Review

Pioneering beginnings of fluorine chemistry research at the Jožef Stefan Institute[1]

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Dedicated to the memory of Prof. Dr. Boris Žemva

Abstract

The article presents a historical personal account of the pioneering development of fluorine chemistry at the Jožef Stefan Institute in Ljubljana. The origins of this research date back to the early 1950s, when the Department of Fuel and UF_6 was established. Early work included the development of electrolytic cells for the production of elemental fluorine and the synthesis of fluorine-containing compounds under challenging laboratory conditions. In the early 1960s, the group successfully synthesized XeF_4 and XeF_6, contributing to the emerging field of noble-gas chemistry. Subsequent research expanded to photochemical fluorination reactions and to the synthesis and characterization of numerous complex fluorides. The article highlights the scientific achievements of the group, the development of specialized experimental equipment, and the role of international collaboration in establishing the Jožef Stefan Institute as an internationally recognized center for fluorine chemistry.

The Jožef Stefan Physics Institute was founded in 1949 as the successor to the former Slovenian Academy of Sciences and Arts Institute of Physics. Its principal mission was research related to the peaceful use of nuclear energy. The Institute moved into a new building on Jamova Street in 1952, and already the following year the Department of Fuel and UF_6 was established. Its objectives were twofold: on the one hand, research and development of nuclear fuel based on pure uranium dioxide, and on the other, the development of methods for producing uranium hexafluoride. The history and development of this department as one of the chemical laboratories of the Jožef Stefan Institute (JSI) can today, many decades after its establishment, be reconstructed only fragmentarily; unfortunately, much of its early activity has been lost to oblivion.

The department was initially led by Branko Brčić, Professor of Inorganic Chemistry at the University of Ljubljana. It comprised two large and, for the time, very modern laboratories: one devoted to research on nuclear fuel based on uranium dioxide, and the other to research on the production of uranium hexafluoride.

In 1953, Jože Slivnik (Figure 1) joined the department with the task of developing an electrolytic cell for the production of elemental fluorine, which was required for the preparation of uranium hexafluoride. Today it is difficult to imagine the research equipment available at that time. In the 1950s, scientific equipment from abroad was extremely difficult to obtain. Researchers were largely dependent on their own ingenuity and inventiveness. Fortunately, the Institute had well-equipped workshops, and with the invaluable assistance of skilled technicians it was possible to fabricate many devices that today would simply be purchased on the market. For example, laboratory tube furnaces, were designed and built in-house, while voltage or temperature regulation was still carried out manually using variable autotransformers ("Variacs"), initially imported and later manufactured domestically by Iskra company.

The pioneering work began with the construction of distillation apparatus for the preparation of anhydrous hydrogen fluoride, which at that time could not be imported

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Figure 1. Jože Slivnik at work with a glass vacuum system in the fluorine laboratory.

and constituted the principal component of the electrolyte KHF_2 used for fluorine production. Simultaneously, research commenced on the construction and development of a suitable electrolytic cell. Initially, a von Wartenberg-type cell was built according to literature data, serving primarily to gain initial experience in handling fluorine. Based on this design, a larger electrolytic cell with nickel anodes was constructed; however, it proved unsuitable for experiments requiring small quantities of fluorine. If left unused for some time, the electrolyte absorbed moisture, leading to explosions upon each restart. A smaller 20-A cell with nickel electrodes was subsequently developed for the production of smaller quantities of fluorine. This cell produced sufficient fluorine for the first synthesis of uranium hexafluoride. Nevertheless, it also caused difficulties if the electrolyte was not completely dry, occasionally resulting in explosions. An additional problem was its relatively low mass: a stronger explosion could lift the lid with the anodes. On one occasion, the explosion was so violent that the cell lid, together with the attached glass apparatus for uranium hexafluoride synthesis, was hurled into the ceiling of the fume hood. Furthermore, nickel anodes significantly contaminated the electrolyte with nickel fluoride formed during electrolysis. Despite these difficulties, the JSI researchers succeeded in preparing the first small quantities of uranium hexafluoride.

Glass apparatus for the laboratory synthesis of bromine trifluoride was also constructed, and the first quantities of this compound were prepared.[1]

Through these syntheses, the JSI researchers gained their first experience in working with moisture-sensitive substances. In 1957, Bogdan Volavšek joined the group and devoted himself to work with such materials. For this purpose, he constructed a glass vacuum system that enabled work under high vacuum, which is essential for the isolation of moisture-sensitive compounds. He also investigated the magnetic properties of fluorides and converted a highly sensitive standard Mettler balance into a magnetic balance suitable for measuring magnetic susceptibilities.

