

## TI-021 – Does fluorine free mean no Fluorine?

The term "fluorine-free" is increasingly used these days in connection with firefighting foam agents.

However, the understanding of what is meant by this term stretches between "products to which no fluorine compounds have been added intentionally and with the purpose of increasing performance" all the way to "no - i.e. zero – i.e. not a single molecule of - (organically bound) fluorine".

But what can users realistically expect from a "fluorine-free" firefighting foam concentrate? Is zero Fluor organic compounds (still) possible?

### Inorganic Fluorine Chemicals:

In principle, a distinction is made between so-called **inorganic compounds** and **organic compounds** of the element fluorine. Inorganic fluorine compounds do occur in nature e.g. as salts (fluorides) or minerals (e.g. fluorite). Water-soluble salts are contained in natural drinking water in traces as well and are used, for example, for caries prophylaxis in medical preparations, toothpastes or are in some countries even added to drinking water.



Fluorite, a Fluor mineral – by Rob Lavinsky, iRocks.com – CC-BY-SA-3.0, CC BY-SA 3.0; <https://commons.wikimedia.org/w/index.php?curid=10155362>

Inorganic fluorine compounds **do not belong to** the group of fluorine compounds known as **PFAS<sup>1</sup>** and **are therefore not subject to the legal regulations** concerning this group, hence firefighting agents!

### Organic Fluorine Compounds

PFAS are organic fluorine compounds characterized by fluorine atoms being exclusively bonded to carbon. In contrast to many inorganic fluorine compounds, their organic counterparts – the so called **PFAS - do not occur in nature**. They are extremely stable and are considered non-degradable (persistent). All fluorine compounds used in firefighting agents belong to this group.

PFAS are used in large quantities<sup>2</sup> in many industries and applications and therefore are – also because of their persistence - now widespread in the environment globally.

<sup>1</sup> PFAS = Perfluoro alkyl substances means the entirety of all chemicals consisting of or containing carbon-Fluorine bonds

<sup>2</sup> According to ECHA (rest\_pfhxa\_bd\_draft\_19694\_en.pdf) about 64% of all emissions of short chain C6-Fluoro compounds are

### The Detection Limit

Envision an analytical method as a magnifying glass used to look into a solution to detect the type and amount of organic fluorine compounds present in it. Like any given magnifying glass, each analytical method has only a certain "magnification" and is blind to everything that is too "small" for it. This is called *the measurement- or detection limit*.

But the detection limit also depends on the test environment or *background*: finding a small bread crumb on a white tablecloth it is not a problem, but doing so on a lawn would be almost hopeless.

Not only does the absolute size of the particle (which in our example would correspond to the magnification of the magnifying glass) influence the detection limit, but also the test environment. Analysts call this "*matrix effects*". The measuring limit of individual PFAS (e.g. PFOS or PFOA) in drinking- or groundwater (in our picture the white tablecloth) is very low and can be as low as 0.001µg/kg (=0.001 ppb), depending on the laboratory.

In firefighting foam agents or fire water (in our example the lawn), on the other hand, a realistic measurement limit is 1-10ppb, i.e. 1000-10000 times higher.

A measurement limit >0 therefore means that one cannot say whether a sample is actually fully free of fluorine compounds, but only that it does not contain more than the value of the measurement limit.

### PFAS Analysis

There are in general two different options to analyse for PFAS in a sample material:

#### Analysis of individual substances

This method, for example, is required to determine the content of individual substances such as PFOS and PFOA, or small groups of substances such as the group of C9-C14 perfluoro carboxylic acids or their precursors in firefighting agents, as accurately<sup>3</sup> as

emitted by the paper industry, 35,8% by the textile industry and 0,2% by firefighting foams.

<sup>3</sup> This means an analytical resolution good enough to safely meet the legal limits

## Technical Information

possible in accordance with current legal regulations<sup>4</sup>. For this purpose, reference substances are needed for any molecule which is to be determined in order to be able of assigning a measurement signal to a particular substance and its content in a sample without any doubt.

Currently, about 30 individual substances can be determined in this way, but with a rather high accuracy of 1-10µg/kg (=1-10ppb).

### Measuring Total Organic Fluorine

If the type or identity of fluorine compounds present in a sample is unknown, or if the target is to prove a sample doesn't contain any fluorine compounds (within the boundaries of what is technically possible), one has to analyse for the *total organic fluorine content*.

One method for the determination of the total content of organically bound fluorine is *TOPA*<sup>5</sup>. Here, all organic fluorine compounds present in a sample are chemically converted into known degradation end-products<sup>6</sup> for which there are also reference substances. Their contents are then measured as in the individual determination method.

Care must be taken to ensure that the limit value applicable to the respective (legally regulated) group of substances is observed, i.e. the sum of the determination limits of all substances in a group must still be significantly lower than the legal limit value for this group.

In another method<sup>7</sup>, samples are incinerated at high temperatures in pure oxygen and the amount of the formed fluoride is then measured. This test is not substance specific.

### So what does „Fluorine-free“ actually mean?

In spite of the many suggestions from the industry, the legislator has so far not attempted to define the term "fluorine-free". However, we know from the above that "fluorine-free" cannot mean the *complete absence of any fluorine compounds*, because we cannot measure down to a zero level. The detection limits of any method are always greater than zero.

In the case of firefighting foam agents, or premixes made up thereof or fire runoff waters, a further problem arises from the fact that they have a matrix that is very unfavorable for trace analysis. In our breadcrumb example, this would compare to a particularly high lawn, which pushes the detection limits to significantly higher numbers.

