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On the track of the Will-O'-The-Wisp

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The will-o'-the-wisp [1 a-c] is a rare luminous phenomenon that can sometimes be seen at night, near the ground, in natural environments such as marshes or graveyards, and it consists of of a faint flame or flickering glowing fog. Its occurrence as a real event is fairly certain, and, although its spooky appearance may have given rise in the past to supernatural superstitions, its natural origin was later generally accepted.

Unless a will-o'-the wisp will be observed under proper condition, captured and/or chemically analyzed, its real nature will still remain the object of speculation.

It is often stated that the phenomenon originates from the spontaneous combustion of gases generated undeground by anaerobic fermentation processes. These gases consist mainly of methane and carbon dioxide (ca 30%). Small amounts of phosphine (PH_3) and diphosphine P_2H_4 (self-igniting on contact with the air) would act as a "chemical match" for the combustible methane.

Although this hypothesis is one century old , the presence of PH_3 in marsh gases had never been convincingly proven. If, however, the will-o'-the-wisp indeed is a hot flame, this conjecture might be correct.

A different hypothesis - not excluding the former, since two distinct phenomena might well coexist - is that the will-o'-the-wisp is a sort of *cold flame*, inconsistent with a normal combustion of methane, as reliable eye-witnesses have reported.

"Cool flames" can indeed been generated if vapours of suitable organic compounds like ethyl ether, come in contact with a hot surface kept at temperatures around 200-300 °C [2] . These luminescent pre-combustion haloes are sufficiently cool that a hand or a piece of paper can be put in them without being burned. The main objections to this interesting hypothesis are that the necessary vapours are not known components of marsh gases, and that the presence of surfaces at such high temperatures is difficult to admit in nature.

Thus, the cold *chemiluminescence* of some compound naturally occurring in marsh gases appears to be a more appealing explanation.

Recently, the presence of PH_3 in anaerobic fermentation processes has indeed been detected by reliable means [3 a,b]. The easy oxydation of lower alkyl phosphines in the presence of air is well known, and chemiluminescence can be easily observed in the dark when e.g. tri-buthyl phosphine is finely dispersed on an inert support like glass wool.

The chemiluminescence of PH_3 (the only naturally occurring term) is also known, but in laboratory environments it has appearently been little investigated. Most of the early researches concentrated on the explosion limits of this toxic gas, while recently its chemiluminescence has been studied at low pressures and/or high temperatures and/or by means of such oxidants as ozone, NO, etc. [4]

However, we reconsidered with this regard a century-old observation [5] in which PH_3, O_2 and an inert gas were fed, through three small nozzles, at the base of a vertical glass tube. By carefully adjusting the flow of the inlets, in the dark a faint flickering luminescence could be seen near the top of the tube due to the chemiluminescence of PH_3.

PH_3 can be generated as described elsewhere [6a-c] from non-toxic red P and KOH, from the thermal decomposition of phosphorous acid or from calcium phosphide and a diluted acid.

Our first equipment (Fig. 1 and Scheme 1) consisted of a 500 mL flat-bottomed glass Erlenmeyer flask in which we put a small amount of solid phosphorous acid (H_2PO_3). The flask was stoppered by a silicone septum through which a mixture of air and nitrogen, stored on water within a gas tank, could be fed by a needle. A second needle in the septum, connected to a long rubber tubing leading to the lab hood, provided for the necessary outlet. The flask was flushed with nitrogen, then it was put on a hot plate which was heated at ca 200 °C. The decomposition of phosphorous acid generated PH_3 *in situ* and a fog formed in the flask. When the air/nitrogen stream was fed into the phosphine vapours, a faint pale greenish light was clearly visible in the darkness. (Fig. 2)

Three experiments were run (Table 1) using different amounts of air and nitrogen. We are now planning to improve the design of this experimental demonstration by mixing the gases from three separated nozzles at measurable flow rates.

