TOTAL ORGANIC FLUORINE IN TEXTILE MATERIALS: FALSE POSITIVE PFAS RESULTS FROM USE OF REACTIVE DYES FOR CELLULOSIC FIBRES

Over the past few years, numerous regulations and proposals have been enacted to restrict the use of poly and perfluorinated substances (PFAS) in various matrices, including textiles. Among the most significant restrictions is AB 1817, passed by the state of California, which introduced a radical change from the past. This law adopts a new method to test for contamination or intentional use of PFAS in fabrics, based on the presence of total organic fluorine (TOF); an analysis known as 'untarget'.
The 'untarget' analysis is an innovative and recently applied technique that allows for a wide-range screening of all substances present in the sample under investigation, including high levels of organic fluorine. This analytical approach contrasts with conventional analyses, which focus on the search for specific PFAS molecules ('targets'), for which analytical standards are available. Unfortunately, to date, of the approximately 10,000 PFAS molecules synthesized, only a few dozen standards are available that can be used for 'target' analyses. The regulatory limit for this new parameter, based on a non-specific ('untarget') approach to PFAS detection and quantification, will be set (e.g. California AB 1817) at 100 mg/kg from January 2025 and decrease to 50 mg/kg from January 2027.

TOF technology for analytical search and verification is extremely reliable in identifying the presence of PFAS in materials, especially when the traditional target search for individual substances does not detect free PFAS in textiles. When TOF results are extremely high (even above 1,000 mg/kg), there is no doubt about the presence of perfluorinated substances. However, if the contamination is minor, with values close to or below 50 mg/kg, further investigation is necessary to determine the sources of pollution of the tested materials.

With this in mind, TIL carried out a research project in collaboration with the company Fratelli Ciampolini spa in Prato (a company specialized in fabric dyeing and finishing processes). The research aims to verify the impact of some reactive dyes for cellulosic fibers on the TOF parameter. In fact, it is known that some of these dyes have the presence of fluorine in their molecules; for this reason, both the dyes themselves and their dyeing applications were subjected to the 'untarget' test used to detect the presence of PFAS; specifically, Total Organic Fluorine (TOF) and Total Fluorine (TF) were determined.

Test & Innovation Lab

Reactive dyes for fluorine-containing cellulosic fibers

There are numerous chemical classes of reactive dyes for cellulosic fibres that contain fluorine in their molecules. These dyes are still widely used in the dyeing of cotton-type textiles and man-made cellulosic fibres.
Below are the chemical classifications of these dyes and their dyeing functionality:

Chemical classification	**Abbreviation**	**Reactive group functionality**
ammino-fluoro-s-triazine	MFT	mono functional
difluoro-chloro-pyrimidine	DFCP	mono functional
fluoro-chloro-methyl-pyrimidine	FCMP	mono functional
monofluoro-s-triazine and vinylsulphonics	MFT-VS	hetero-bifunctional
monochloro-s-triazine and monofluoro-s-triazine	MCT-MFT	hetero-bifunctional
monochloro-s-triazine and difluoro-chloropyrimidine	MCT-DFCP	hetero-bifunctional
difluoro-chloropyrimidine and vinylsulphonics	DFCP-VS	hetero-bifunctional
monofluoro-s-triazine and bis(vinylsulphonics)	MFT/bis-VS	hetero-bifunctional

Fig. 1 - TIL elaboration

The presence of the (organic) fluorine atom within the molecule of these dyes in no way classifies them as PFAS substances. In fact, the most recent definition of PFAS is as follows: 'Per and polyfluoroalkyl substances (PFAS) are defined as any substance that contains at least one fully fluorinated methyl (CF3-) or methylene (-CF2-) carbon atom (without any H/Cl/Br/I attached to it).'
This definition (OECD - Organization for Economic Co-operation and Development), released in 2021, thus allows the identification of around 10,000 substances that can instead be classified as PFAS.

If the TF or TOF analysis obtains an analytical screening for the 'untarget' detection of the possible presence of PFAS products, it becomes of paramount importance to identify whether the source of the fluorine is indeed from PFAS molecules, or from other organic molecules that, although containing fluorine, do not belong to the PFAS category. Especially considering the upcoming legal restrictions of PFAS, such as the legislation of California and other US states or the proposed restriction of the European Union.

