a factor of ~ 2 , because then the only sensitive volume of the detector is within the thickness of the chamber, which is equal to 6 mm. Major proof of the negligible contribution of EF vapour came from the cooling of the detector, under working conditions, from 27°C to 2°C . According to the EF vapour pressure (see fig. 1), the sensitivity, which must decrease linearly with it, should have dropped by more than one order of magnitude. We measured a decrease of only ~ 2 for the number of counts under these conditions. Taking into account the tests made at low pressure, all these experiments demonstrated clearly that the major contribution to the sensitivity indeed comes from the EF layer adsorbed on the BaF_2 crystal and not from the vapour.

The second important series of measurements made at atmospheric pressure concerned the stability of the layer when the gas mixture was flushed through the detector. The gas mixture, composed of helium and different concentrations of CH_4 , was bubbled through a bottle of liquid EF before reaching the SSPC. The detector and the bottle of EF were kept at room temperature. The efficiencies measured compared with those achieved with TMAE vapour at full light absorption were $\sim (15 \pm 2)\%$ with $\text{He} + 50\% \text{CH}_4$, $\sim (10 \pm 3)\%$ with $\text{He} + 10\% \text{CH}_4$. The stability in time was tested for several days, and no modification in the efficiency of the adsorbed EF layer within the above-mentioned interval of error was observed. In these measurements, the stability of the gas gain

was estimated to be $\sim 30\%$. We expect that the stability in the accuracy of this type of operation would essentially be disturbed by small variations in the outside pressure and the detector temperature. In future, this would be compensated by electronic regulation of the gain according to the high voltage applied in the chamber.

4. DISCUSSION AND CONCLUSION

Our investigation proves that EF can be used as a replacement for TMAE vapour as the photosensitive element in gaseous detectors, with three possibilities:

1) Under the condition of full light absorption, *EF vapour* has an efficiency comparable to that of TMAE vapour: our measurement showed it to be only $(67 \pm 5)\%$ of it. The EF vapour pressure is, however, much lower than that of TMAE. For practical applications, particularly for good time resolution compatible with high detection efficiency for VUV photons from BaF₂ emission, it is necessary to reach a higher temperature ($\sim 100^\circ\text{C}$ with EF compared with $40\text{--}50^\circ\text{C}$ with TMAE) in order to decrease the mean free path of VUV photons and obtain a thin absorption gap in SSPCs. A prototype chamber—a multistep parallel-plate avalanche chamber (PPAC) designed to work at high temperature ($\sim 100^\circ\text{C}$)—is under development. With large detectors, for example an electromagnetic (e.m.) calorimeter, it may be a technical challenge to use this type of SSPC. However, the disadvantage of higher temperature could be compensated by the good properties of non-interaction with air and with the standard materials used in the construction of the chambers, and by the simplicity of manipulating EF compared with TMAE. Ethyl ferrocene vapour may be an attractive alternative to TMAE where small-size detectors are commonly used, such as in positron-emission tomography (PET) [19, 20].

2) We have demonstrated the capability of *condensed layers of EF* deposited, as photocathodes, on a metallic cathode in a single-wire counter and on the surface of a BaF₂ crystal in an SSPC. The preliminary measurements of the quantum efficiency of the condensed layer of EF gave results comparable to those obtained with different substances, such as TMAE, in ref. [26]. When the layer was deposited on a BaF₂ crystal in an SSPC, we measured a sensitivity, at low pressure, of $\sim (10 \pm 3)\%$ of that obtained with TMAE vapour under the condition of full light absorption. The efficiency of liquid photocathodes in gaseous detectors usually increases according to the applied electric field [26]. This means that, at atmospheric pressure, a condensed layer of EF in an SSPC would reach even higher sensitivity. To verify this and to study the properties of liquid photocathodes, more extensive investigations will be necessary. With its property of non-interaction with air, EF used as a liquid photocathode in a gaseous detector should find a wide range of applications.