In 1958, Jože Slivnik, previously the operational head, assumed leadership of the department, which was expanded with new coworkers.

In 1959, Boris Frlec (Figure 2) joined the department and initially focused on the calciothermic reduction of uranium tetrafluoride to metallic uranium. He constructed a suitable reactor lined with calcium fluoride, containing a mixture of uranium tetrafluoride and metallic calcium shavings. After evacuation to remove residual moisture, the reactor was heated to initiate the reaction. Molten metallic uranium collected at the tapered bottom, where it solidified into a small metal rod. Frlec also developed apparatus for converting uranium dioxide with halogen fluorides, such as bromine trifluoride, into volatile fluorides. This equipment served as a model for the processing of spent nuclear fuel and separation of higher fluorides by distillation. To measure the pressure of elemental fluorine and highly corrosive higher fluorides, he developed a membrane pressure transmitter enabling measurements with conventional manometers.

Figure 2. The authors of the article, Andrej Šmalc (left) and Boris Frlec (right), in the laboratory in front of a metal high-vacuum system for work with volatile fluorides.

In 1960, Andrej Šmalc (Figure 2) joined the department and undertook the development of a larger 120-A electrolytic cell (Figure 3). Due to earlier problems with non-sealed cells, the new cell was more robust and featured a sealed lid to prevent electrolyte moisture uptake during downtime. The electrolyte consisted of a melt with approximate composition KF·2HF at 110–120 °C. The cell was equipped with electrical heaters for preheating, while during operation the temperature was maintained by ohmic heating. Nickel anodes were replaced by carbon electrodes, as they were more suitable for high currents and did not contaminate the electrolyte.

The maximum capacity of the cell was approximately 120 L of gaseous fluorine per hour, necessitating fluorine storage. Since each cell startup involved difficulties in re-

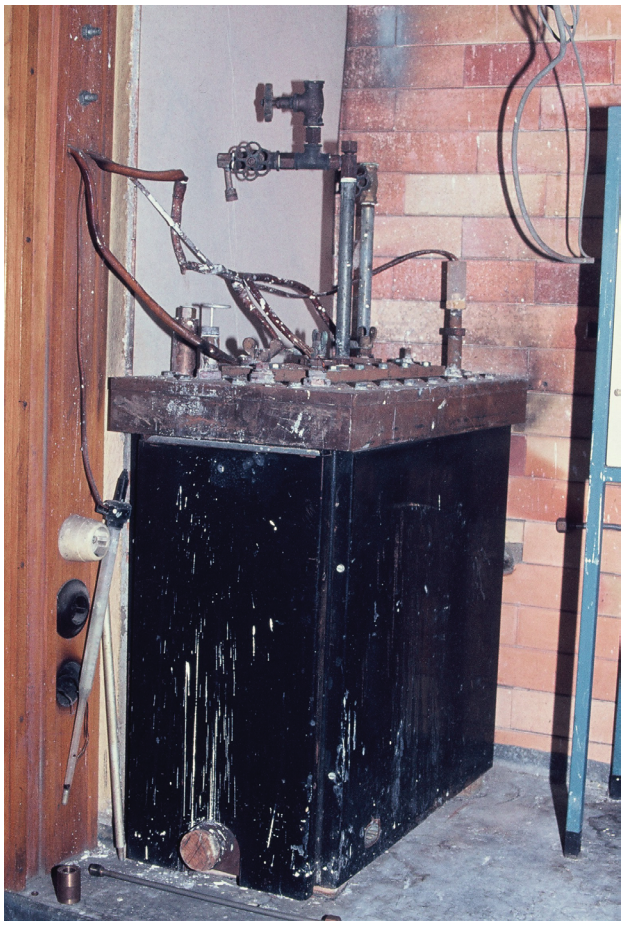

Figure 3. 120-A electrolytic cell for fluorine production in the fluorine laboratory.

moving residual moisture from the electrolyte regenerated with anhydrous HF, it was considered advantageous to liquefy fluorine at –196 °C and store it in cylinders, ensuring ready availability. The principal challenge was the low vapor pressure of fluorine at liquid nitrogen temperature (~400 mbar), which could draw molten electrolyte into the outlet line, where it would freeze and cause blockage. To address this, a glass contact manometer was designed using fluorine-resistant halocarbon oil as the barrier liquid and concentrated sulfuric acid to establish electrical contact. This device controlled a magnetic valve within ±10 mm water column pressure, admitting only as much fluorine as produced by the cell. Pressure deviations triggered an alarm. Once a vessel was filled, fluorine flow was diverted to a second vessel cooled to –196 °C, while the first was connected to a steel cylinder and slowly warmed to room temperature. Fluorine pressures in the cylinders did not exceed 30 bar. Modified 10-L oxygen cylinders equipped with stainless-steel valves and PTFE seals, passivated with fluorine, were used for storage (Figure 4).

