New insights into the accessibility of native cellulose to environmental contaminants toward tritium behavior prediction

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Highlights

- Hydroxyl reactivity of native cellulose is correlated to its crystallinity.
- A linear relationship describes OH group accessibility versus Crystallinity Index.
- Fast XRD analysis gives access to hydroxyl reactivity of native cellulose.
- Tritium retention capacity of native cellulose is deduced from the model.
- The model is applicable to environmental samples depending on cellulose parameters.

Abstract

Tritium speciation and behavior in the environment directly rely on accessible OH groups of organic molecules and their hydrogen exchangeability properties. As one of the most widespread biomolecule, cellulose role in reducing the exchange capacity of the hydrogen atom has been previously highlighted experimentally in various environmental matrices. In this paper, a robust and reliable T/H gas-solid isotopic exchange procedure has been implemented to assess the OH group accessibility of native celluloses with an increasing degree of crystallinity. A linear relationship was found between hydroxyl reactivity and the Crystallinity Index (CrI) of native celluloses, as determined by the analysis of their crystalline structure from XRD characterization. The application of the obtained linear experimental model to cellulosic materials was then evaluated and an acceptable minimum value of 12% for the CrI parameter on environmental matrices could thus be established. The authors have therefore proposed an environmental matrices relevant and efficient analytical process in order to determine the accessibility of native cellulose hydroxyl groups to tritium in the environment from a single and quick sample characterization procedure.

Keywords: tritium, speciation, isotopic exchange, cellulose, pollutants

1. Introduction

Tritium is the natural radioactive isotope of hydrogen and one of the main radionuclides released into the environment by nuclear installations (IRSN, 2017). According to current forecasts, the release rates of this radionuclide are expected to rise significantly over the upcoming decades from changes in fuel management methods along with new tritium-emitting facilities, such as the International Thermonuclear Experimental Reactor (ITER) and Evolutionary Power Reactor (EPR) (ASN, 2010; Song et al., 2019). To understand the behavior of this radioactive pollutant in the environment and thus evaluate its potential impact, the main scientific challenge calls for identifying its mobility and bioavailability characteristics, which are mainly governed by its speciation. In environmental matrices, tritium can integrate organic matter in the form of organically bound tritium (OBT) by replacing stable hydrogen isotopes and taking up exchangeable positions (exchangeable OBT) or else remaining in the molecule until its degradation (non-exchangeable OBT) (Diabaté and Strack, 1993; Kim et al., 2013; Sepall and Mason, 1961). As such, monitoring OBT has become a major concern in many countries for both public and regulatory assurance and several studies have focused on the non-exchangeable form (NE-OBT) as a reliable environmental marker (Kim et al., 2013; Péron et al., 2016; Baglan et al., 2018; Nivesse et al., 2021a, 2021b). Among those previous investigations, cellulose has been repeatedly identified as one of the organic molecule with great impact on OBT speciation and was found to be responsible for the decrease in tritium exchangeability rates within various cellulosic environmental matrices (Nivesse et al., 2021a; Péron et al., 2018). Beyond these properties specific to the cellulose biomolecule, the work presented in Nivesse et al. (2021a) has also highlighted the total control of major constituent over the hydrogen transfer mechanisms and OBT speciation found in related environmental matrices. As the most abundant biopolymer on earth and the main structural component of cell walls in plants, cellulose reactivity to hydrogen isotopes

62 binding is thus key to understanding tritium behavior in the environment and its transfer into food
63 chain samples.