Table 1

Entry	g H_2PO_3	mL air	mL nitrogen	% O_2	notes
1	3	80	5600	0.3	
2	1	180	6150	0.61	
3	1.6	360	5320	1.42	brighter luminescence

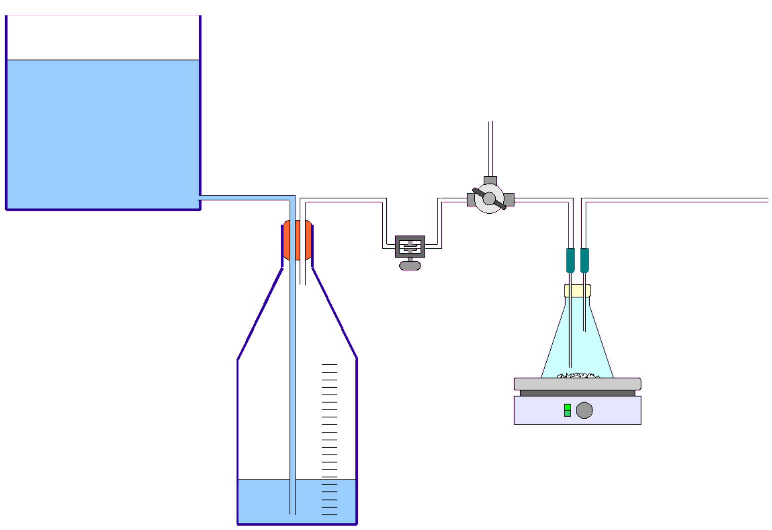
Mills [1b] reports, giving no experimental details, that injecting crude phosphine into a current of natural gas (i.e. $CH_4 + CO_2$) at a level insufficient to cause ignition produces a bright green luminescent "flame"; but there was plenty of smoke, a characteristic smell, and the color did not match what was expected, according to the eye-witnesses. We notice, however, that under different condition (relative and absolute amounts of the gases, temperature and humidity, etc.) smoke and smell could be not present; or even – if present - they might have gone unnoticed. Furthermore, under condition of feeble light, the human eye cannot easily discriminate between colours.
We therefore suppose that, as far as we know, the chemiluminescence of PH_3 might well be a likely explanation for this elusive phenomenon; given the right conditions, the suitable range of concentrations of the appropriate gases for which it takes could possibly be found also in nature, generating a will-o'-the-wisp.
Of course, this or other speculations could be confirmed or disproved by generating a chemiluminescent gas by biological fermentation processes, or - even better - by capturing a real will-o'-the-wisp.

In a second line of research, we reasoned that, if indeed PH_3 is involved in the generation of the will-o'-the wisp, there is no need for hunting it during the night. Will-o'-the wisp may occur even during the daytime, when its appearence will be invisible because of the stronger light. Also, PH_3 might be present in lower concentration than those required for the phenomenon to arise; nevertheless, its detection in the presence of decaying organic matter (most easily in cemeteries) might provide an indirect evidence of its involvement in the occurrence of will-o'-the-wisp.

Consequently, we are planning the monitoring of air samples from graveyards, marshes, etc. using a very sensitive PH_3 detector, a portable Draeger Xam-7000. [7 and Fig. 3]

The first few trials in the cemetry of Pavia, at night and during the day [Fig. 4], gave until now negative results; but the the hunting season is always open.