Later, when helium became commercially available, the contact manometer and magnetic valve were replaced by a helium buffer reservoir at the end of the liquefaction

Figure 4. Fluorine dosing system in the fluorine laboratory; the electrolytic cell is shown at the far left.

apparatus, since helium neither liquefies nor dissolves in liquid fluorine.

Through work with fluorine cylinder filling, the JSI researchers gained experience handling pressurized fluorine. In 1962, Neil Bartlett published the synthesis of the first true noble-gas compound, xenon hexafluoridoplat-

Figure 5. Nickel reaction vessel ("*nikljenica*"), in which xenon tetrafluoride was synthesized in 1962—the first noble-gas compound prepared in what was then Yugoslavia.

inate, $XePtF_6$.[2] In the same year, American researchers reported the synthesis of the first binary noble-gas compound, xenon tetrafluoride, prepared at 400 °C and 4 bar.[3] The publication of the synthesis of xenon tetrafluoride naturally stimulated other suitably equipped research groups to undertake investigations in this entirely new field—the chemistry of noble gases.

Given their experience with pressurized fluorine, the Ljubljana group, at Slivnik's initiative, repeated the synthesis of XeF_4 in the same year,[4] using a 700 mL nickel vessel (Figure 5) under identical conditions to those described by the American researchers. The experiment was conducted overnight as a precaution. Once the reaction vessel was placed in the furnace, tension eased; notably, Volavšek went to the Figovec tavern and returned with sausages to sustain the team during the wait.

It should also be noted that relations among the members of the laboratory were always genuine, and for this reason the work was undertaken with pleasure and enthusiasm. An indispensable contribution to this atmosphere was made by Jože Slivnik, with his good-natured, though somewhat complex and at times controversial, personality. He was firmly convinced that intuition is essential in research and that reliance solely on the experiences of others leads to indoctrination that stifles creativity. At the same time, he infused his surroundings with what appeared to be inexhaustible energy.

After completion of the synthesis, Volavšek isolated colorless XeF_4 crystals using the vacuum system. Mass spectrometry indicated traces of a higher xenon fluoride, prompting repetition of the synthesis with a larger excess of fluorine at pressures up to 250 bar. For measuring the pressure of the reaction mixture, the JSI researchers replaced the pressure transmitter with a relatively rigid nickel diaphragm by a newly developed transmitter employing a tombac bellows as the elastic element. This device was more compact and, moreover, had a smaller influence on measurement accuracy. Pressure measurements during the reaction showed that the reaction was complete at 320 °C; the calculated fluorine consumption, within the limits of experimental error, indicated the formation of xenon hexafluoride, XeF_6, which was also confirmed by chemical analysis. The synthesis was published in January 1963,[5] simultaneously with two reports on XeF_6 from American laboratories.[6,7]

The synthesis of xenon hexafluoride at the Jožef Stefan Institute was in fact the result of an international competition in this field, which, of course, did not end with this discovery. The Ljubljana group, as well as several others, hypothesized that a xenon octafluoride might also exist. Considerable effort was invested in the search for this compound before it became clear that it does not exist; however, this pursuit opened up a broad field of complex fluorides. It should be emphasized that the fluorine chemistry group at the Jožef Stefan Institute, which until then had been a completely unknown research group in this field, attracted the interest of numerous established research centers worldwide, so that after just over a decade, in 1972, the organization of the 4th European Symposium on Fluorine Chemistry was entrusted to Slovenian researchers.

Due to the increasing scope of research activities, the Department of Fuel and UF_6 was divided in 1965 into the Department of Fluorine Chemistry (K-1), headed by Jože Slivnik, and the Department of Ceramics (K-5), headed by Drago Kolar. The Department of Fluorine Chemistry moved into newly renovated premises that had previously housed research on heavy-water electrolysis, which had by then been discontinued, while the Department of Ceramics expanded into the entire area formerly occupied by the Department of Fuel and UF_6.