3) The third possibility studied was to use an *adsorbed layer of EF* as a photocathode for SSPCs. We discovered that an efficient layer of EF is adsorbed on the BaF₂ crystal in the SSPC when the detector is filled, at room temperature, with EF vapour. We found that the efficiency of this layer, for the BaF₂ component, is $\sim (10 \pm 3)\%$ of that of TMAE vapour (under the condition of full light absorption) at low pressure, and reaches $\sim (25 \pm 2)\%$ at a higher pressure. In large detectors (e.g. high-energy e.m. calorimeters) based on SSPCs—which are being considered for high-energy machines [30, 31]—the lower efficiency of the EF adsorbed layer compared to the vapour is not really a limitation. Again, the sensitivity of the EF photocathode depends on the electric field applied near the cathode (i.e. it increases with the electric field) and therefore on the type of gas mixture used and on the pressure. The stability of the layer seemed to be rather good, even when we flushed the gas mixture through the SSPC at atmospheric pressure.

For applications where the speed of the detector is an essential factor, it is interesting to detect only the signal that comes from the fast component (decay-time 600 ps) of BaF₂ emission, and not the one from the slow component (decay-time 620 ns). In fact, if the spectral efficiency cut-off of EF vapour is around 200 nm, the tail of efficiency between 200 and 280 nm observed for condensed

liquid EF (see fig. 7) can in principle show some sensitivity for the slow component of BaF₂ emission peaked at 310 nm. Unfortunately, we cannot estimate it correctly because we do not measure the quantum efficiency of a liquid EF layer for $\lambda < 200$ nm. If we assume that here the efficiency is constant, then, as a pessimistic estimate, the contribution of the slow component of BaF₂ emission is not more than 10% of the photoelectrons detected with our electronics (1 μ s integration time).

In SSPCs with TMAE vapour as the photosensitive element, it is necessary to work at a high temperature (40–50 °C) in order to decrease the thickness of the absorption gap. With an EF adsorbed layer at room temperature, a considerable fraction of all the photoelectrons is produced on the surface of the BaF₂. It is then possible to eliminate the conversion gap in the SSPC, which may allow more compact devices and better time resolution to be obtained because the jitter coming from the conversion position of VUV photons in this gap disappears. Without drift space in which to collect photoelectrons, a direct amplification could probably start at the surface of the crystal, and the detector would then work in parallel-plate avalanche mode.

The concept of the SSPC is based historically on the association of BaF₂ scintillators and low-pressure MWPCs. This type of chamber was used essentially for two reasons. First, low pressure allows minimization of direct ionization, which adds to the signal coming from the BaF₂ VUV light. The second reason is its good timing properties compared with those of MWPCs at atmospheric pressure; the SSPC achieves time resolutions that are two orders of magnitude better [18], and the positive-ion drift velocity is only a few microseconds for ~ 100 μ s at atmospheric pressure. In low-pressure MWPCs, this latter property leads to much less sensitivity to the space-charge effect produced by the drift of positive ions, which at high rates decreases the gain of the chambers. The PPACs at atmospheric pressure also have good timing properties—in particular, the drift-time of the positive ions could be only a few microseconds. Furthermore, with an adsorbed layer of EF as the photosensitive element in a PPAC, only photoelectrons produced near the crystal are detected because only the photoelectrons produced near the BaF₂ surface receive the total amplification. Then again, in the PPAC, only a small area close to the face of the crystal may be sensitive to direct ionization that would add to the signal coming from the photoelectrons produced in the layer. This means that even at atmospheric pressure, a gas mixture with a low sensitivity to direct ionization could give a negligible direct contribution from ionizing particles. For example, with a gas mixture based on helium, where approximately only eight ion pairs per centimetre are produced by minimum-ionizing particles (MIPs)—and assuming that a gas gap of only 1 mm after the crystal is the sensitive detection volume—the level of this contribution will be less than one electron per MIP crossing the SSPC. In BaF₂, the energy deposited by one MIP is ~ 6.5 MeV/cm. In one radiation length ($X_0 = 2.05$ cm), 13 MeV will be deposited, which may produce ~ 13 photoelectrons. (Under these conditions the efficiency of the EF adsorption layer is estimated to be one photoelectron per MeV deposited in BaF₂, while that of TMAE is 10 photoelectrons per MeV.) The contribution from direct ionization will be small (less than 10%) compared with the signal from the adsorbed layer.