The two PFAS restrictions in the US laws and the European proposal are in this approach 'different', in fact:

- The California law (AB 1817), sets TOF limits of 100 and 50 mg/kg and does not allow any exemption for articles exceeding these limits.
- The European proposal, on the other hand, provides for the following exemption if the proposed limit of 50 mg/kg TF is exceeded: 'This proposed restriction shall apply unless the manufacturer, importer or downstream user demonstrates to inspectors that the product contains fluorine from substances other than those covered by this proposed restriction.'

In view of this, it is of critical importance to verify the impact of TOF and TF measures on the class of 'NON-PFAS' substances, which are widely used in cellulosic fibre dyeing processes.

Analyses for TF and TOF determination in reactive dyestuffs

Many reactive dyes for cellulosic fibres containing fluorine were subjected to analysis for the determination of **TF** in the dyestuffs in question using the CIC (Combustion Ion Chromatography) technique, following the procedures described in EN 17813 – ASTM D7359.
The test for the possible presence of inorganic fluorine (**IF**) was carried out by leaching/solubilization in an aqueous medium of the dyestuffs and subsequent determination of the fluoride ion concentration by potentiometry with a specific ion electrode.
The **TOF** value was calculated by subtraction of the inorganic fluorine (**IF**) from the **TF** value.

The impossibility of tracing the chemical structure of many of the 51 commercial dyes examined with sufficient certainty (Colour Index Numbers - CAS Numbers), required the use of an 'arbitrary' description for these dyes.

The following table shows the results obtained on the tested dye materials.
TF and **TOF** values were considered to be overlapping, as the contribution of inorganic fluorine (**IF**) in all samples was very low and close to the Limit of Quantification (LOQ) of 2 mg/kg.

Dye	TF/TOF content (mg/kg)	Dye	TF/TOF content (mg/kg)
1- Reactive dye DL amber color	18.543	16-Reactive dye HN brown color	12.536
2- Reactive dye DL olive color	8.486	17-Reactive dye HN ocean blue color	1.033
3- Reactive dye DL solid-red color	7.837	18-Reactive dye HN navy blue-2 color	3.314
4- Reactive dye HN blue color	11.832	19-Reactive dye HN balck-1 color	888
5- Reactive dye DL blue color	19.075	20-Reactive dye HN black-2 color	938
6- Reactive dye CT black-1 color	186	21-Reactive dye HN red-1 color	6.963
7- Reactive dye DL bright Yellow color	20.449	22-Reactive dye HN yellow- 1 color	571
8- Reactive dye DL bright red color	17.371	23-Reactive dye HN orange color	424
9- Reactive dye DL orange color	15.9767	24-Reactive dye HN red-2 color	776
10-Reactive dye DL marine color	22.734	25-Reactive dye HN scarlet color	721
11-Reactive dye DL red color	37.511	26-Reactive dye HN deep red color	14.306
12-Reactive dye HN lemon yellow color	16.368	27-Reactive dye CT black- 2 color	678
13-Reactive dye HN navy blue-1 color	1.617	28-Reactive dye HN olive color	20.288
14-Reactive dye ZR black color	719	29-Reactive dye HN red-3 color	2.662
15-Reactive dye HN bright turquoise color	1.295	30-Reactive dye DR bright violet color	630,6

Dye	TF/TOF content (mg/kg)	Dye	TF/TOF content (mg/kg)
31-Reactive dye DR scarlet color	987	42-Reactive dye DR green color	562
32-Reactive dye HN Atlantic blue color	548	43-Reactive dye DR bright red color	566
33-Reactive dye DR yellow-1 color	532	44-Reactive dye DR orange color	1.516
34-Reactive dye HN yellow-2 color	13.063	45-Reactive dye DR yellow-2 color	899
35-Reactive dye CT marine color	746	46-Reactive dye DR carmine color	614
36-Reactive dye CD blue color	19.316	47-Reactive dye DR crimson color	894
37-Reactive dye DR turquoise blue color	1.405	48-Reactive dye DR black-2 color	492
38-Reactive dye DR blue color	5.609	49-Reactive dye DR black-3 color	1.330
39-Reactive dye DR black-1 color	2.492	50-Reactive dye DR bright orange color	738
40-Reactive dye DR deep red color	616	51-Reactive dye DR red color	727
41-Reactive dye DR bright blue color	1.624		