In subsequent work involving high-pressure syntheses with elemental fluorine, the original massive reaction vessels machined from solid nickel rods were replaced by lightweight pressure reactors fabricated from nickel tubes with a diameter of 50 mm, fitted with a welded domed bottom and a top made of nickel sheet. The principal advantage of these vessels was the substantially reduced consumption of liquid nitrogen required for cooling during fluorine liquefaction, as well as the markedly shorter times needed to cool the vessels to –196 °C or to rewarm them to room temperature.

High-pressure syntheses were carried out in reaction vessels with a volume of 235 cm^3, charged with a weighed amount of the appropriate reactant, onto which a measured quantity of fluorine was subsequently condensed. The course of the reactions was monitored by measuring pressure and temperature. For experiments whose behavior could not be predicted in advance, a furnace equipped with an aluminum block and a thermocouple was used; this furnace was installed underground outside the laboratory. The reaction vessel containing the reactants, cooled with liquid nitrogen, was lowered into the preheated furnace using a pulley system operated from inside the laboratory. This safety measure proved justified (Figure 6), as

Figure 6. This also happened occasionally—consequences of an explosion in a small fume hood of the fluorine laboratory.

an attempt to react diarsenic trioxide with fluorine under pressure resulted in an explosive reaction, during which the explosion hurled the reaction vessel several tens of meters into the air, where it eventually landed on the roof of a nearby storage shed.

By high-pressure synthesis from the elements, the hexafluorides of tungsten, rhenium, osmium, iridium, and platinum were prepared. A major advantage of high-pressure synthesis of higher fluorides, which are highly sensitive to traces of moisture, lies in the fact that the reactions proceed in a closed system. As a result, isolation of the reaction products by sublimation under vacuum is straightforward, since contact with atmospheric moisture is avoided.

Once fluorine production no longer posed any difficulties (Figure 7), it became possible to obtain larger quantities of uranium hexafluoride for studies on the preparation of metallic uranium by direct reduction of uranium hexafluoride with calcium. For this reaction, a reactor lined with calcium fluoride was constructed, containing calcium in the form of shavings. Attached to it was a vessel containing uranium hexafluoride, surrounded by a steam-heated coil to keep the compound molten. The liquid uranium hexafluoride was then rapidly introduced into the heated reactor in a single stream. The resulting molten uranium collected in the narrowed lower section of the reactor and was, after cooling, removed in the form of a metallic rod.

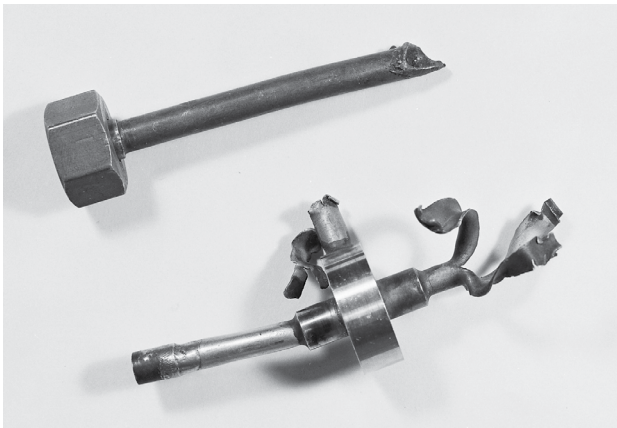

Figure 7. Copper tubing ignited due to an organic impurity (paraffin oil from a damaged pressure transmitter); during the explosion, the T-joint "blossomed" open—the cause was the same as in the previous case, but at a higher fluorine pressure.

The laboratory equipment steadily improved, aided significantly by international collaborations. The head of the department, Slivnik, possessed the valuable quality of encouraging his coworkers and enabling their personal development. An important part of this development consisted of postdoctoral training in foreign laboratories. Thus, Bogdan Volavšek worked in 1955 in Germany at the University of Münster with Prof. Wilhelm Klemm; Boris Frlec spent the years 1965–1967 at Argonne National Laboratory in the United States; Andrej Šmalc worked in 1968 and 1969 at the University of Göttingen in Germany with Prof. Oskar Glemser; and Boris Žemva undertook postdoctoral training in 1972 at the University of California, Berkeley, with Prof. Neil Bartlett. Each of these researchers returned not only with specialized personal expertise, but also with new methods, approaches, and a broad network of international scientific contacts. Over time, the group evolved into one of the internationally recognized research centers in the field of fluorine chemistry.