Fig 1



Scheme 1

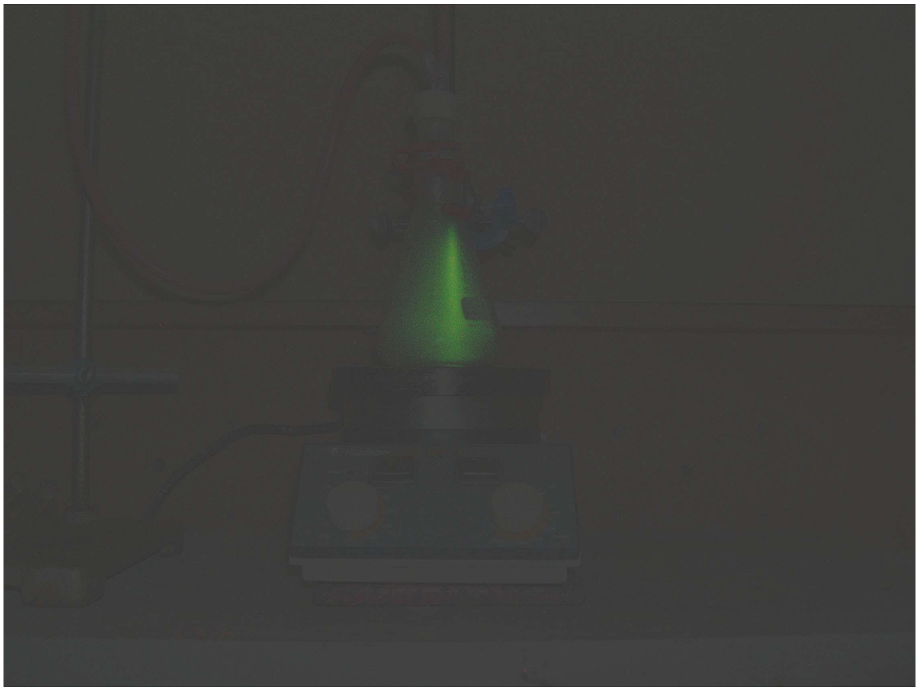


Fig. 2


DrägerSensors
Equipped with 3 electrochemical and 2 catalytic bead or infrared sensors
Alarm functions
360°all around visible and > 100 dB multitone audible alarm
Large display
Clearly structured, scratch resistant display with information in plain text
Robust enclosure
Rugged, waterproof with standard rubber-boot
Dräger
X-am 7000
OK

Fig 3

Fig. 4

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About the author:

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In 1975-76 he worked on organic synthesis as research assistant at the Politecnico di Milano. In 1976-77 he was Research Specialist on a U.S.A. grant at the School of Pharmacy of the University of Wisconsin (Madison, Wisconsin, U.S.A.). Here, he performed studies on the biosynthesis of nicotine and of the antibiotic brefeldin A. From 1977 to 1981 he was a R&D chemist with Farmoplant (Montedison) company, at the Centre for Pesticide Research (Milano), working on the synthesis of new pesticides active against the downy mildew (Plasmopara viticola). Montedison issued 4 patent applications for these compounds, one of which was developed, and is still traded as "Galben" (see Merck Index, 11. ed.). Since 1981 he became Researcher for Organic Chemistry, worked again at the Politecnico di Milano and in 1984 he returned to the Department of Organic Chemistry at the University of Pavia. Here, as a member of a team, he has been busy for many years with natural organic compounds, particularly with the extraction, purification an synthesis of terpenic compounds extracted from mushrooms (Basidiomycetes). From 1992 to 2001 he has taught a course of Chemistry of Natural Organic Compounds. His recent interests have been in the synthesis of fullerene derivatives in cooperation with the Department of Organic Chemistry at the University of Padua , and later in proton-conductive polymers for fuel cells. From 2001 to 2005 he was lecturer for a course of Organic Chemistry at the University S.Raffaele (Milan). He authored or co-authored about 50 papers and patens. Besides his official duty, Garlaschelli is since several years interested in paranormal phenomena, scientific anomalies, pseudoscience and mysteries. Since 1991 he is fellow of CICAP (Comitato Italiano per il Controllo delle Affermazioni sul Paranormale, Italian Committee for the Investigations of the Claims of the Paranormal), where he is in charge of the experimental works. The results of some of his investigations were printed on international journals dealing with parapsychology and the paranormal, as well as on chemistry journals. He has been co-relator of two graduation works at the Department of General Psychology at the University of Padua: one on the perceptive illusion of the "Spook Hills", the other on the near- death experiences. Consistently with the aims of CICAP, he is concerned with the popularization of science and of the scientific and rational method. He appeared countless times in national and foreign TV services, and gives very often lectures on these topics in high schools and Universities. He writes for CICAP's magazine, and has published several articles on other magazines as well. He was a columnist for “La Chimica e l'Industria”, the magazine of the Società Chimica Italiana, with his page “Chimica e misteri” (“Chemistry and mysteries”). As an amateur magician he gave a few lectures for the local groups of Circolo Magico Italiano (Italian Magic Club), on 'chemical magic' and 'fakirs performances'. He authored several books: “I Segreti dei fachiri” and “Investigatori dell’occulto” (with Massimo Polidoro), “Rabdomanzia” (with Andrea Albini), “Processo alla Sindone”.(Avverbi Ed), and the mystery “Corpi di pietra” (Neftasia Ed.). In 2009 he has been the editor of the Quaderno Cicap n°10 (“Indagatori del Mistero”) and Quaderno Cicap n°11 (“In cerca di miracoli”) and in 2011 he has been the editor of the volume “LOURDES - I dossier sconosciuti” (Italian university Press). In dicember 2009 he was nominated Fellow of the C.S.I. (Center for Skeptical Inquiry).

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