SOLVAY

asking more from chemistry®

Elemental Fluorine

Contents

1 Introduction

The element fluorine (chemical symbol: F) belongs to the halogen group. The name "fluorine" derives from the mineral "fluorspar".

Fluorine is the most reactive element in the periodic table. This is why fluorine occurs in nature only in chemically bonded form as fluoride.

Fluorspar (CaF_2) was added to the metal ores to lower their melting point and thus make them more fluid (hence the name, from the Latin = fluere, "to flow"). Among the halogens, fluorine is the element that occurs most abundantly in nature. Solvay owns two fluorspar mines in Namibia and Bulgaria to secure the raw material for its fluorine production sites in Europe and Asia.

The manufacture of fluorine, together with its inorganic and organic compounds has given remarkable new impulse to fluorine chemistry. Typical areas of application include metallurgy, aluminum electrolysis, the manufacture and processing of glass, abrasives, electroplating processes, ceramics, electrical engineering, electrochemical elements, energy storage, nuclear technology, flat panel production, photovoltaic production and semiconductor production.

In the field of organic fluorine chemistry the development of new products continues. Fluorine containing polymers are highly valued for their remarkable properties. The most known examples are polytetrafluorethylene (PTFE) and polyvinylidene fluoride (PVDF). Fluorinated organic compounds are also used as:

- Electrolyte in Lithium ion batteries
- Solvents
- Surfactants
- Pharmaceuticals
- Pesticides
- Lubricants
- Blood substitutes
- Insecticides
- Starting material for organic synthesis

And many more.

Today the main industrial applications for elemental fluorine are fuel tank fluorination for cars and cleaning of CVD tools during the production of semiconductors.

Fig. 01: The raw material: fluorspar crystal from the Solvay mine in Okorusu, Namibia.

2.1 Technical Application of Fluorine

Fluorine is widely used in applications for the direct reaction with organic substances.

The reaction between the pure fluorine and the organic substance results in the formation of the thermodynamically more stable end products CF_4 and HF:

$$C_nH_{2n+2} + (3n + 1)\,F_2 \rightarrow$$
$$\downarrow -E$$
$$nCF_4 + (2n + 2)HF$$

This entails that the aim in all methods of fluorine treatment is to minimize the formation of by-products or waste products as far as possible. At the same time it is essential to maximize the yield of the target compound. An optimum reaction is achieved through control of the process parameters:

- Concentration of reagent
- Reaction temperature
- Reaction time.

In simplified terms, the various processes used may be divided into two categories:

- Single-phase fluorination
- Two-phase fluorination.

In the single-phase method, the substance to be fluorinated and the fluorinating agent (F_2 diluted with an inert gas) are present in one and the same phase. A number of different variants have been developed for both the gaseous-phase and liquid-phase fluorination technique. In the case of two-phase fluorination the compound to be fluorinated and the fluorinating agent are present in different phases. As early as 1954, Rudge filed a patent application in which the fluorination of polyethylene surfaces by means of a fluorine/inert gas mixture was described. A whole series of processes specifically designed for direct fluorination of plastic surfaces have subsequently been developed, some of them differing in terms of the steps involved. Foam sheeting can be treated in a continuous fluorination process. Selective fluorination of hollow plastic containers can now be carried out during the actual blow moulding process (in-line treatment) so that only the inner walls are treated.

Off-line fluorination, carried out when blow-moulding is completed, is a discontinuous process. Fluorination may be confined to the inner walls of the container; alternatively, both inner and outer walls may be treated. In another process, plastic surfaces are treated with elemental fluorine i.e. in solution with inert solvents or solvent mixtures.

Fig. 02: Fluorinated plastics for high performance applications.

Plastic Processing

The finishing of plastic surfaces is of great significance in the foil industry. For the production processes of gluing, coating, laminating, painting and printing good adhesion is absolutely essential.

During the nineteen eighties a continuous fluorinating process was developed for the treatment of foils. With this method the surfaces of foils can be activated, on one or both sides, independent of the size and length of the rolls, in a continuous process from roll to roll. The fluorination of almost all types of foils consistently results in a significant increase in surface energy.

Fluorination of Tanks

Polyethylene, the plastic employed for the production of fuel tanks and containers for different chemicals, has often the disadvantage of being relatively permeable to the stored vapour. This undesirable property leads to permeate to the extent of a few grams per day from a PE container.

For this reason the automobile industry performs the fluorination process to reduce the permeability of fuel through petrol tanks walls. A layer of CF_2 will be formed. The permeation of fuel through polyethylene fuel-container walls can be dramatically reduced by the chemical process of forming a layer which is almost impermeable.

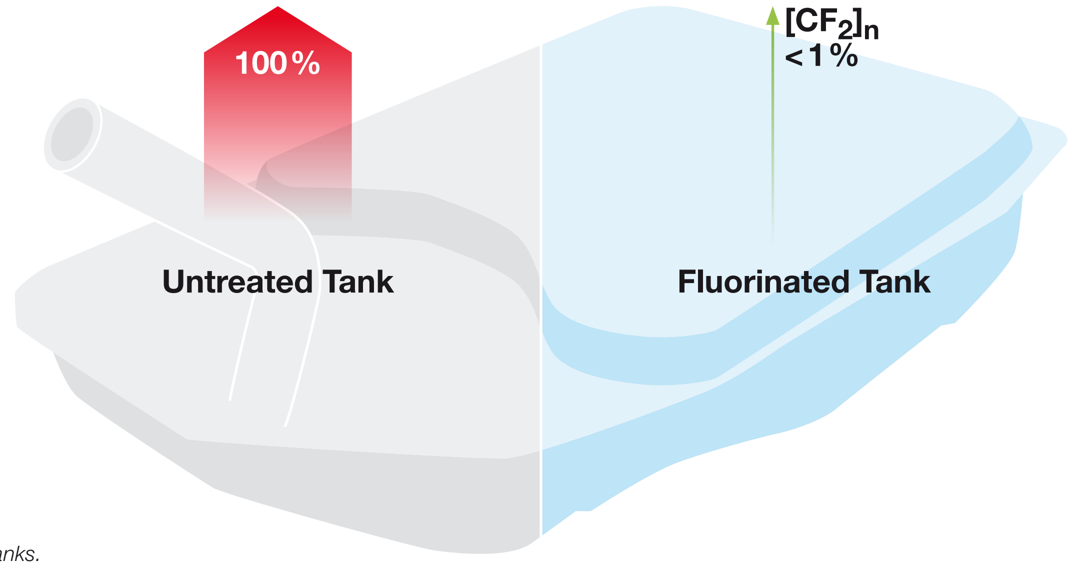


Fig. 03: Permeation in plastic fuel tanks.

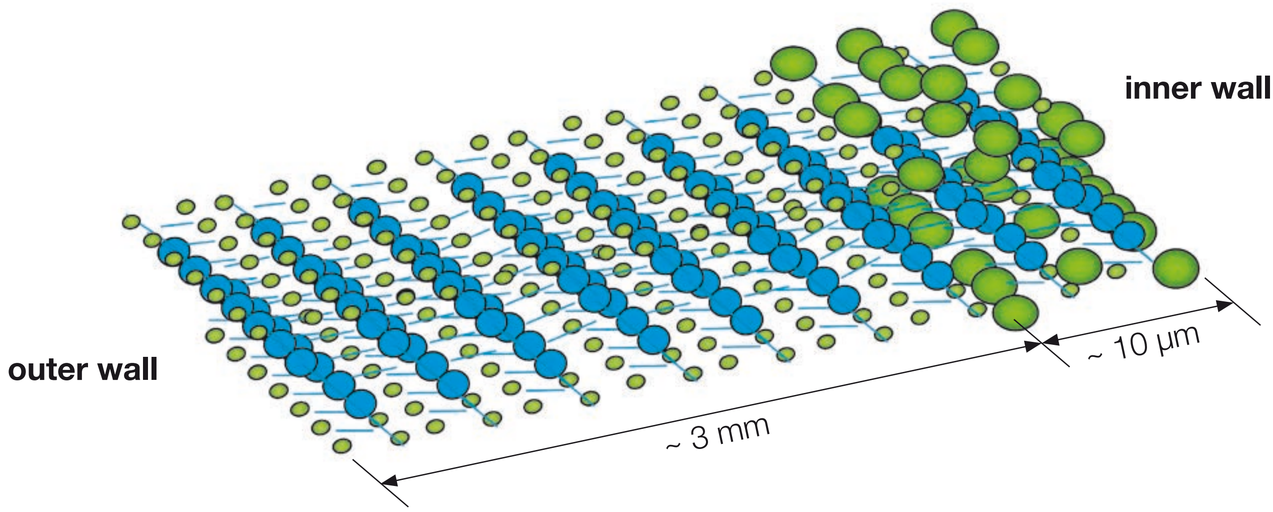


Fig. 04: Cross-Section of a container wall with a fluorinated inner layer.