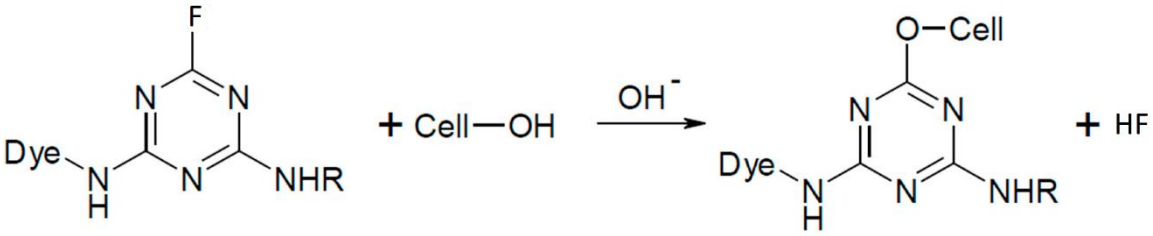
Fig. 2 – TIL elaboration

High TF and TOF values confirm the presence of organic fluorine (fluorine-carbon bond) in all molecules of the tested dyes. The differences in the quantitative values found between the dyes can be attributed to the various weight ratios between the fluorine present in the individual molecules and the molecular weight of the respective dyes.

Analyses for TF and TOF determination in cellulosic fabrics dyed with fluorine-containing reactive dye stuffs

The teorical results of TF and TOF in dyed fabrics, calculated on the basis of dye percentages applicable to the fibre, suggest extremely high fluorine contents (as can be seen in the specific column of the following tables). This situation could lead to restrictions based on TF and TOF contents being incorrectly correlated with the presence of PFAS, resulting in a so-called 'false positive' situation.

It is well known that the fluorine present in reactive dyes is an atom embedded in the 'reactive group' of the molecule itself, which is also referred to as the 'leaving group'. This means that this component of the molecule, following the reaction between fibre and dye, leaves the structure of the dye itself and is found in the dye bath as a fluoride anion (alkaline environment).



For this reason, experimental TF/TOF results on textile materials dyed with this type of dye stuff should show much lower values than those that were theoretically calculated.

To verify the above, four of the listed dyes were selected, characterised by amounts of TF/TOF in the molecule that could be defined as low, medium, high and very high.
For each of the four dyes, dyeing tests were performed at varying concentrations of 0.1%, 1%, 2% and 3% weight/fibre dye.
The dyeing was carried out following the usual pad-batch dyeing procedures, adapted to the various types of reactive dyes used.
The fabric subjected to dyeing was a 100% cotton fabric, GOTS certified.
The results of the experimental fabric tests are reported in the following tables.

17- Reactive dye HN ocean blue color - TF content 1,031 mg/kg

Dyeing tests (fabrics)	Theoretical TF content (mg/kg)	Dyed fabric: TF/TOF (mg/kg)
100% GOTS cotton fabric - **undyed**	//	**< LOQ ***
17-Reactive dye HN ocean blue color– **dye 0,1%**	1,0	**11,2**
17-Reactive dye HN ocean blue color – **dye 1%**	10,3	**6,6**
17-Reactive dye HN ocean blue color – **dye 2%**	20,7	**6,8**
17-Reactive dye HN ocean blue color – **dye 3%**	31,0	**7,3**

Fig. 3 – TIL elaboration
LOQ (Limit of quantification): 5 mg/kg

2- Reactive dye DL olive color - TF content 8,486 mg/kg

Dyeing tests (fabrics)	Theoretical TF content (mg/kg)	Dyed fabric: TF/TOF (mg/kg)
2- Reactive dye DL olive color – **dye 0,1%**	8,5	**5,8**
2- Reactive dye DL olive color – **dye 1%**	84,9	**10,5**
2- Reactive dye DL olive color – **dye 2%**	169,7	**13,4**
2- Reactive dye DL olive color – **dye 3%**	254,6	**15,4**

Fig. 4 - TIL elaboration

12- Reactive dye HN lemon yellow color - TF content 16.366 mg/kg

Dyeing tests (fabrics)	Theoretical TF content (mg/kg)	Dyed fabric: TF/TOF (mg/kg)
12-Reactive dye HN lemon yellow color – **dye 0,1%**	16,4	**6,9**
12-Reactive dye HN lemon yellow color – **dye 1%**	163,7	**10,4**
12-Reactive dye HN lemon yellow color – **dye 2%**	327,4	**12,9**
12-Reactive dye HN lemon yellow color – **dye 3%**	491,0	**14,2**

