In an attempt to cross the Daugava River close to Riga on early morning July 19th 1701, King Charles XII of Sweden had his men set fire to a few dinghies filled with manure and straw. The evolving smoke nicely blended with the natural fog typical for an early morning on a river and allowed half the division to cross the water before being spotted by the Polish-Saxon forces emplaced at the East bank. Though this is surely not the first military use of smoke it is quite accurately passed on historic account of a combined deception and camouflage operation which allowed a small force to successfully take a superior force by surprise [1].

Until the end of the 19th century, military smoke compositions were exclusively based on sulphur-rich black powder, which sometimes was blended for slower burning rate with high boiling hydrocarbons such as pitch and various wood resins. However, not very much attention was payed to the chemistry and the mode of action of smokes until the naval forces by beginning of the 20th century realized a general need to conceal their large vessels. In Germany, for that purpose both oleum (solution of SO\(_3\) in H\(_2\)SO\(_4\)) and chlorosulphonic acid (HSO\(_3\)Cl) were investigated while US and British Navy investigated using “funnel smoke” that is the vaporization (white) and incomplete combustion (black) of the ships fuel oil [2].

In the lead up of the looming war, the systematic and forced exploitation of science for warfare began. It was also the time when the uneven footage between new toxic chemicals and protective countermeasures began.

As the French forces lacked enlisted personnel with detailed knowledge in chemistry, the chemical laboratory of the artillery in Versailles near Paris appointed Ernest-Édouard-Frédéric Berger (Fig. 1) as a civilian chemist in 1908 [3]. Later during World War I (1914–1918) he was assigned the rank of a captain and was in charge of explosives and propellants.

Berger had a good overview of the chemical research going on in France and was in contact with key people at that time such as the Nobel Prize laureate Victor Grignard (1871–1935) or Camille Matignon (1867–1934) a famous specialist in thermochemistry.

Matignon - possibly inspired by Vautin’s and Goldschmidt’s work on the aluminothermic reduction of metal oxides [4] - tried to prepare aluminium carbide (Al\(_4\)C\(_3\)), which was then thought a source of methane. For this purpose, he mixed hexachlorobenzene with aluminium [5]. When heated sufficiently the mixture becomes red hot to give the carbide and aluminium chloride, which due to its high volatility emanates as a dense smoke. Matignon already noted the thick fumes in his first paper [5a].

\[
10 \text{Al} + C_6\text{Cl}_6 \rightarrow 2 \text{AlCl}_3(\text{g}) + 2 \text{Al}_4\text{C}_3(\text{s}) \tag{1}
\]

Berger recognized this type of reaction, which he later referred to clearly [6] as a fundamental principle to generate metal chlorides smokes and consequently expanded this by using other metals and metallic fuels such as zinc and calcium silicide and by varying the chlorine source including even inorganic chlorides such as FeCl\(_3\) and SbCl\(_5\) and finally hexachloroethane (C\(_2\)Cl\(_6\), HC), which would later become

Figure 1. Ernest-Édouard-Frédéric Berger (1876–1934)

[a] E.-C. Koch
Lutradyn- Energetic Materials Science & Technology.
Kaiserslautern, Germany
e-mail: e-c.koch@lutradyn.com
synonymous with any obscurant mixtures of that type. The French naval forces adopted his formulations to protect their vessels earning him the “Grand Prix de la Marine” in 1918.

However one would belittle Berger’s achievement for pyrotechnics and obscurants in particular if one would stop telling the story right here. It is less known but fortunately precisely documented in the reports of the French Academy of Science that Berger also applied the aluminothermic principle to other reactive systems [8]. He, therefore, coined the French term “reactions arrondies” to describe reactions between solids that require initial high heating. Today, these reactions are commonly referred to as Self Propagating High Temperature Synthesis (SHS) reactions [9].

Berger found that boron phosphate (BPO₄) can be reduced with aluminium to give fumes which upon contact with air give intense yellow flame and thick smoke indicative of combustion of thermally excited BP, the latter one is a fuel that was theoretically investigated recently as a replacement for red phosphorus (P₃) [10].