2.2 Electronic Application of Fluorine

Solvay is producing F_2 electronic grade in two plants in Germany and South Korea. This is unique in the world so far and enables the highest possible supply security among all F_2 high purity manufactures.

As fluorine is the most reactive element, it is obvious that it is a strong oxidizer. This ability is useful for the removal of Siliconoxide (SiO_2) and Siliconnitride (Si_3N_4). This process is done in a CVD Tool (Chemical Vapour Deposition) and the residues of these compounds are deposited at the chamber walls of these tools. After removing the wafer, the tool has to be cleaned with fluorine containing gases like NF_3, SF_6, CF_4, C_2F_6 and others. These gases however have global warming potential.

An environmental friendly alternative to these cleaning gases are F_2/N_2 or $F_2/N_2/Ar$ mixtures. Fluorine reacts spontaneously already at ambient temperature with deposits of silicon and all its compounds to generate SiF_4, which is gaseous and can be therefore easily removed from the chamber to be cleaned. In order to have the reaction better controlled fluorine is diluted with nitrogen.

F_2/N_2 Mixtures

Within the production process of semiconductors, one process step is the etching process. Within this step a structure is etched into the semiconductors. The step takes place in a so called etcher. The etched material is as well deposited on the wall of the etching tool. Therefore a separate process to clean this tool is required. In most of the cases it is cleaned with NF_3, but there are etchers on the market using F_2/N_2 mixtures with high purity. Solvay is producing this F_2/N_2 mixture with high purity. A basic specification can be seen on page 9.

F_2 Laser Gas mixtures

Within the production of semiconductors, the lithographic process is one of the most important ones, because here the structure of the wafer is created. In the higher technology nodes below 128 nm wavelength excimer laser with F_2 and Ne, Ar, Kr as mixtures are used. The radiation of these gas mixtures is reflecting the minimum size of the structure.

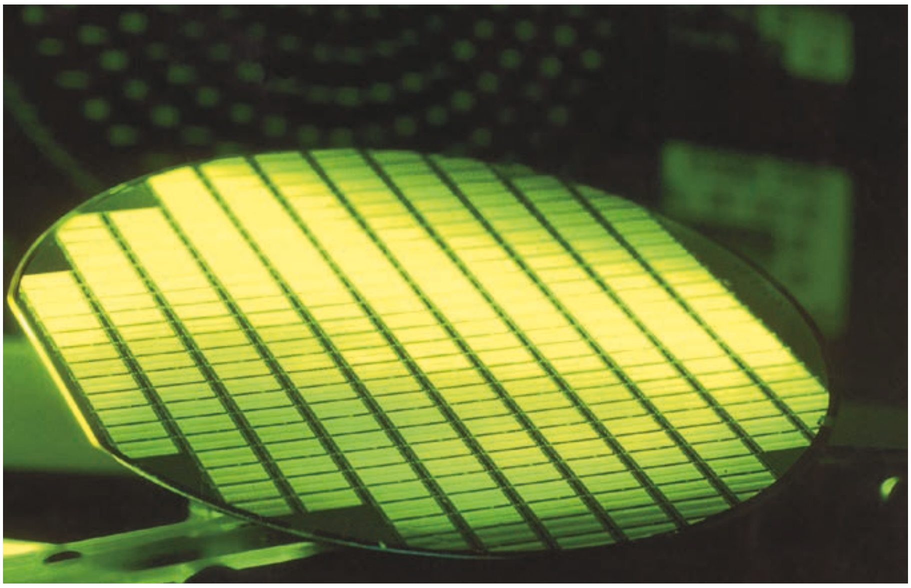


Fig. 05: Chamber cleaning in the semiconductor industry with F_2 mixtures.

F_2 Nitrogen Mixtures as Replacement for Other Cleaning Gases

F_2 in dilution with nitrogen at 20 % is a very competitive cleaning gas for cleaning CVD tools. Tests at the Fraunhofer Institute in Munich have proven the full compatibility of the F_2 mixtures on the AMAT P 5000 tool. It has been demonstrated that it is possible to reduce the cleaning time of SiO_2 and Si_3N_4 up to 44 % vs. CF_4 and up to 21% vs. NF_3 based on the cleaning recipes.

The fluorine gas consumption has also been drastically reduced compared to both NF_3 (49%) and CF_4 (in this case 1 kg F_2 can substitute 35 kg of CF_4).

In addition to the savings, the applied F_2 process will reduce the environmental impact enormously, because the GWP of F_2 is ZERO, compared to the values of 7,390 for CF_4 and 17,200 for NF_3. /1/

2.3 Fluorine On-Site Plant

Fig. 06: F_2 onsite plant.

Fig. 07: Solar panels.

The development of the F_2 on-site concept for the production of fluorine by electrolysis of hydrogenfluoride in an on-site production-unit is based on existing Solvay F_2 production-technology. The onsite plant concept was developed for high fluorine demands as for example photovoltaic and flat panel manufacturers.

The concept is based on a skid mounted F_2 on-site production plant. This F_2 electronic grade onsite modular approach includes the scale-down of common technology parts and process improvements. It allows a safe and reliable production of F_2 e-grade on-site, delivered over-the-fence to the customer on demand. The unit is designed for connection to standard utilities on customer site. Base case is a module with 100 to/a F_2 capacity.

Detailed safety studies were performed on the F_2 skid-mounted concept. Inventories of HF and F_2 in the unit are limited and pressures for HF and F_2 are low. Gas detection sensors for HF and F_2 are installed and the skids are ventilated with connection to the emergency response scrubber system. Additionally, scrubbers for HF abatement and F_2 off-spec destruction are included in the concept.

A new concept for HF supply as raw material for the process and handling is realized via transportable HF tanks à 2 to HF per tank. Analysis equipment is installed to monitor the impurities in the fluorine, like HF, CF_4 and others.

Specifications for T-grade Fluorine (Technical Grade)

Characteristics	Unit	Specification
F_2	vol %	≥ 99.0
HF	vol %	≤ 0.2

Specifications for T-grade Fluorine (20) / Nitrogen (80)

Characteristics	Unit	Specification
F_2 content	vol %	19.5 – 20.5
N_2 content	vol %	79.5 – 80.5
HF	vol %	≤ 0.05

Specifications for T-grade Fluorine (10) / Nitrogen (90)

Characteristics	Unit	Specification
F_2 content	vol %	9.5 – 10.5
N_2 content	vol %	89.5 – 90.5
HF	vol %	≤ 0.05

Specifications for E-grade Fluorine (20) / Nitrogen (80) (Electronic Grade)

Characteristics	Unit	Specification
F_2 content	vol %	19.5 – 20.5
N_2 content	vol %	79.5 – 80.5
HF	vppm	≤ 500
CF_4	vppm	≤ 160
O_2	vppm	≤ 400

There are other F_2/N_2 mixtures and F_2 noble gas mixtures available upon request.