Fig. 5 - TIL elaboration

11- Reactive dye DL red color TF 37.509 mg/kg

Dyeing tests (fabrics)	Theoretical TF content (mg/kg)	Dyed fabric: TF/TOF (mg/kg)
11-Reactive dye DL red color – **dye 0,1%**	37,5	**7,3**
11-Reactive dye DL red color – **dye 1%**	375,1	**9,5**
11-Reactive dye DL red color – **dye 2%**	750,2	**14,8**
11-Reactive dye DL red color – **dye 3%**	1.125,3	**12,9**

Fig. 6 - TIL elaboration

The results obtained, described in the tables above (Nos. 3-6), confirm the above hypothesis. The experimental values of residual organic fluorine (TF/TOF) in fabrics dyed with dyes characterized by amounts of TF/TOF in the molecule classified as low, medium, high and very high, are at low values and are always below the more stringent limits of the PFAS restrictions in the various legislations, including that of California (January 2027) and the current proposals in EU legislation, which set a limit of **50 mg/kg**.

As a further investigation, we also wanted to analyse the influence of the final post-dyeing phases; these phases consist of washing and rinsing for the elimination of the dyeing electrolytes, and above all the **soaping** phases in an aqueous bath at high temperature, which are **useful for the elimination of the reactive dye not bound by covalent chemical bond (hydrolysed dye**) from the

fibre. To do this, dyeing tests were carried out with the 4 dyes described above, without performing the soaping steps.

Dyeing test without soaping	Fabric: Total Fluorine (TF) (mg/kg)	Fabric: Total Organic Fluorine (TOF) (mg/kg)
17-Reactive dye HN ocean blue color - dyeing 2% - without soaping step	10,3	6,7
2- Reactive dye DL olive color - dyeing 2% - without soaping step	110,3	11,6
12-Reactive dye HN lemon yellow color dyeing 2% - without soaping step	153,1	12,9
11-Reactive dye DL red color - dyeing 2% - without soaping step	101,3	13,4

Fig. 7 – TIL elaboration

As can be seen from Table 7, the presence of high levels of Total Fluorine (TF) determined by the CIC technique is evident. On the other hand, the concentrations of Total Organic Fluorine (TOF), calculated by subtracting the inorganic fluorine (IF) from the TF values, are very low. It is also confirmed that any residues of hydrolyzed dyes (not fixed to the fibers), present in the textile materials, do not contribute to a significant increase in TOF levels.

Conclusions

The aim of this study is to verify how the use of reactive dyes for cellulosic fibres containing fluorine influences the determination of Total Fluorine (TF) and Total Organic Fluorine (TOF), calculated using the innovative 'untarget' methods. These methods of analysis are recognised and referred to in numerous international legislations concerning restrictions on the use of PFAS substances.

The testing described above outlined the following situation:

- Reactive dyes for cellulosic fibres containing one or more organic fluorine atoms in their molecules (fluorine-carbon bond) are marketed.
- The chemical classes of these dyes are numerous and are described in table 1.
- Determination of Total Fluorine (TF) and Total Organic Fluorine (TOF) in commercial formulations of these dyestuffs have shown fluorine concentrations ranging between approx. 200 and 37,000 mg/kg.

- These situations - very high values of organic fluorine in dye formulations and very low values of organic fluorine found in textiles dyed with these dyes - are attributable to the nature of the organic fluorine in the dye molecules. In fact, the fluorine in these dyes acts as an 'leaving-group' in the molecule, which is released from the dye as a result of the chemical reaction between the cellulose and the dye.

- The application of these dyestuffs on cotton textiles with suitable dyeing processes and at various levels of dye concentration/fibre weight resulted in low TF and TOF values; values, however, always below the strictest restriction levels in international legislation (50 mg/kg).

- The low TF and TOF values could be increased in cases where post-treatment procedures, such as soaps, are not performed correctly; however, such variations should not exceed the established restriction levels (50 mg/kg).

- It is important to consider that the TF/TOF values detectable in textile materials dyed with reactive dyes could, under certain conditions, exceed the limits for PFAS-related TF/TOF required by some fashion brands in their PRSL (Product Restricted Substances List), where values below 50 mg/kg are present.