3 BPO₄ + 8 Al → 4 Al₂O₃(s) + 3 BP₃(g) (2)

Mixtures of P₃ with nitrates are quite sensitive and prone to accidental explosions Berger introduced calcium sulphate as an oxidizer that smoothly reacts with P₃ according to

5 CaSO₄ + 8 P₃ → 5 CaS(s) + 2 P₅O₁₀(s) (3)

He also found that the amount of phosphorus could be increased up to three – four times the amount given in Eq. (3) to volatize surplus phosphorus. This composition should then become the basis for naval float and smoke markers for the next 60 years [11].

Berger was also the first to recognize the superior exothermicity available with fluorides as oxidizers. He prepared silicon tetrafluoride, SiF₄, and boron trifluoride, BF₃, by the following reactions.

2 PbF₂ + Si → SiF₄(g) + 2 Pb(g) (4)

B₂O₃ + 2 Al + 3 PbF₂ → 2 BF₃(g) + Al₂O₃(s) + 3 Pb(g) (5)

Generating SiF₄ and BF₃ as reaction products, Berger was not so much aiming at using these highly hydrolysable gases to produce smoke but rather to exploit their antiseptic behaviour to kill common germs in quarters. If we consequently develop Berger’s idea this was the first pyrotechnic attempt to fight biological warfare agents and so we can assign Berger with the basic idea for energetic materials in use as agent defeat weapons (ADW) [12]. Among other research he also investigated the self-ignition (hypergolic action) upon contacting calcium silicide with alkali bifluorides (MHF₃, with M=Na, K, etc.).

Unfortunately, we don’t know much about Berger’s activities after the war though it’s reported that he applied for a professor’s position in 1922 at the École Polytechnique de Palaiseau [13].

As the Berger smoke mixture was very successful it also triggered numerous refinements over the decades.

One of the early modifications stems from Gowdy and concerns the replacement of zinc by magnesium and the addition of an aromatic hydrocarbon as a combined coolant and aerosol [14]. While these mixtures were initially patented for making black signalling smoke, later in the 20th century, it was recognized that they also are very effective in blocking infrared rays [15].

As zinc is prone to be attacked by moisture but aluminium or titanium are not, common variants of Berger’s smoke mixture use Al/ZnO and Ti/ZnO for in-situ generation of Zn [2].

The main aerosol forming species in HC smokes is ZnCl₂ which due to its high negative enthalpy of solvation is highly deliquescent and is able to condense moisture already at low relative humidity. However, the solutions formed contain acidic species and hence are heavily corrosive and even dissolve organic tissue. In the same way, inhalation of HC smoke effects severe lung injury and can cause fatalities [16]. To overcome these issues Krone developed a modified composition codenamed NT-smoke, containing ammonium salts to effect complexation of ZnCl₂ [17]. The resulting complexes such as Zn(NH₄)₂Cl₂·H₂O indeed have near neutral pH but still decompose when in contact with the mucous membranes [18].

While replacement of zinc by magnesium circumvents the formation of acidic species in the aerosol the reductive elimination of the halocarbon still yields extensive amounts of particulate carbon that can be contaminated with mutagenic chloro-organic compounds [19]. To avoid the formation of carbon in general, a disclosure therefore teaches the use of Mg/MgO [20].

Other modifications of Berger’s mixture saw the partial [21] and complete replacement of organochlorine compounds with fluorocarbons such as polytetrafluoroethylene [22] and graphite fluoride the latter yielding an aerosol capable to screen in the visual, infrared and millimetric wavelength range [23].

Berger was a true pioneer of pyrotechnics [8], and hence his name remains inseparably tied to the field and in particular to the invention of a paramount military smoke mixture.
References


[13] Files at the Bibliothèque de l’École Polytechnique Palaiseau contain a letter of application of E. Berger though the outcome of his application is not documented. I gratefully acknowledge M. Olivier Azolla (*École Polytechnique Palaiseau*) and M. Patrice Bret (CEHD) for providing facsimile of E. Berger’s picture and this letter.