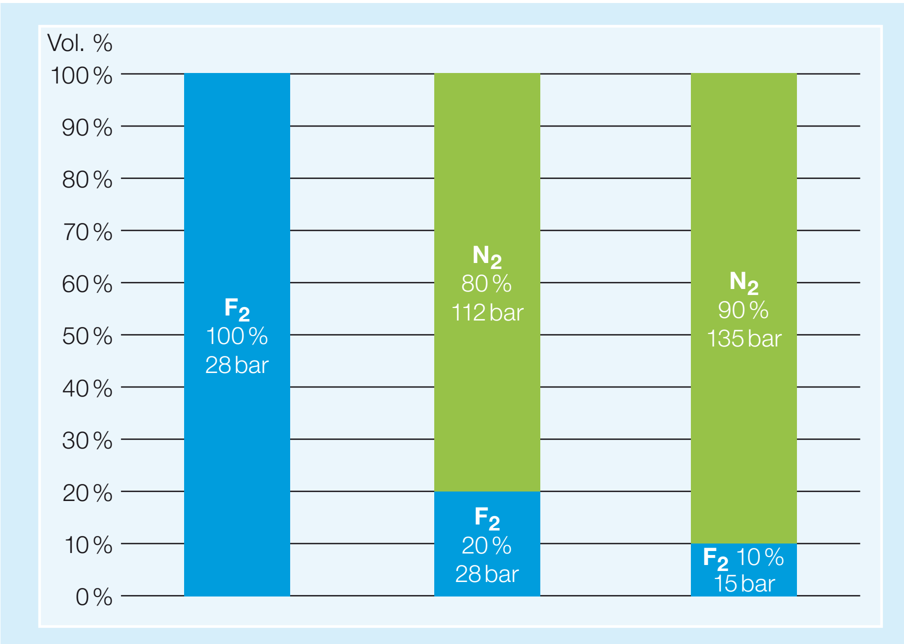


Fig. 08: Pressure of the components.

4 Safety

When handling fluorine it is essential to observe the rules and regulations laid down by the government of the respective country. “Technical Regulations for Hazardous Materials” define the latest government safety standards relating to all aspects on the use and handling of hazardous industrial materials including technical advice, occupational medicine, hygiene and transport. The extreme reactivity of fluorine makes special safety precautions essential. To ensure safe handling of this product, we recommend an extended safety code, based on industrial recommendations and government regulations.

Due to the reduced oxidizing behavior, fluorine mixtures (mixed with inert gases) with lower F_2 concentrations than 30 % show some difference in handling and material use compared to elemental fluorine (F_2 ~ 100 %).

Handling of F_2 100 % and Mixtures Thereof

Fluorine, as the most electronegative element in the periodic system, is a highly reactive substance. The extreme reactivity of fluorine makes special safety precautions essential.

Fluorine can be transported in compressed form in an approved gas cylinder at 30 bar (435 psi) following the international rules for transport. Gas cylinders for F_2 need a recurrent approval every five years by a surveyor. Checks of valves, valve connections and the condition of cylinder surfaces need to be carried out at every filling.

The size of side adapters are regulated by national and international standards. Cylinders, bundles and tube trailers are designed for safest handling. e.g. bundles are equipped with pneumatic valves for remote controlling the gas flow.

Leakage Check

Already small leakages are technically detectable. Leakages can be detected by gas monitors. Fluorine can be recognized by F_2 odor at ~ 0.1 ppm (TLV level 1 ppm).

An easy method to check connections can be done by using a potassium iodide paper. In the case of existing small fluorine releases the paper will change color from yellow to black (this relates to a concentration of approx. less 1 ppmw).

Passivation

Fluorine reacts with all materials, depending on temperature or other properties. This reaction could be very fast or slow. To prepare metal parts for fluorine transport these materials need to be passivated beforehand. Therefore a smooth fluorination under regulated fluorine conditions is necessary. Passivation will result in a metal fluoride containing surface preventing raw metal surfaces against fast oxidation of fluorine and fluorine burning. New passivation investigations conclude that post heating to ~ 200 °C will increase the solidity of the passivation layer. /2/

Basic needs for passivation: parts have to be cleaned carefully, parts must be oil and grease free and dry, system must be proven free of leakages and all parts must be carefully passivated.

Workplace and Personnel

Fluorine should be handled only by qualified, well-trained personnel!

When working on components or systems that contain fluorine!

1. Safety goggles must be worn at all times!
2. Heavy duty clean neoprene (or leather) gloves must be worn at all times!
3. Protective helmets with visors made of a chemically resistant material must be worn if fluorine valves need to be manipulated manually!
4. Personnel must refrain from eating, drinking, smoking and the use of inhalants while handling fluorine.
5. Adequate ventilation must be provided in all enclosed spaces where fluorine is handled or processed.
6. Emergency showers and eye wash stations should be installed at easily accessible places within the working area.
7. Personnel working on a fluorine containing system must always work in pairs. Everyone should remain within sight and calling distance at all time.

Fluorine 100%	**Fluorine Mixture < 20 % F_2**
Metal burn can occur in case of impingement or increased flow rate	In clean tubes metal burns of F_2 mixtures are very unlikely
Only Ni alloyed metals recommended for higher temperatures	Stainless steel is recommended for use at higher temperature applications
Flow rate must be limited	No flow rate limitation necessary
185 ppm (or ml/m³ = LC50) (LC = Lethal Concentration)	925 ppm (or ml/m³ = LC50) calculated

Fig. 09: Safe handling comparison./3/

Pressure regulator

- Monel regulators with special sealing for work with 100 % fluorine are available from the market
- Monel regulator is recommended for fluorine nitrogen gas mixtures $> 20\,\%\ F_2$
- Stainless steel can be used for fluorine mixtures $< 20\,\%\ F_2$ up to 200 bars

Pressure Determination

- Special edition for fluorine – Monel gauge

Scrubber

The handling of scrubbers needs to be split in two applications of fluorine use.

- $CaCO_3$ solid absorber can be used if fluorine concentration is between 1–2 % in the application (eg. the use of fluorine in the online fluorination of petrol tanks). In order to use $CaCO_3$ scrubbers properly, the waste gas stream should be humidified.
- Higher concentrated F_2 mixtures need to be scrubbed using a wet scrubber with ~ 20% KOH solution, or solid materials (e.g. Al_2O_3), which react with F_2 in a compatible way. In some cases OF_2 will be generated – this can be avoided by using oxidative substances.

Sealing compounds

For fluorine and fluorine mixtures in inert gas at concentrations equal to or below 20 % of fluorine, Monel, nickel, copper or stainless steel systems can be used.

PTFE is used, out of the flow path for systems of fluorine and fluorine mixtures, such as for valve packing, gasket material and pipe thread sealant. PTFE may be used up to 10% F_2 concentration.

Fig. 10: Material compatability. /3/

Material	**F_2 Concentration**	**Application**
Monel and Nickel	> 4 bar F_2 100 %	Piping
Stainless steel	< 4 bar F_2 100 %	Piping (up to 30 bar F_2 systems with additional safe guard)
Stainless steel	< 4 bar F_2 in mixtures with inert gases	Piping for 20 % F_2 up to 150 bar
Carbon steel	> 1 bar or less F_2 100 %	Piping (gas cylinder up to 30 bar)
Brass	< 4 bar F_2 100 %	Valve material (caution, as they are susceptible to de-zincification)
Copper	< 4 bar F_2 100 %	Seals and washer
Aluminium and Aluminium Alloys	< 4 bar F_2 100 %	Tests at Solvay showed good resistance and ductibility for use as Al gaskets up to 200 °C
PTFE	< 10 % F_2	Piping
Filled PTFE	< 10 % F_2	Regulator valve seat

4.1 Maintenance of the F_2 system

During maintenance any contamination and exposure to moisture must be avoided. Moisture can not only be a possible source of F_2 ignition but also can hydrolyze the passivation layer and result in the formation of hydrofluoric acid. The hydrogen fluoride can lead to accelerated corrosion in the system. It is not advisable to use a vacuum pump or fan to allow air to be sucked into a fluorine system. To minimize air infiltration when a system must be momentarily opened, consider the use of low flow inert gas purge as protection against moist air infiltration.