From his work at Argonne National Laboratory in the United States, Frlec brought the technique for fabricating reaction vessels from the fluoropolymer Kel-F (polychlorotrifluoroethylene), as well as the associated handling methods, which enabled the use of equipment made from this material. Kel-F enabled work in anhydrous hydrogen fluoride, and reaction vessels fabricated from this polymer allowed visual observation of reactions during their course. These vessels—more accurately described as test tubes—were manufactured from commercially available tubing, while the valves were machined from solid Kel-F plates. Later reaction vessels were made from the fluoropolymer FEP (a copolymer of tetrafluoroethylene and hexafluoropropylene), which had the advantage over Kel-F of containing no chlorine and exhibiting greater chemical resistance.

Frlec upgraded the existing glass vacuum system with a metal vacuum system (Figure 8). This enabled work with elemental fluorine, gaseous aggressive higher

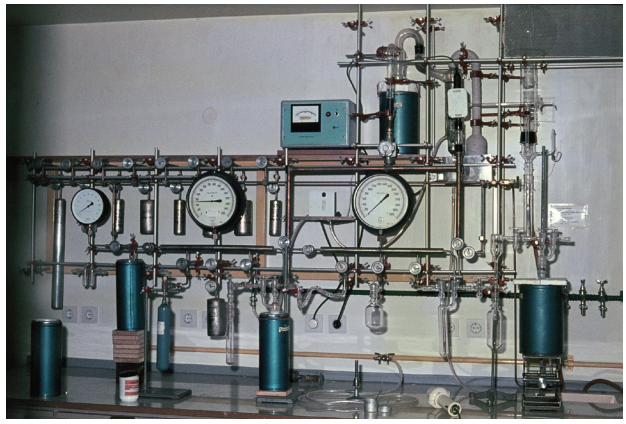

Figure 8. Metal vacuum system for work with volatile fluorides.

fluorides, and anhydrous hydrogen fluoride as a solvent. It also allowed straightforward isolation of volatile reaction products and their preparation for identification and characterization. In this context, studies on the reaction between hydrazinium(2+) fluoride and uranium hexafluoride in anhydrous hydrogen fluoride as the solvent should be mentioned; these led to the isolation of a new complex compound containing pentavalent uranium—hydrazinium(2+) heptafluoridouranate, $N_2H_6UF_7$.[8] Compounds of this type and their derivatives, hydrazinium fluoridometallates, later became the subject of numerous investigations by the K-1 research group.

In the Institute's workshops, a glovebox for working with moisture-sensitive substances was also constructed according to designs prepared by the JSI researchers, representing an important addition to the available equipment. At that time, due to general difficulties with imports and additional export restrictions imposed by foreign manufacturers on strategic materials, the group was compelled to develop certain pieces of equipment independently. These included electrolytic cells for fluorine production, valves, pressure transmitters, cells for recording IR spectra of reaction products, precise absolute manometers for measuring the pressure of fluorine and gaseous aggressive fluorides on vacuum systems, and related devices. This equipment, which was gradually improved by the JSI researchers themselves, was also essential for studies on the calciothermic reduction of uranium hexafluoride. These investigations still formed part of the broader research program related to nuclear fuel development, which was discontinued in subsequent years.

In collaboration with the physicist the late Borut Lavrenčič, a Raman spectrometer was constructed, enabling the recording of spectra of reaction products directly in reaction vessels made of Kel-F or FEP.

During his stay in Göttingen, Šmalc investigated the synthesis of tribromine hexafluoridoarsenate, Br_3AsF_6,[9] as the first isolated compound containing the tribromine cation, as well as the use of dioxygenyl hexafluoridoarsenate, O_2AsF_6, as a powerful oxidizing agent, for example in the synthesis of peroxydisulfuryl difluoride, $S_2O_6F_2$.[10]

