

What were the difficulties in the preparation of fluorine? Explain how these difficulties were overcome

In 1810, French physicist André-Marie Ampère suggested that hydrofluoric acid was a compound of hydrogen with an unknown element, analogous to chlorine. Fluorite was then shown to be mostly composed of calcium fluoride. Progress in isolating the element was slowed by the exceptional dangers of generating fluorine: several 19th century experimenters, the "fluorine martyrs", were killed or blinded. Davy, as well as the notable French chemists Joseph Louis Gay-Lussac and Louis Jacques Thénard, experienced severe pains from inhaling hydrogen fluoride gas.

The isolation of this new element continued to occupy many researchers for most of the nineteenth century. A first step was the preparation of pure water-free hydrofluoric acid by L.J. Thénard (1777-1857) and L. J. Gay-Lussac (1778-1850). Their product fumed strongly in air, rapidly dissolved glass and caused extraordinary burns if it entered into contact with the skin - a phenomenon the authors described in great detail. Later on, J. J. Berzelius (1779-1848) characterised ammonium fluoride. Other researchers paid a high price to the even more toxic effects of this element, without for so much succeeding in isolating the element: G. and T. Knox were severely intoxicated and the Belgium chemist P. Louyet lost his life. Meanwhile, J. C. Marignac (1817-1894) described in minute detail around 1860, the preparation and crystal morphology of a good number of anhydrous or hydrated fluorosalts, such as fluorotitanates or fluorozirconates, and most of his accurate conclusions are still valid today. Many new inorganic fluorides were also characterised by scientists such as H. Sainte-Claire Deville (1818-1881) or E. Frémy (1814-1894). Nevertheless it seemed almost impossible to synthesise fluorine, despite numerous attempts carried out during the latter part of the century. An important step was made by Frémy, Moissan's first mentor, when he succeeded in preparing pure, anhydrous HF and also KHF_2 , so-called Frémy's salt, expressed "KFl.HFl" using the notations of that time. Frémy had come very close to finding the solution by electrolysing anhydrous HF, molten calcium fluoride or potassium fluoride, but he seemed not to have had the idea of replacing these compounds by KHF_2 , perhaps because of the high melting point of the compound, $T_f = 293^\circ\text{C}$, which would have led to insurmountable technical difficulties.

Finally, on June 1886, the French chemist Henri Moissan (1852-1907), a former student of Frémy, succeeded in isolating fluorine gas. His genius laid in his idea of turning the bath into a conductor by adding a molten fluoride potassium salt, KHF_2 . Indeed pure hydrogen fluoride, HF, could not suffice as its capacity as an electric conductor was too weak. Henri Moissan devised a platinum electrolyser and lowered the reaction temperature of the electrolytic solution of HF + KHF_2 to limit corrosion. The platinum electrolyser was U-shaped and was stopped with fluorine stoppers, CaF_2 . The cathode and the anode were made of irradiated platinum to provide better resistance to the fluorine. The traces of hydrogen fluoride were condensed at the end of the apparatus in a low temperature trap and also by sodium fluoride. On 28th June 1886, a gaseous product was identified at the anode of the electrolyser - the fluorine (F_2) had been successfully isolated, thus resolving one of the most difficult challenges in the realm of inorganic chemistry.

More information on the web-site: <http://zafira.univ-lemans.fr/LABO/reseau-fluor/en/angdomaines-d-application/histoire-du-fluor>

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