Fig. 11: Twelve cylinders building a bundle.

Install blank flanges, pipe caps etc., on any open ports of a F_2 system.

Piping systems that use fluorine mixtures will become contaminated with a powdery residue over time. This material is composed of metal fluorides and should be handled with caution since the material may contain hydrofluoric acid. It should also be assumed that any liquids or moisture found in these fluorine systems would contain hydrofluoric acid. This material is very corrosive to many other materials of construction.

If the system is exposed to atmosphere for extended periods re-drying and re-passivation is recommended as a safeguard prior to re-introducing F_2 at full operating pressure.

Storage

Storage conditions should always be in line with the local fire department regulations. According to pressure vessel regulations, compressed gases are substances whose vapour pressure at 50 °C is above 3 bar. In line with the regulations governing pressure vessels these gases may only be transferred to approved and labelled gas-tight gas cylinders or containers. Wherever these containers are handeld, there must be no open flames or heat sources (e.g. hot metallic surfaces) or reactive products. An important precondition is strict adherence to the threshold limit value (TLV).

Handling

Be sure to close all cylinder valves when not in use. The valves of empty cylinders should also be closed.

Ensure that gas cylinders are transported so that they do not tip, fall or roll. Gas cylinders should be secured to the cylinder trucks or carts. Regulators should be removed and valve protection caps should be secured in place before moving cylinders. Also, cylinder valves should be closed before moving cylinders. Appropriate lifting devices, such as cradles or nets, must be used when using a crane, hoist or derrick to transport gas cylinders. Do not use magnets or slings to lift gas cylinders. Do not use the valve protection cap to lift a gas cylinder. It is necessary to take precautions to prevent gas cylinders being dropped or striking each other or other objects. Dropping or striking may damage the cylinder valve, which could turn the cylinder into a dangerous torpedo with the potential to destroy property and/or injure personnel.

Gas cylinders should be properly secured at all times to prevent tipping, falling or rolling. They can be secured with straps or chains connected to a wall bracket or other fixed surface, or by using a cylinder stand.

Store cylinders in a cool, dry, well-ventilated, fire-resistant area in accordance with local regulations.

A cylinder storage area should be located in an area where the cylinders will not be knocked over or damaged by falling objects.

When a cylinder is not being used, the valve should be closed and the valve protector secured in place.

Inspection

Gas cylinders should be visually inspected to ensure that they are in a safe condition.

If necessary, a cylinder can be tested ultrasonically for hidden defects. Leaking and malfunctioning regulators, cylinder valves or other equipment should be taken out of service. A cylinder's contents should be identified at all times. Cylinder status should also be identified; for example, whether the cylinder is full, empty or in service.

SDS

Consult the appropriate SDS for detailed information on the chemical contained in the gas cylinder.

Specific chemical handling and storage precautions will be outlined in the SDS. The SDS will also have specifications for appropriate personal protective equipment for worker protection.

Rescue

First protect yourself and afterwards bring injured people out of the hazardous area. Place injured people in quiet, uncontaminated and well ventilated area.

Contaminated Bodyparts

Inhalation:

- Give fresh air immediately, oxygen or cardiopulmonary resuscitation if necessary.
- Keep insured people warm (blanket).
- If possible perform therapy with (inhalable corticoid) e.g. Auxiloson™.
- In all cases consult with a physician – take insured people to hospital.
- If possible use O_2 portable cylinder nebulizer during emergency transport. Corrugated tubing and mask; 500 cc. of a 2.5 % calcium gluconate nebulizing solution.

Eyes:

- Rinse with fresh water or better calcium gluconate 1 % solution in physiological serum.

Skin:

- Remove contaminated clothes immediately, under shower if necessary. Wash the affected skin with running water. Immediately apply calcium gluconate gel 2.5 % and massage into affected area using rubber gloves; continue to massage while repeatedly applying gel until 15 minutes after pain is relieved.
- Keep insured people warm (blanket).
- In all cases consult with a physician – take insured people to hospital.

If daily work with fluorine is your business, an informative precaution meeting with the next hospital should take place, before an accident happens. /4/

Fig. 12: First Aid set.

5.1 Chemical Properties

Fluorine is an almost colourless gas. In dense concentrations and in the liquid state it is seen to have a pale greenish-yellow colour. It has a characteristic odour, similar to a mixture of ozone and chlorine. As the most reactive of all the elements and the most powerful known oxidizing agent, fluorine is able to react with almost all elements and compounds, with the exception of lighter, noble gases and fluorides of the highest valency. Fluorine reacts with many substances even at room temperatures, sometimes explosively, and often accompanied by combustion.

Reaction with hydrogen

Fluorine and hydrogen react with extreme violence, in a highly exothermic reaction [$\Delta H°$ HF (g) 25°C = – 271.7 kJ/mol]. Even at very low temperatures (solid fluorine, liquid hydrogen) a violent reaction is produced.

Reaction with silicium

Fluorine reacts significantly with silicon at 120 °C to SiF_4. Simultaneously a chemiluminescence can be observed. The reaction with silicon is increasing with increasing partial pressure of fluorine, at the same time the intensity of the chemiluminescence is reduced. An increase of the fluorine reaction rate with silicon can be achieved by increasing the temperature to 600 °C, but less relevant compared to the partial pressure increase of fluorine.

$$SiF_{2(chemisorbed)} + F_2 \leftrightarrow [SiF_2{\cdot}F_2]_{surf}$$

$$[SiF_2{\cdot}F_2]_{surf} \rightarrow SiF_2 + F_{2\ (chem.)} \rightarrow SiF_x \quad (x > 2)$$

$$SiF_2 + F_2 \rightarrow SiF_3^* + F \rightarrow SiF_3 + F$$

$$SiF_3^* \rightarrow SiF_3 + h\nu$$

$$SiF_3^* + F_2 \rightarrow SiF_3 + F_2 \qquad /5/$$

Reaction with water

Fluorine reacts with water to form oxygen, oxygen difluoride and hydrogen fluoride. Small quantities of ozone and hydrogen peroxide may also be formed. Passing fluorine through dilute sodium hydroxide or potassium hydroxide is the standard method for preparing oxygen difluoride. Mixtures of fluorine and water vapour are potentially explosive.

Reaction with halogens

If fluorine is combined with any of the other elements in Group VII of the periodic table, it leads into an highly exothermic reaction, from which a series of interhalogen compounds are formed (ClF, ClF_3, ClF_5, BrF, BrF_3, BrF_5, IF, IF_3, IF_5, IF_7). Halogen fluorides are also widely used as fluorinating agents.

Reaction with carbon

Carbon reacts variously with fluorine, depending on its structure and surface configuration. Active carbon may ignite at room temperature in presence of fluorine; the resulting reaction produces CF_4, C_2F_6 and small quantities of higher perfluorinated alkanes. If the mixture does not ignite, the fluorine is absorbed and carbon monofluoride $(CF)_x$ formed. This may decompose explosively at higher temperatures to form carbon and fluorocarbon compounds. When combined with graphite, fluorine forms graphite fluorides, which are likewise liable to decompose violently at higher temperatures.

At temperatures below 500°C, or in the presence of metal fluorides, fluorine reacts smoothly with carbon to form CF_4 and higher perfluorinated alkanes or cycloalkanes.