It is therefore *technically impossible* to prove that a firefighting foam concentrate actually does not contain any fluorine compounds. Hence, "fluorine-free" cannot mean zero content of fluorine organics in the sense of not a single molecule.

### „Fluorine free“ foams in the environment

This becomes particularly precarious if traces of fluorine compounds are suddenly found in the soil, water or groundwater after a foam application, even though a "fluorine-free" foam extinguishing agent has been used. However, this does not necessarily mean that the foam concentrate is contaminated; other reasons may be possible:

One possible reason could of course be a contaminated firefighting foam agent, but other root causes are thinkable too:

- the detection limit for PFAS e.g. in groundwater is much lower than in the firefighting foam agent itself, or
- fluorine compounds are not only present in firefighting foam agents, but also in an almost infinite number of products.
- PFASs are also widespread in the environment and can even be detected in drinking water.

One could now assume that a finding below the legally anchored limit values is no cause for concern. Unfortunately, this is not the case for two reasons:

- There is no harmonized or legally binding Europe-wide definition of the term "fluorine-free" in connection with foam extinguishing agents available as guidance.
- there is no harmonised legal standard in the EU with harmonized thresholds for soil, natural waters or groundwater. Thus, it is often up to local authorities to set limit values for tolerable contamination or contamination requiring remediation.

Thus, the detection of fluorine compounds in orders of magnitude of a few hundredths or thousandths of the legal thresholds can nevertheless lead to remediation being scheduled and to disputes about its costs.

The limiting values discussed for environmental contamination are sometimes low enough that even the background contamination now present in water, packaging materials, equipment or storage vessels can lead to them being reached or exceeded.

### „Fluorine-free“ foams in international standards

But how can "fluorine-free" be understood?

There are various approaches to defining the term "fluorine-free". The European foam standard EN1568:2018 states: "*fluorine free foam concentrates (F3): these foam concentrates are dedicated to meet fire*

<sup>4</sup> (EU) 2019/1021; (EU) 2017/1000; (EU) 2020/784; (EU)2021/1297; see also our Technical Information Nr. 64 „Regulation of per- and polyfluorinated substances in Europe “

<sup>5</sup> TOPA= Total Oxidizable Precursor Assay

<sup>6</sup> These are the perfluoro carbon acids

<sup>7</sup> TOF = total organic fluorine: electrochemical or chromatographic detection of Fluorides

## Technical Information

performance ratings and are targeting applications similar to AFFF and/or AR-foams without using fluoro-organic compounds. These foam concentrates are based upon mixtures of hydrocarbon surface-active agents and non-fluorine containing stabilizers. "

Like other similar definitions (e.g. UL 162), it is assumed that organo-fluorine compounds can only get into foaming agents by deliberate addition. This is not the case, however, because many other sources of low-level contamination can also be considered (e.g. water, packaging materials, equipment or storage vessels).

### How we define „Fluorine-free“

Due to the lack of official/legal definition/-s of the term “fluorine free” and in the course of open and clear communication, we have therefore decided to develop our own definition of what we understand by “fluorine-free” and can guarantee our customers:

**We define fluorine-free products as being manufactured without the intentional addition of fluoro-organic compounds (PFAS) for the purpose of improving performance in such a way that, according to current commercially available analysis, they do not contain any fluoro-organic substances in excess of the regionally ubiquitous background contamination (e.g. in the drinking water used for production).**

### What can users do?

Users of foam extinguishing agents can currently minimise their risk by taking the following measures<sup>8</sup>:

1. thorough *professional*<sup>9</sup> cleaning of all equipment by experienced service providers before switching to fluorine-free extinguishing agents and (ideally) replacement of all plastic parts that have been in contact with fluorine-containing extinguishing agents;
2. only refill systems and vehicles with fluorine-free foam agents if PFAS contamination is below detection limit;
3. purchase of F3 foam extinguishing agents only from manufacturers who can prove physical separation of production lines for fluorine-free foam agents from those for fluorine-containing products.

<sup>8</sup> Please contact us for further technical information on this subject

<sup>9</sup> Of many cleaning recommendations circulating on the market, only a few are really suitable for reducing the residual fluorochemical build-up after cleaning to such an extent that the

4. proof of the fluorine content in fluorine-free products through current testing by an accredited laboratory.
5. complete and up-to-date documentation of all measures for submission to the authorities.

### Disclaimer

All information given in this technical information are based on our best knowledge at the time of this revision. This Technical Information remains subject to alterations and revisions. Please do not hesitate to contact us for the most recent edition.

level of contamination of fluorine-free extinguishing agents can be reduced below the detection limit. Rinsing with water alone is not suitable for this in most cases. Please contact us for recommendations on this.

				
<b>Main Office Hamburg</b> Liebigstraße 5 D-22113 Hamburg Tel.: +49 (0)40 73 61 68-0 Fax: +49 (0)40 73 61 68-60	<b>Sales Office Hannover</b> Hartenbrakenstraße 54 D-30659 Hannover Tel.: +49 (0)511 768 358 45 Fax: +49 (0)511 768 358 46	<b>Sales Office Jena</b> Wöllnitzer Straße 97a 07749 Jena/Germany Tel.: +49 (0)3641 63538-57 Fax: +49 (0)3641 63538-59	<b>Office Frankenthal</b> Siemensstraße 4 D-67227 Frankenthal Tel.: +49 (0)6233 3796 – 605 Fax: +49 (0)6233 3796 – 622	<a href="mailto:info@sthamer.com">info@sthamer.com</a> <a href="http://www.sthamer.com">www.sthamer.com</a>