Our observation shows that in single-wire counters working in the Geiger mode, the effect of ageing on the properties of EF is, at least, not worse than on TMAE (in the case of wire chambers [28]). In the case of PPACs, which in the future will be used with the adsorbed layer of EF as the photocathode, we expect the ageing effect to be even less noticeable because laterally the avalanches would be larger; this would reduce the local charge density, and the gas gain would be less disturbed by the non-uniformity on the mesh surface than would be the case with wire chambers.

If the ageing characteristics are really favourable, then the use of an adsorbed layer of EF at room temperature as the photosensitive element in PPACs at atmospheric pressure, may be a simple and attractive solution for calorimetry in high-energy physics, particularly compared with TMAE vapour and low-pressure MWPCs. However, further extensive research will be required.

Acknowledgements

This work is part of the research on BaF_2 calorimetry within the framework of the LAA project.

We thank Professor W. Schmidt for his contribution to discussions, and R. Bouclier, G. Million and I. Crotty for technical assistance.

We are indebted to G. Aleksandrov, of the Institute for Chemical Physics of the USSR Academy of Sciences, Moscow, for supplying us with our first samples of ethyl ferrocene.

We also wish to thank P. Müller and J. Pfyffer of the Organic Chemistry Laboratory, University of Geneva, who kindly synthesized for us more than 0.1 litre of ethyl ferrocene within a very short time.

REFERENCES

- [1] D.F. Anderson, IEEE Trans. Nucl. Sci. **NS-32** (1) (1985) 495.
- [2] J. Séguinot and T. Ypsilantis, Nucl. Instrum. Methods **142** (1977) 377.
- [3] G.D. Bogomolov, Yu.V. Dubrovskii and V.D. Peskov, Instr. Exp. Tech. **21** (1978) 779.
- [4] G. Charpak et al., Nucl. Instrum. Methods **164** (1979) 419.
- [5] V.D. Peskov, Instr. Exp. Tech. **23** (1980) 507.
- [6] V.D. Peskov, Proc. All-Union Conf. on Vacuum Ultraviolet, 'VUV-78', Leningrad, 1978 (Acad. Sci. USSR, Leningrad, 1978), p. 99.
- [7] A. Policarpo, Nucl. Instrum. Methods **153** (1978) 389.
- [8] G. Charpak, A. Policarpo and F. Sauli, IEEE Trans. Nucl. Sci. **NS-27** (1980) 212.
- [9] D.F. Anderson, Nucl. Instrum. Methods **178** (1980) 125.
- [10] D.F. Anderson, Phys. Lett. **118** (1982) 230.
- [11] D.F. Anderson, R. Bouclier, G. Charpak and S. Majewski, Nucl. Instrum. Methods **217** (1983) 217.
- [12] D.F. Anderson, G. Charpak, Ch. von Gagern and S. Majewski, Nucl. Instrum. Methods **225** (1984) 8.
- [13] M. Laval, M. Moszynski, R. Allemand, E. Cormorèche, P. Guinet, R. Odru and J. Vacher, Nucl. Instrum. Methods **206** (1983) 169.
- [14] P. Schotanus, C.W. van Eijk, R.W. Hollander and J. Pijpelink, Nucl. Instrum. Methods **A238** (1985) 564.
- [15] M. Suffert and G. Charpak, CERN EP Internal Report 86-03 (1986).
- [16] S. Majewski and D. Anderson, Nucl. Instrum. Methods **A241** (1985) 76.
- [17] A.J. Caffrey et al., IEEE Trans. Nucl. Sci. **NS-33** (1986) 230.
- [18] A. Breskin, Nucl. Instrum. Methods **196** (1982) 11.
- [19] P. Miné et al., IEEE Trans. Nucl. Sci. **NS-34** (1987) 458.
- [20] P. Miné et al., Nucl. Instrum. Methods **A269** (1988) 385.
- [21] R. Bouclier et al., Nucl. Instrum. Methods **A267** (1988) 69.
- [22] G. Melin, Handbuch der Anorganischen Chemie, Band 14, Teil A, Ferrocen 1 (Springer-Verlag, Heidelberg, 1974), p. 259.
- [23] R. Arnold et al., A ring-imaging Cherenkov detector: the DELPHI Barrel RICH prototype, to be published in Nucl. Instrum. Methods.
- [24] G. Charpak et al., Studies of light emission by continuously sensitive avalanche chambers, to be submitted to Nucl. Instrum. Methods.
- [25] G. Charpak, W. Dominik, V. Peskov and F. Sauli, Investigation of light emission from a parallel-plate avalanche chamber filled with noble gases, and with TEA, TMAE, and H₂O vapours at atmospheric pressure (in preparation).
- [26] V. Peskov et al., Nucl. Instrum. Methods **A269** (1988) 149.
- [27] R.A. Holroyd et al., Nucl. Instrum. Methods **261** (1987) 44.
- [28] C.L. Woody, IEEE Trans. Nucl. Sci. **NS-35** (1988) 493.
- [29] R.A. Holroyd, S. Ehrenson and J.M. Preses, J. Phys. Chem. **89** (1985) 4244.
- [30] A. Zichichi, in Report on the LAA project, 9 December 1986.
- [31] G. Anzivino et al., in Report on the LAA project, 25 June 1987.