Reaction with other non-metals

Boron, silicon, phosphorus, sulphur, selenium and tellurium all react with fluorine to cause combustion and the formation of fluorides of the highest valency. Normally, oxygen and nitrogen do not react with fluorine, but reactions may occur under special conditions, such as dark electrical discharges, plasma arcs, etc. Of the noble gases, radon and xenon react readily with fluorine while krypton reacts only under special conditions.

Reactions with organic compounds

All organic compounds react with fluorine. Ignition usually occurs, and under certain circumstances the reaction may be explosive. The end product of the reaction is invariably carbon tetrafluoride. Under suitable reaction conditions, organic compounds may be partially or completely fluorinated with elemental fluorine, without causing destruction of the molecule.

With the exception of carbon tetrafluoride, all fully halogenated carbon compounds also react with fluorine. In many cases, however, this reaction proceeds so slowly that some of these materials, such as polytetrafluoroethylene, can be used as construction materials or sealants, providing that certain reaction conditions are maintained.

Reaction with metals

Fluorine attacks metals at room temperature, but some metals and alloys form a protective layer of fluoride that effectively prevents further attack. When deliberately induced, the process is known as passivation. Treated in this way, some metals and alloys (Mg, Al, Fe, Ni, Cu, Cr, etc.) become valuable materials for the handling of elemental fluorine.

5.2 Physical Data

Parameter	Value	Unit	Bibliography
Molar mass	37.997	g/mol	/6/
Transition point	– 227.61	°C	/6/
Melting point	– 219.62	°C	/6/
Boiling point	– 188.14	°C	/6/
Critical temperature	– 129.16	°C	/7/
Critical pressure	55.715	bar	/8/
Critical densitiy	573.76	g/l	/9/
Density (liquid at boiling point)	1.513	g/cm^3	/10/
Density (gas, 0°C, 1.013 bar)			
F_2 100%	1.695	g/l	/11/
F_2 10% | N_2 90%	1.294	g/l	/11/
F_2 20% | N_2 80%	1.339	g/l	/11/
F_2 20% | N_2 70% | Ar 10%	1.392	g/l	/11/
F_2 20% | N_2 40% | Ar 40%	1.552	g/l	/11/
Refractive index (n_D^{bp}, liquid)	1.20		/12/
Refractive index (n_D^0 at 1.013 bar)	1.000214		/12/
Molar refractivity	3.22	cm^3/mol	/12/
Heat of transition	728.09	J/mol	/6/
Heat of fusion	510.79	J/mol	/6/
Heat of vapourization (at boiling point)	6548	J/mol	/6/
Kirchhoff formula (temperature range: – 219.6 to – 183 °C) (p: Torr, T:K)	$\log p = 7.08718 - (357.258/T) - ((1.3155 \cdot 10^{-13}) / T8)$		/6/
Entropy of transition (– 227.61 °C)	15.99	J/mol K	/6/
Entropy of fusion (– 219.62 °C)	9.55	J/mol K	/6/
Entropy of vapourization (at boiling point)	76.6	J/mol K	/6/
Standard entropy $S°_{298}$	203.09	J/mol K	/13/
Surface tension (at boiling point)	$13.6 \cdot 10^{-5}$	N/cm	/10/
Eötvös constant	2.1		/10/
Viscosity (liquid at boling point)	0.24	mPa · s	/14/
Viscosity (Gas, 0 °C, 1.013 bar)	0.0218	mPa · s	/15/
Thermal conductivity (Gas, 0 °C, 1.013 bar)	$2.48 \cdot 10^{-4}$	W/cmK	/16/
Coefficient of self-diffusion (Gas, 0 °C, 1.013 bar)	0.170	cm^2/s	/15/
Impulse diameter	$0.37 \cdot 10^{-8}$	cm	/15/
Internuclear distance	$1.435 \cdot 10^{-8}$	cm	/17/
Dissociation energy (0 °C)	156.6	kJ/mol	/18/
Electron affinity of atoms	340	kJ/mol	/18/

Fig. 13: Table of Physical Data.

Fig. 14: Best etch rates found for selected materials at 150°C.

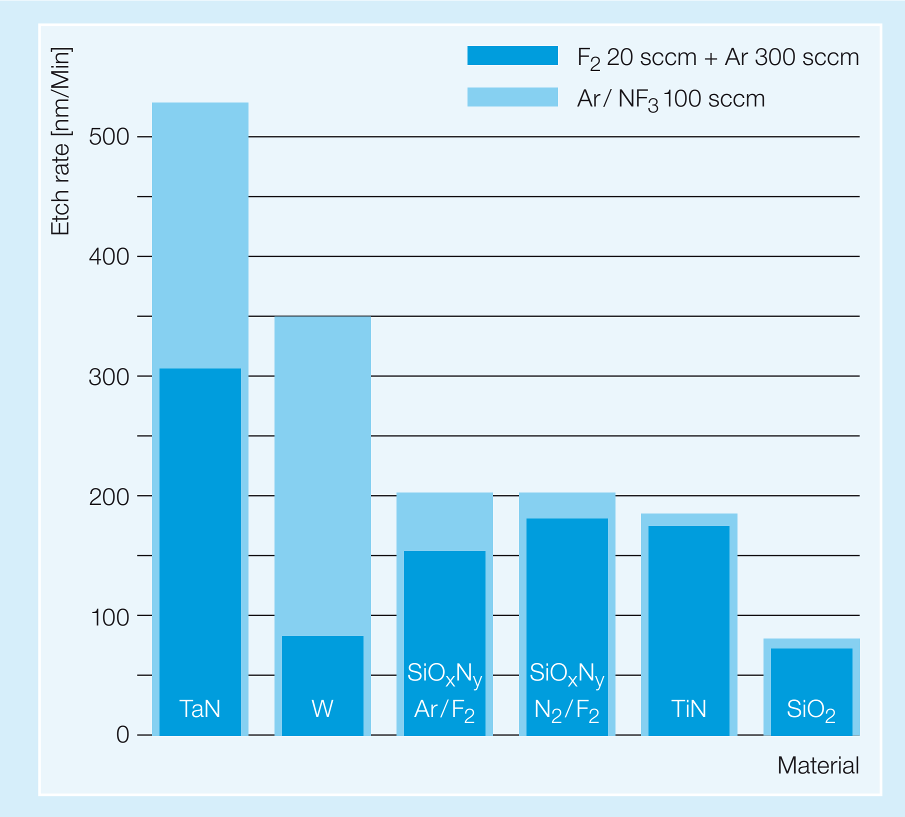
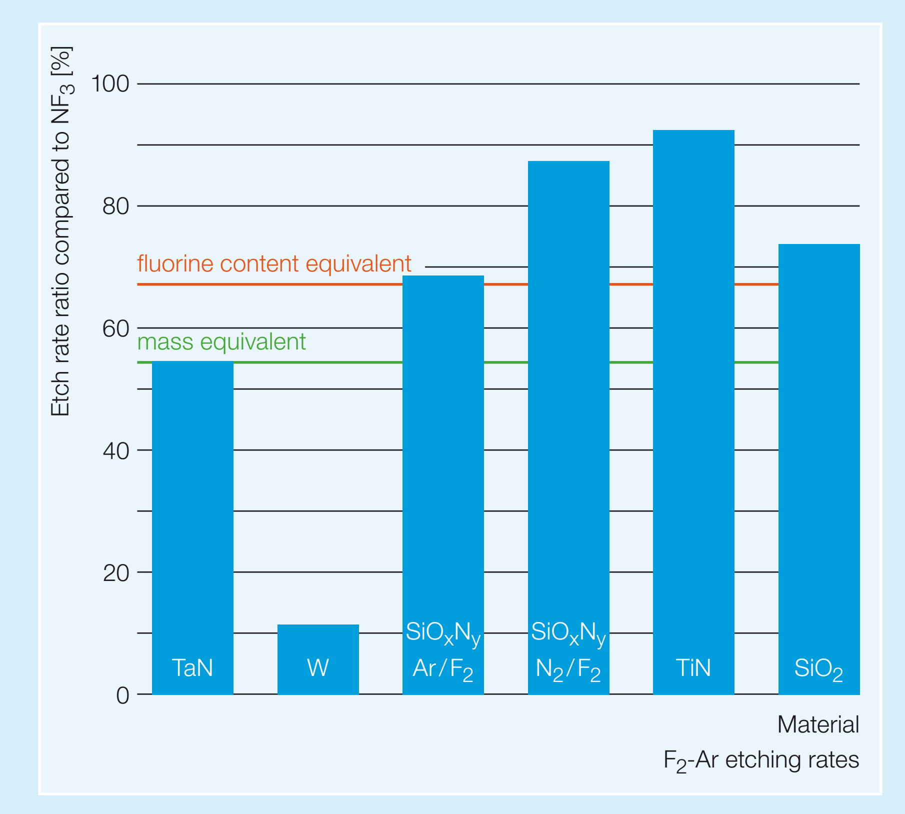


Fig. 15: Best etch ratio of 20 sccm F_2 in Ar compared to 20 sccm NF_3 best known method.