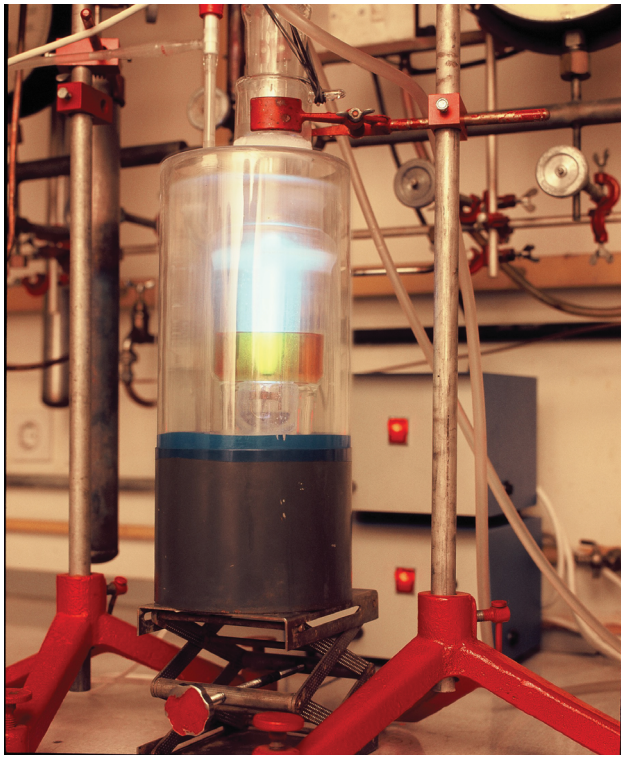

Figure 9. Glass reactor for UV photochemical reactions in liquefied fluorine at –196 °C.

At the Jožef Stefan Institute, he continued his research on compounds containing halogen cations, including the synthesis of dibromine hexafluoridoarsenate in the Br_2–BrF_3–AsF_5 system.

In the 1970s, the group expanded its research to photochemical syntheses involving elemental fluorine,[11] such as the photosynthesis of xenon fluorides,[12,13] uranium hexafluoride,[14] and chlorine pentafluoride.[15] The course of the photochemical synthesis of dioxygenyl hexafluoridoarsenate was also investigated in the O_2–F_2–AsF_5, OF_2–AsF_5, and OF_2–O_2–AsF_5 systems.[16]

During this period, a glass reactor for photochemical reactions with liquefied fluorine (Figure 9) was designed and constructed, and the photosynthesis of dioxygen difluoride was tested in a liquefied mixture of fluorine and oxygen.[17] On this basis, a process for the purification of elemental fluorine was developed and patented in 1975.

In 1975, the photochemical synthesis of krypton difluoride was achieved by irradiating a mixture of liquefied fluorine and solid krypton at –196 °C (Figure 10). This procedure enabled the synthesis of gram-scale quantities of KrF_2,[18] which had not been possible using earlier methods. As a result, krypton difluoride became readily accessible, allowing the emergence of a new field of research in noble-gas chemistry—namely, reactions involving exceptionally powerful oxidizing agents. This area remains an active field of research at the Institute to this day. Such work is by no means without risk, as the presence of moisture can lead to the formation of highly explosive compounds, for example xenon trioxide, which is dangerous even in quantities of only a few tens of milligrams.

As is customary internationally, members of the group were invited to present their work at universities, professional colloquia, and conferences around the world. At the invitation of foreign universities, they also served for extended periods as visiting professors, for ex-

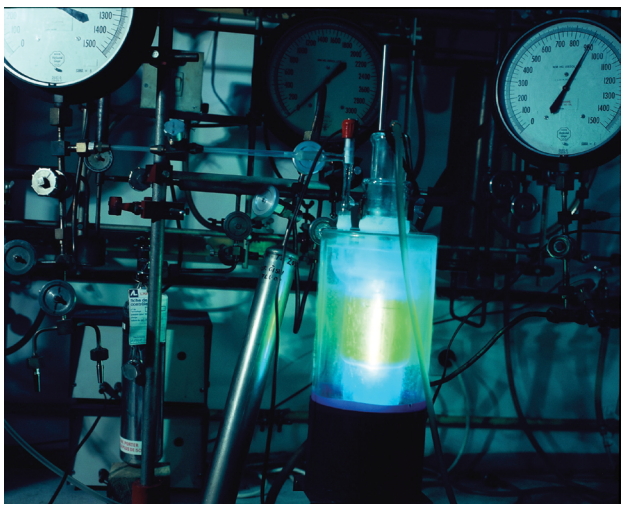

Figure 10. Photochemical reaction between krypton and liquid fluorine at liquid-nitrogen temperature.

ample Boris Frlec in 1973 at the University of Leicester (United Kingdom) with Prof. John H. Holloway, Boris Žemva in 1993 at the University of California, Berkeley (USA) with Prof. Neil Bartlett, and in 1997 at the Institute of Condensed Matter Chemistry in Bordeaux–Pessac (France) with Prof. Alain Tressaud. Collaborations with foreign research groups became routine, as the fluorine chemistry group at the Jožef Stefan Institute had become established as one of the more prominent groups worldwide.