Table 1
Efficiency of EF vapour (see text)
with 59 keV gammas from a ^{241}Am source

Detector	Temperature T_{EF} (°C)	Gap ℓ_{EF} (mm)	$N_{\text{TMAE}}/N_{\text{EF}}$
Single-wire	80	36	1.5 ^{a)}
SSPC	52	40	7 ^{b)}
	80	35	1.5 ^{b)}

a) with $\ell_{\text{TMAE}} = 36$ mm and $T_{\text{TMAE}} = 27$ °C

b) with $\ell_{\text{TMAE}} = 40$ mm and $T_{\text{TMAE}} = 30$ °C

Figure captions

- Fig. 1: EF vapour pressure as a function of temperature [22].
- Fig. 2: Light-to-charge ratio as a function of charge gain. 1) Argon + 50 Torr of TEA [24]; 2) argon + EF + 2 Torr of water vapour; 3) argon + 0.5 Torr of TMAE [24]; 4) argon + EF.
- Fig. 3: Set-up of the single-wire counter [26]. 1) Body of the counter; 2) anode wire; 3) CaF_2 window; 4) BaF_2 crystal; 5) lead collimator; 6) ^{241}Am gamma source; 7) cathode mesh; 8) ceramics; 9) cathode that can be cooled; ℓ is the absorption gap.
- Fig. 4: Set-up of the SSPC.
- Fig. 5: a) Estimated quantum efficiency of EF vapour as a function of wavelength. This result was obtained with a vapour pressure corresponding to the liquid at $T_{\text{EF}} \approx 70^\circ\text{C}$ and $\ell_{\text{EF}} = 16\text{ mm}$.
b) Comparison of the efficiency of EF and TMAE vapours for BaF_2 photon emission: 1) BaF_2 fast emission spectrum; 2) quantum efficiency of EF in the same conditions as in (a); 3) quantum efficiency of TMAE vapour for full light absorption [27].
- Fig. 6: Count rate measured in a BaF_2 counter (SSPC) filled with EF vapour, irradiated by 59 keV gammas from ^{241}Am , as a function of temperature and for different gaps: $\ell_{\text{EF}} = 35\text{ mm}$ (+); 25 mm ($\diamond$); 15 mm ($\square$); 10 mm (∇). Dashed line is TMAE vapour, $\ell_{\text{TMAE}} = 35\text{ mm}$.
- Fig. 7: Quantum efficiency measured with a single-wire counter [26]: 1) EF vapour, corresponding to the liquid EF, at $T_{\text{EF}} = 40^\circ\text{C}$ and $\ell_{\text{EF}} = 15\text{ mm}$; 2) thin layer of EF condensed on a copper cathode; 3) clean copper cathode.
- Fig. 8: Efficiency of the layer of condensed EF as a function of the time from the start of condensation, at constant temperature and gain.
- Fig. 9: Count rate measured in the SSPC irradiated by gammas from ^{60}Co for $\ell_{\text{EF}} = 5\text{ mm}$: $\bullet$ EF vapour (and probably adsorbed layer); * layer of condensed EF.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9