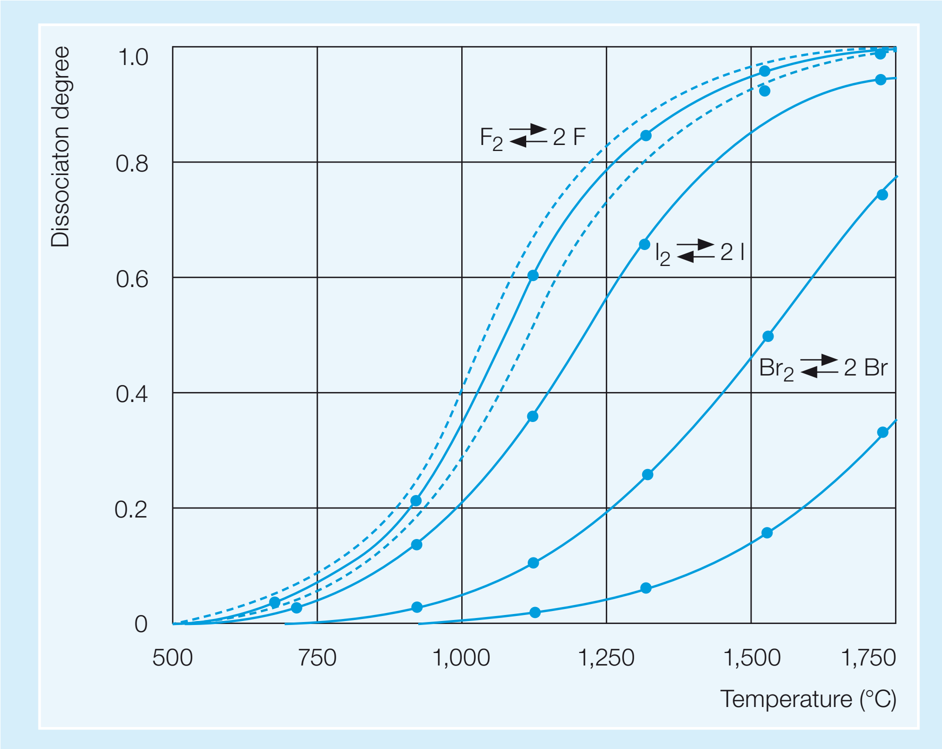


Fig. 16: Dissociaton degree of the halogens /18/.

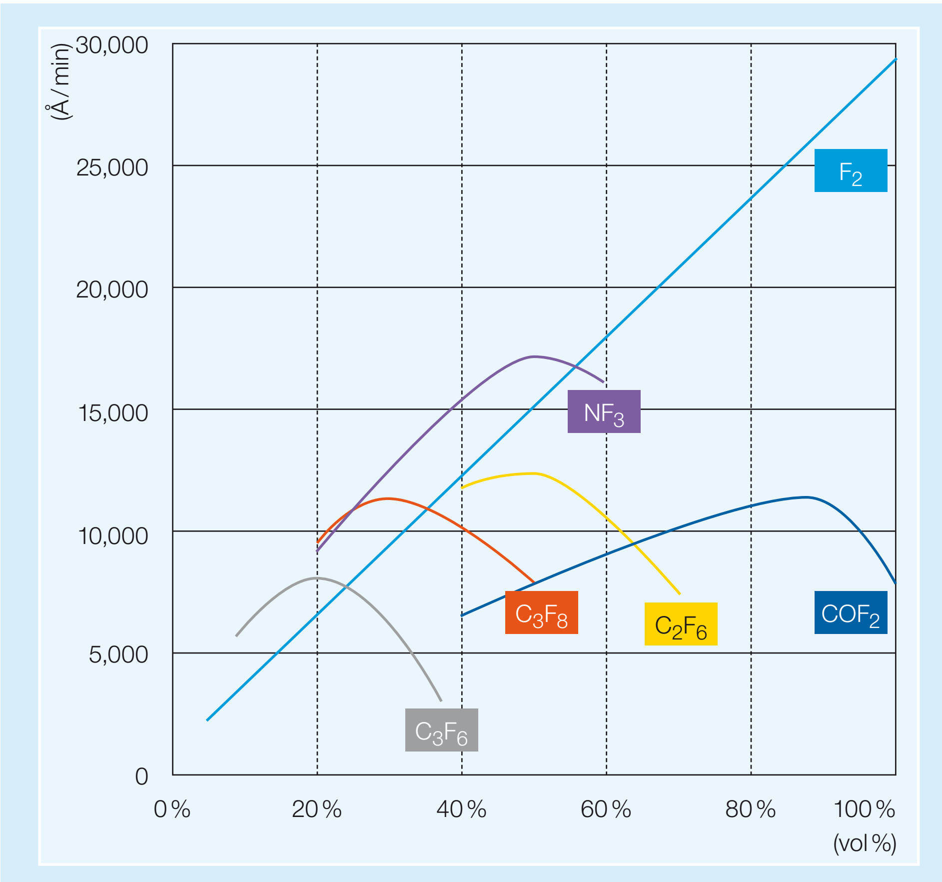


Fig. 17: Rite report etching comparison of different gases. /19/.

6 Toxicity

Fluorine gas is classified as a highly toxic gas for handling, use and transport. The established maximum limits of fluorine exposure reflects this. Please refer to the governing agency in the country where the fluorine is being used.

Threshold Limit Value (TLV)	1.0 ppm
Short Time Exposure Limit (STEL)	2.0 ppm
Permissible Exposure Limit (PEL)	0.1 ppm
Workplace Exposure Limits (WEL)	1.0 ppm

Fig. 18: Common established maximum limits of fluorine exposure.

TLVs or WELs are the maximum average airborne concentrations of a hazardous material to which healthy adult workers can be exposed during an 8-hour workday and 40-hour work week – over a working lifetime – without experiencing significant adverse health effects.

Under emergency conditions, the following maximum exposure limits are established.

Emergency Exposure Level (EEL) .	25 ppm for 5 min
Immediately Dangerous to Life and Health (IDLH)	25 ppm (NIOSH)

Fig. 19: Maximum limits of fluorine exposure under emergency conditions.

Established LC50 (lethal concentration 50%) values

LC50 (1h, rat) pure fluorine	185 ppm
LC50 (1h, rat) for 20% fluorine in nitrogen	925 ppm (calculated)
LC50 (1h, rat) for 10% fluorine in nitrogen	1,850 ppm (calculated)

Fig. 20: Established LC50 values.

Reference: ISO 10298 Determination of gas or gas mixture toxicity.

The Destructive Effects on Human Body Tissue are due to three Causes

- The immediate oxidizing effect of the fluorine
- The termic damage resulting from the heat generated when fluorine reacts with the tissue
- Poisoning of the tissue by hydrogen fluoride – this is formed when fluorine reacts with water in the tissue.