The standing of the fluorine chemistry research group is further reflected in the awards and recognitions received by individual members both domestically and internationally. A few examples are listed below:

- **1963**: Boris Kidrič Fund Award for the work *Über die Synthese von XeF_6* by Jože Slivnik, Bogdan Volavšek, Vinko Vrščaj, Boris Frlec, Branko Brčić, Jože Marsel, Andrej Šmalc, and Anton Zemljič.[5]
- **1972**: Boris Kidrič Fund Award for inventions and improvements, awarded for the inventions *Pressure Transducer for Measuring the Pressure of Elemental Fluorine and Other Highly Corrosive Gases* and *Low-Temperature Cell for IR Spectroscopy of Highly Corrosive Fluorides* by Boris Frlec and Andrej Šmalc.
- **1977**: Boris Kidrič Fund Award for achievements in the synthesis and characterization of krypton and xenon fluoridometallates, published in articles in 1975 and 1976, awarded to Boris Frlec.[19,20]
- **1984**: Boris Kidrič Fund Award for work on metal(II) hexafluoridoarsenates(V) and hexafluoridouranates(V) by Darja Gantar and Boris Frlec.[21,22]

In 1983, following the death of the long-time head of the department, Jože Slivnik, leadership was assumed by Boris Žemva (Figure 11). Together with his coworkers, he continued and expanded research in xenon and krypton chemistry, extending it to complex noble-gas fluorides.[23] Particularly significant was his contribution to the chemistry of high oxidation states, which represents another peak in the group's scientific achievements and has placed Žemva among the internationally leading researchers in this field.[24,25]

Figure 11. Boris Žemva with visitors (secondary-school students) in fluorine laboratory.

Finally, a brief remark on laboratory safety practices of that time may be appropriate. It must be acknowledged that the group was accompanied almost constantly by what can only be described as extraordinary good fortune. By today's standards, the laboratory would have been closed immediately if research had been conducted as it was then, without adherence to basic safety and occupational protection standards. The only protection worn was a laboratory coat. No one wore safety goggles; extremely cumbersome gloves were used only rarely, as they severely impeded work. Face shields were employed only occasionally, when a particular operation was deemed potentially hazardous.

Nevertheless, the properties of fluorine and reactive fluorides were well known to us, as they were demonstrated to various visitors and guests of the Institute who were brought to our laboratory during tours. We demonstrated, for example, how not only an unlit cigarette ignites in a stream of fluorine, but even asbestos—a textbook example of a nonflammable material—or how acetone reacts with a sharp detonation and flame when a drop of bromine trifluoride falls into it. We even maintained a small "museum collection" of stainless-steel valves and fittings that had ignited in pressurized fluorine for various reasons, as well as ruptured reaction vessels (Figure 7). And yet, almost no one was ever injured.

This "almost" refers to our colleague Boris Frlec, who was splashed in the face with anhydrous hydrogen fluoride. He was immediately taken to the hospital, where it was first necessary to convince the physicians that they did not, in fact, know everything about burns—especially not about burns of this type. Fortunately, we had in the laboratory our "bible": a book documenting the experiences with fluorine gained by American researchers involved in the so-called Manhattan Project—the nuclear program that ultimately produced the atomic bombs dropped on Hiroshima and Nagasaki. Among other things, it contained a protocol for first aid in cases of burns caused by fluorine and hydrogen fluoride. The suspension described therein contained two essential active components: procaine for pain relief and magnesium oxide to neutralize hydrogen fluoride and prevent its further penetration into tissue. The latter is particularly dangerous, as it causes deep and extremely painful necroses. Only with great difficulty did Slivnik persuade the physicians to use this treatment instead of conventional burn ointments, such as the then-popular Jekoderm. Only in this way did our colleague Frlec, after receiving 42 injections of this medication to the face, escape with minor injuries and no lasting scars.

Over the more than sixty years since the beginnings of our work, life and research conditions have changed profoundly, and it would therefore be inappropriate for these memories to be lost entirely.

Chronological Summary of the Pioneering Beginnings of Fluorine Chemistry at JSI

1952

Establishment of the Department of Fuel and UF_6, from which the Department of Fluorine Chemistry later developed, i.e., the Department of Inorganic Chemistry and Technology; Honorary head: Branko Brčić, Head of the Institute of Inorganic Chemistry at the University of Ljubljana

1953

Arrival of Jože Slivnik at the Jožef Stefan Institute, Department of Fuel and UF_6

1954

Arrival of technician Anton Zemljič at the Department of Fuel and UF_6

First steps in the production of elemental fluorine

Preparation of anhydrous HF and electrolyte KHF_2 from KF and HF

Construction of a von Wartenberg-type electrolytic cell

Development of a 20-A fluorine electrolytic cell; startup difficulties when the electrolyte was not completely dry, leading to explosions

First attempts at synthesizing uranium hexafluoride from uranium tetrafluoride using elemental fluorine produced directly in the 20-A cell

1957

Arrival of Bogdan Volavšek at the Department of Fuel and UF_6

Construction of the first glass high-vacuum system for working with moisture-sensitive substances

Construction of a magnetic balance and measurements of magnetic susceptibilities of fluorides

1959

Arrival of Boris Frlec at the Department of Fuel and UF_6.

