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 fluorides are present in traces in natural waters and are used for caries prophylaxis in medicines, toothpastes or are even added to drinking water in some countries.

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***[1] 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[2] in many industries and applications and therefore are – also because of their persistence - now widespread in the environment globally.

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 detection 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[3] as possible in accordance with current legal regulations[4]. For this purpose, reference substances are needed for any molecule which is to be to be determined in order to

[1] PFAS = Perfluoro alkyl substances means the entirety of all chemicals consisting of or containing carbon-Fluorine bonds

[2] According to ECHA (rest_pfhxa_bd_draft_19694_en.pdf) about 64% of all emissions of short chain C6-Fluoro compounds are emitted by the paper industry, 35,8% by the textile industry and 0,2% by firefighting foams.

[3] This means an analytical resolution good enough to safely meet the legal limits

[4] (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 "

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***[5]. This method does not look for particular organic fluorine compounds but chemically converts all of them into their degradation end-products[6]. Hence, any C6-compound is converted into the C6-perfluoro carbon acid[7], any C8-compound gives the corresponding C8-acid[8] etc..

The carbon acids of organic fluorine compounds are a much smaller group of chemicals compared to the group of their precursors, hence easier to identify and quantify (e.g. by comparison of their detection signals to those of reference substances). The information which particular organic fluorine compound a certain detected carbon acid originated from gets lost in the process for the benefit of

a) not needing a pure reference substance for each and every substance that might be in a sample and
b) therefore, being able to also detect unknown organic fluorine compounds.

Care must be taken to ensure that the sum of the detection limits of all individual substances in a group must still be significantly lower than the legal threshold for this group.

In another method[9], organic fluorine compounds are completely converted into inorganic Fluoride by incineration of sample material at high temperatures in pure oxygen atmosphere. The resulting Fluoride is then analysed. 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, premixes made up thereof or fire runoff waters, yet another 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 present*.

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

a) the detection limit for PFAS e.g. in groundwater is much lower than in the firefighting foam agent itself, or
b) fluorine compounds are not only present in firefighting foam agents, but also in an almost infinite number of products.
c) 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 limiting values is no cause for concern. Unfortunately, this is not the case for two reasons:

1) There is no harmonised or legally binding Europe-wide definition of the term "*fluorine-free*" in connection with foam extinguishing agents available as guidance.
2) there is no legal standard in the EU harmonizing thresholds for PFAS in soil, natural waters or groundwater. Hence, it is often up to local authorities to set the limits for a tolerable contamination or a contamination level requiring remediation.

The detection of fluorine compounds in orders of magnitude of a few hundredths or thousandths of the legal thresholds can nevertheless result in remediation being scheduled and in disputes about associated costs.

[5] TOPA= Total Oxidizable Precursor Assay
[6] These are the perfluoro carbon acids
[7] Perfluor hexanoic acid - PFHxA
[8] Perfluor octanoic acid - PFOA
[9] TOF = total organic fluorine: electrochemical or chromatographic detection of Fluor*ides*

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 reaching or even exceeding them.

„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 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, however is not the case, 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[10]:

1. thorough ***professional***[11] 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.
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.

[10] Please contact us for further technical information on this subject

[11] 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 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.

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