The effect to the human body resembles that of hydrogen fluoride. Hydrogen fluoride is a deep-acting protoplasmic poison. It is unlike other acids because it cannot be rapidly neutralized and can destroy tissue for several days after exposure to skin. The fluoride ion readily penetrates the skin, causing destruction to deep tissue layers including bone.

Since fluorine , even in small concentrations, is already detectable by its pungent odor, cases of poisoning are relatively rare. The gas is detectable by human smell at concentrations starting at 0.1 ppm.

Routes of Exposure

Inhalation

Inhalation of vapours is irritating to the respiratory system and may cause throat pain and cough. Aspiration may cause pulmonary oedema and pneumonitis. There is a risk of hypocalcemia with nervous problems (tetany) and cardiac arrhythmia. Symptoms after inhalation could be: breathing difficulties, sore throat, nose bleeding. Repeated exposure could result in chronic bronchitis.

Skin contact

Skin contact with fluorine causes severe burns and intoxication hazards by simultaneous inhalation of the product. There is a risk of shock due to the reduction of free available calcium (hypocalcemia) following the extent of the lesions. Symptoms after skin contact could be skin irritation, redness, swelling of tissue and burn.

Eye contact

Eye contact may cause permanent eye injury up to blindness and intoxication hazards by simultaneous inhalation of the product. Symptoms after eye contact could be: lachrymation, redness, swelling of tissue and burn. /20/

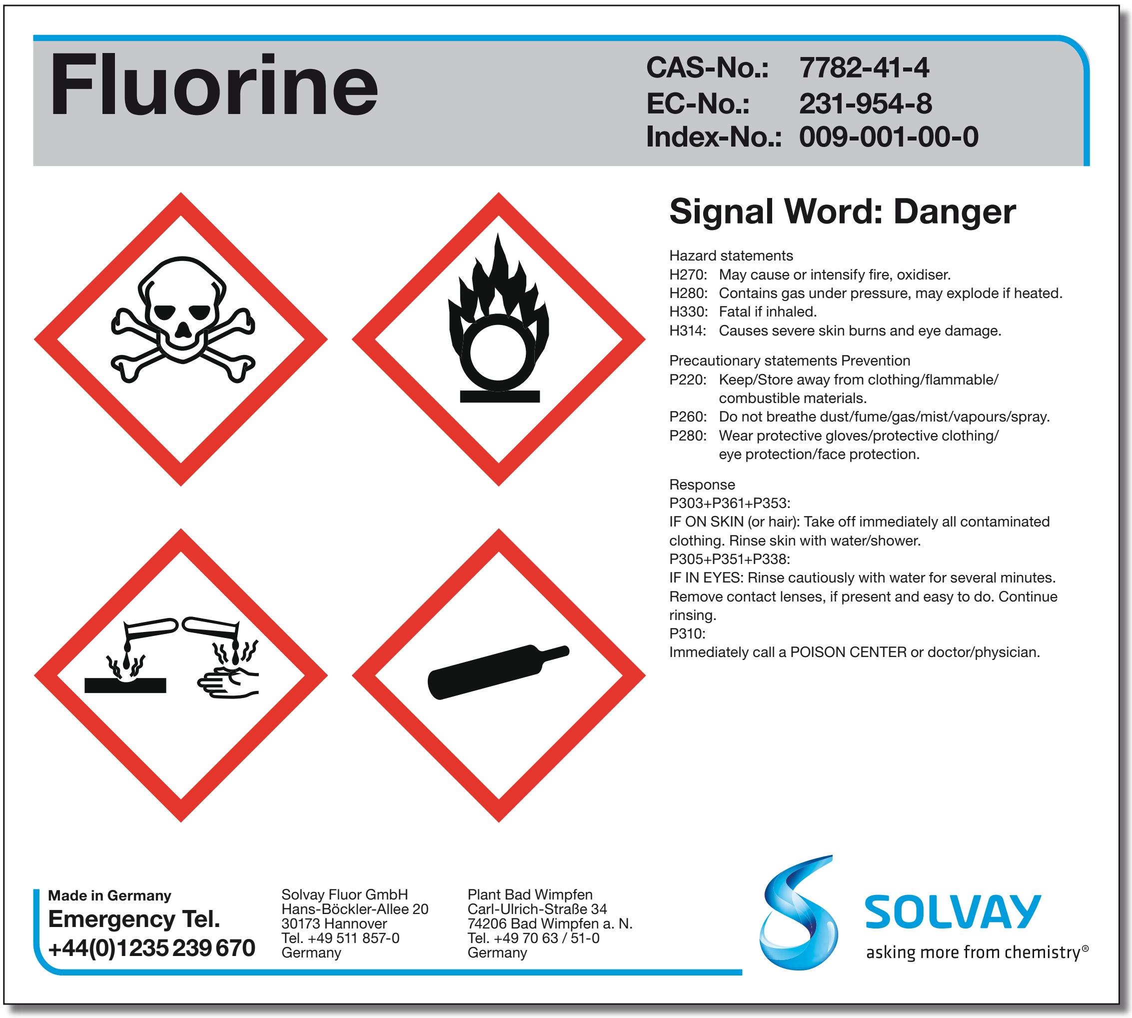


Fig. 21: Labeling according to the Global Harmonized System for dangerous goods from Wimpfen plant, Germany.

7 Shipping and Transport

Fig. 22: Bundle trailer.

Elemental fluorine is shipped by Solvay as compressed gas either pure or as a mixture with nitrogen (other gases for mixture on request). The product is available in individual cylinders, in stacks, bundle- or tube trailer. Fluorine cylinders are fitted with specially designed valves. The valve plug closure must be gas-tight and firmly attached to the valve (chain). Fluorine cylinders should never be emptied to the point where an internal vacuum is created, since this could cause other gases to be sucked inside. After emptying the cylinder its valve should be closed immediately. Please return empty cylinders for refilling.

Land transport

Compressed fluorine and fluorine mixtures in inert gases are authorized for shipment in containers with the appropriate service pressure. However, the LC_{50} of the mixture is used to determine the UN Number and the proper shipping name of the gas or gas mixtures. Certain shipping restrictions are linked to the UN numbers according to International transport regulations, namely;

- Pure 100 % fluorine is transported under UN1045 Fluorine, compressed. The transport is not authorized in tubes or pressure drums. The filling pressure is limited to 30 bar and the quantity of fluorine to a maximum of 5 kg in a single vessel.

Fig. 23: Packaging forms of fluorine gas.

- Mixtures containing fluorine with a LC_{50} of less than 200 ml/m³ (e.g. 92.5 % or more of F_2 in N_2) are transported under UN3306, compressed gas, toxic, oxidizing, corrosive, N.O.S. The transport is not authorized in tubes or pressure drums. Bundles containing fluorine and fluorine mixtures may be divided into assemblies (groups) of cylinders not exceeding 150 litres total water capacity.
- Mixtures containing fluorine with a LC_{50} of between 200 ml/m³ and 5,000 ml/m³ (e.g. between 3.7% and 92.5% of F_2 in N_2) are transported under UN3306, compressed gas, toxic, oxidizing, corrosive, N.O.S. but are authorized to be transported in tubes and pressure drums. /21/

Air Transport

IATA (International Air Transport Association) prohibits the shipment of dangerous goods identified by UN3306 and UN1045.

Sea Transport

Compressed fluorine and fluorine mixtures of all concentrations are permitted for sea shipment following provisions detailed in IMDG (International Maritime Dangerous Goods) Code.

Fig. 24: Fluorine cylinders are fitted with specially designed valves.

Fig. 25: Container volume.