Preparation of UF_4

Construction of a vacuum-tight reaction vessel for calciothermic reduction of UF_4

Calciothermic reduction of uranium tetrafluoride to metallic uranium

Development of a metal-membrane pressure transmitter for measuring the pressure of elemental fluorine

1960–1961

Military service of Boris Frlec

1960

Arrival of Andrej Šmalc at the Department of Fuel and UF_6

Synthesis of larger quantities of uranium hexafluoride

1961–1962

Military service of Andrej Šmalc

1962

Jože Slivnik becomes Head of the Department

Repetition of the synthesis of XeF_4 from the elements at 400 °C in a sealed nickel vessel

Development of a bellows-type pressure transmitter for measuring the pressure of elemental fluorine

High-pressure synthesis of XeF_6 from the elements at temperatures up to 700 °C and pressures up to 250 bar in a massive pressure vessel

1963

Development of a 120-A electrolytic cell for fluorine production

Development of lightweight nickel pressure vessels for high-pressure syntheses with elemental fluorine (up to 250 bar)

Development of techniques and apparatus for fluorine liquefaction in a closed system, including a contact manometer and magnetic valve for regulating fluorine flow from the electrolytic cell

Development of valves for fluorine storage cylinders and conversion of 10-L oxygen cylinders into fluorine cylinders

Development of fluorine cylinder filling techniques via liquefaction and controlled expansion to pressures up to 30 bar

Development of a method for determining the purity of gaseous fluorine using mercury

1965

Departure of Boris Frlec for postdoctoral training at Argonne National Laboratory (USA)

Division of the Department of Fuel and UF_6 into the Department of Fluorine Chemistry (K-1) and the Department of Ceramics (K-5)

Calciothermic reduction of uranium hexafluoride to metallic uranium

High-pressure synthesis of hexafluorides of tungsten, rhenium, osmium, iridium, and platinum from the elements

Studies of vanadium pentafluoride synthesis from divanadium pentoxide and fluorine under pressure

1967

Construction of a dry box for working with moisture-sensitive substances

Construction of a glass–metal high-vacuum system for working with corrosive fluorides

Development of reaction vessels and valves made of fluoropolymers (Kel-F and FEP)

1968–1969

Postdoctoral training of Andrej Šmalc at the Institute of Inorganic Chemistry, University of Göttingen (Federal Republic of Germany)

1975

Photochemical synthesis of larger quantities of krypton difluoride

Development of a method for photochemical purification of elemental fluorine

Development of photochemical syntheses of XeF_2, XeF_6, and ClF_5

Photochemical synthesis of O_2AsF_6 and its use as an oxidant for the synthesis of $S_2O_6F_2$ from HSO_3F

Investigation of O_2AsF_6 formation in the O_2–F_2–AsF_5 and OF_2-based systems

Notes

We note with great sadness that Prof. Boris Frlec passed away in February 2026, shortly before the publication of this article.

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Povzetek

Prispevek predstavlja osebni zgodovinski pregled pionirskega razvoja kemije fluora na Institutu »Jožef Stefan« v Ljubljani. Začetki teh raziskav segajo v zgodnja petdeseta leta prejšnjega stoletja, ko je bil ustanovljen Odsek za gorivo in UF_6. Delo je sprva obsegalo razvoj elektroliznih celic za pridobivanje elementarnega fluora ter sintezo fluorovih spojin v zahtevnih laboratorijskih razmerah. V začetku šestdesetih let je skupina uspešno sintetizirala XeF_4 in XeF_6 ter s tem prispevala k nastajajočemu področju kemije žlahtnih plinov. Poznejše raziskave so se razširile na fotokemijske reakcije fluoriranja ter na sintezo in karakterizacijo številnih kompleksnih fluoridov. Prispevek poudarja znanstvene dosežke skupine, razvoj specializirane eksperimentalne opreme ter vlogo mednarodnega sodelovanja pri uveljavitvi Instituta »Jožef Stefan« kot mednarodno priznanega raziskovalnega središča na področju kemije fluora.