		Cylinder				Bundle			Bundle Trailer*	Tube Trailer
Volume (water)	l	50	50	50	47	600	600	600	3,600	12,000
F_2 Concentration	%	10	20	100	20	10	20	100	20	20
Pressure	bar	150	140	28	75	150	140	28	140	140
F_2 Capacity	kg	1.19	2.22	2.22	1.12	14.28	26.64	26.64	160	634
Volume (gas)	l	7,500	7,000	1,400	3,525	90,000	84,000	16,800	504,000	1,680,000

** Bundle trailers are available from 6 (here calculated) to 24 bundles per trailer.*

Fig. 26: Valve connector specification for technical and electronical grade Fluorine.

	Technical grade (Brass)*				Electronic grade (Stainless steel)			
	DIN 477 No.8		CGA 679		CGA-DISS 728		JIS (Japan)	
	pneumatic	manual	pneumatic	manual	pneumatic	manual	pneumatic	manual
Asia	■	■			■	■	■	■
Europe	■	■			■	■		
USA			■	■	■	■		

** Stainless steel available on request.*

8 Environment

As Fluorine is a highly toxic gas every effort must be made to avoid contact with personnel and environmental releases. For more detailed information, please see the safety data sheet (SDS).

Because fluorine reacts with moisture, any release will form hydrogen fluoride and this should be taken into account in the control measures adopted.

As fluorine reacts with the moisture from ambient air and is transferred to hydrogen fluorine, F_2 has no ozone depleting (ODP) and no global warming potential (GWP). Therefore it is an ideal replacement gas in the semiconductor industry to sustitude high global warming gases like NF_3 (17,200 GWP) or PFC's like CF_4 (7,390 GWP) and C_2F_6 (12,200 GWP).

8.1 Product Stewardship for F_2

Solvay is a well known manufacturer and a global supplier of Fluorine and Fluorine gas mixtures.

Since Fluorine and its mixtures with other gases are toxic, Solvay has established a detailed product stewardship program for these products.

Within this product stewardship program Solvay supports its customers e.g. in the safe handling, transport and application of Fluorine and its mixtures with other gases.

In principle, for the three kinds of available supply packaging for these products, the following safety requirements are mandatory at the customer location:

In addition to the above mentioned support, Solvay offers to its customers technical training including emergency behavior before the first delivery starts.

Customers are highly recommended to take advantage of the support offered by Solvay within its product stewardship program to minimize risks on their end due to failures in installation or false handling.

Fluorine users shall have an Emergency Rescue Coffin Vehicle (ERCV) available on hand.

Fig. 27: Fluorine user safety requirements.

Packaging	**Fluorine user safety requirements for the packaging**	**Fluorine user safety requirements for gas destruction**
Cylinder	ERCV (Emergency Rescue Coffin Vehicle)	$CaCO_3$ point of use gas scrubber
Bundle	Gas cabinet	Al_2O_3 point of use gas scrubber
Bundle trailer/ISO-container	Sprinkler, ventilation	Central gas scrubber (wet or dry for high volumes)

8.2 Solvay Way

We believe that better chemical solutions need not come at the expense of the environment and have to respect people's lives.

We strive to offer employees a safe and secure working environment that encourages professional development, and maintain a regular dialogue with them in an atmosphere of trust. This exchange is particularly important as they are the key players in our responsible performance.

Our products, such as solutions keeping clothes clean, water purification, home heating solutions that reduce energy consumption or low energy road lighting, are designed to contribute to the quality of life and meet stakeholders' expectations regarding sustainable development. As a supplier to thousands of industries, we continually look at ways to further reduce our impact on the environment, asking chemistry to do more with less.

Because we commit to progress towards our stakeholders, in 2013 we launched Solvay Way, our sustainable development policy that provides a framework to guide and measure our success at meeting our objectives.

Fig. 28: More information www.solvay.com –> Sustainability –> Solvay Way

9 Solvay – The Specialists for Fluorides

Solvay Special Chemicals

Solvay Special Chemicals is active in a range of markets: Energy Conservation and Storage, Semicon/Electronics, Agro & Food, and Performance Materials. It is a world leader in Fluorine Chemistry and maintains this position through innovation, utilising its distinct knowledge for high-end applications such as heat exchangers and Li-ion batteries. The Global Business Unit (GBU) has a global presence: more than 35 sites, HQ in Seoul and 2,300 employees spread across four continents.

Professional Fluorochemistry

Solvay Special Chemicals stands for a professional team of experienced chemists and a sales staff committed to taking on any challenge and to solving problems in close co-operation with our clients. With our state-of-the-art application technologies we offer a full range of fluorochemicals, using fluorspar produced in-house. In line with our commitment to managing challenges we further focus our Fluor business on high value-added specialty products to bring value to our customers.

Fig. 29 Plant Bad Wimpfen, Germany.

Fig. 30 Plant Onsan, South Korea.

Product range of fluorine compounds from GBU Special Chemicals

Product Range Hydrofluoroalkanes

- SOLKANE® 227 pharma
  SOLKANE® 134 a pharma
- SOLKAFLAM® 227
- SOLKANE® 134 a
  SOLKANE® 143 a
  SOLKANE® 227 tech
  SOLKANE® 365 / 227
  SOLKANE® 365mfc
  SOLKANE® 404A
  SOLKANE® 407A
  SOLKANE® 407C
  SOLKANE® 410
  SOLKANE® 507
  SOLKANE® 22 L
  SOLKANE® 22 M
  SOLKANE® 141 b
- SOLKATHERM® SES24
  SOLKATHERM® SES30
  SOLKATHERM® SES36
- SOLVOKANE®
  SOLVOKANE® S
  SOLVOKANE® E1.5

Brominated Polyols

- IXOL® B 251
  IXOL® M125

HF and Inorganic Fluorides

- Ammonium hydrogenfluoride
- Ammonium hydrogenfluoride electronic grade
- Barium fluoride
- Calcium fluoride
- Cryolite, synth powder
- Fluoroboric acid
- Hydrofluoric acid
- Hydrogen fluoride
- Hydrogen fluoride electronic grade
- Lithium cryolite
- Potassium cryolite
- Potassium fluoroaluminate
- Potassium fluoride solution
- Potassium fluoroborate
- Potassium hydrogenfluoride
- Sodium hydrogenfluoride

Aluminium Brazing Fluxing Agents

- NOCOLOK® Flux
  NOCOLOK® Flux Drystatic
  NOCOLOK® Sil Flux
  NOCOLOK® CB Flux
  NOCOLOK® Cs Flux
  NOCOLOK® Zn Flux
  NOCOLOK® Li Flux
  NOCOLOK® Li Flux Drystatic

Aluminium Brazing Supporting Products

- NOCOLOK® Flux plus binder mixture
  NOCOLOK® Sil Flux plus binder
  NOCOLOK® Binder
  NOCOLOK® Thickener
  NOCOLOK® Precoating
  NOCOLOK® Flux Paste

Fluorine Specialties

- Elemental Fluorine (F_2)
  Elemental Fluorine (F_2), electronic grade
- Fluorine Nitrogen Mixtures (F_2/N_2)
  Fluorine Nitrogen Mixtures (F_2/N_2), electronic grade
- Iodine pentafluoride (IF_5)
- Sulphur Hexafluoride (SF_6)
  Sulphur Hexafluoride (SF_6), electronic grade

Materials for Lithium Ion Batteries

- Monofluoroethylene carbonate (F1EC)

Organic Intermediates

- CF_3 Molecules:
  4-Ethoxy-1,1,1-trifluoro-3-buten-2-one (ETFBO)
  Trifluoroacetic acid (TFA)
  Trifluoroacetylchloride (TFAC)
  Trifluoroacetic anhydride (TFAH)
  Trifluoroacetic acid ethylester (TFAEt)
  1,1,1-Trifluoroacetone (TFK)
  Trifluoroacetic acid methylester (TFAMe)
  Trifluoroacetic acid isopropylester (TFAiP)
- CF_2 Molecules:
  1H-Pyrazole-4-carboxylic-3-(difluoromethyl)-1-methyl-ethylester (DFMMP)

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