64 In cellulose molecules, OBT speciation directly relies on accessible OH groups and their hydrogen
65 exchangeability properties. On the supramolecular level, cellulose is composed of linear chains of
66 D-glucose units linked together by (1→4)-beta-D-glycosidic bonds, subjected to aggregation into
67 microfibrils with a sheet organization and a two-phase morphology of crystalline and amorphous
68 regions. The crystalline structure of cellulose is highly ordered and originates from extensive
69 intra-molecular and intra-strand hydrogen bonding between OH groups. As a result, the
70 accessibility of cellulose hydroxyl groups undergoes a drastic reduction, as has been widely
71 demonstrated in the literature during crystalline structure investigations of various cellulose
72 compounds in hydrogen-deuterium exchange experiments (Lindh and Salmén, 2017; Reishofer
73 and Spirk, 2015). Nevertheless, no clear analytical relationship has ever been derived between
74 hydrogen exchangeability and degree of crystallinity in native cellulose. To a global extent,
75 several characterizations methods (SEM, TEM, FTIR, XRD, TGA …) are usually combined to
76 assess the link between the crystalline morphology of cellulose and applications related to its OH
77 group's reactivity (Luzi et al., 2019; Melikoğlu et al., 2019; Trache et al., 2016). However,
78 simplified calculation method could also be fit for purpose in given conditions. For example, the
79 Crystallinity Index (CrI) determined after a single X-ray diffraction (XRD) analysis is commonly
80 used for quantifying the crystallinity rate of native cellulose (Hashem et al., 2020; Johar et al.,
81 2012; Luzi et al., 2019; Madivoli et al., 2016; Melikoğlu et al., 2019; Segal et al., 1959; Trache et
82 al., 2016). The present work therefore aims to provide a simple and environmental matrices
83 relevant linear model to describe OH group accessibility with respect to the Crystallinity Index
84 (CrI) from a series of five native celluloses. While CrI is determined by means of X-ray diffraction
85 (XRD), OH group accessibility is investigated by a robust and reliable T/H gas-solid isotopic
86 exchange procedure (Nivesse et al., 2021a, 2021b, 2020; Péron et al., 2018). By virtue of being

87 extracted or investigated from environmental sources, the application potential of the linear model
88 obtained for the cellulose accessibility determination can then be established for cellulosic
89 materials and from direct measurements conducted on environmental matrices.

90

2. Materials and methods

2.1. Sample preparation and characterization

Alpha (cellulose-C) and microcrystalline (cellulose-E) native celluloses extracted from cotton sources (CAS number: 9004-34-6) were purchased from Sigma-Aldrich. The crystalline structures of these celluloses were modified by partial destruction using ball-milling processes. A series of five native celluloses with increasing crystalline ratios was produced from ball-milling with the following parameters: cellulose-A (142 x g, 15 min) and B (84 x g, 10 min) from cellulose-C (alpha cellulose); and cellulose-D (68 x g, 3 min) from cellulose-E (microcrystalline cellulose). Cellulose-E refers to the microcrystalline cellulose previously studied in Péron et al., (2018).

An amorphous compound of silica SiO_2 (CAS number: 7631-86-9) was purchased from Sigma-Aldrich and added in different ratios to each cellulose of the series (A through E) in order to obtain a modified sequence of increasing cellulose content samples (from 5% to 95% by weight) for each native cellulose of the series (Table 1).

All the samples were directly freeze-dried after the preparation steps and stored under vacuum prior to further use.

2.2. Experimental procedure

2.2.1. X-ray diffraction analysis

X-ray diffraction was employed to determine the crystallinity of the series of five native celluloses and the modified sequences of increasing cellulose content samples. Each milled powder material was placed on the sample holder and leveled to obtain total and uniform X-ray exposure. Analyses were performed at room temperature using a D5000 Brucker X-ray diffractometer (Cu/Kα radiation = 0.154 nm at 40 kV and 30 mA). The XRD patterns were collected within the range of $2\theta = 0° - 50°$ with a scan step of $2\theta = 0.02°$ and a measurement time per step of 4 s.

The Crystallinity Index (CrI) was determined based on the reflected intensity data, according to the method developed by Segal et al., (1959), using the following Equation 1:

$$(\mathrm{CrI})\ (\%) = \frac{(\mathrm{I_{002}} - \mathrm{I_{am}})}{\mathrm{I_{002}}} \times 100 \qquad (1)$$

where $\mathrm{I_{002}}$ is the maximum diffracted intensity by the (002) plane at a 2θ angle of around 22°, while $\mathrm{I_{am}}$ is the minimum diffracted intensity at a 2θ angle of around 18°, representing the intensity scattered by the amorphous region of the sample.

2.2.2. Isotopic exchanges

The (α_{iso}) parameter describes the isotopic exchangeable hydrogen pool versus total hydrogen atoms in a specific matrix and is typically determined by a gas-solid isotopic exchange procedure. The gas-solid isotopic exchange process has already been developed and described in previous publications (Nivesse et al., 2021b; Péron et al., 2018); it is based on a sample set-up vapor phase

experiment performed in a confined glove box (Plas-Labs 890-THC) with controlled and stable temperature (20.0° ± 0.1°C) and relative humidity (85% < RH < 88%) parameters. An isotopic steady state with a defined (T/H) ratio is established between a bath of KCl-saturated solution ($\left(\frac{T}{H}\right)_{l,\ bath}$) with controlled tritium activities, a vapor phase confined in a glove box ($\left(\frac{T}{H}\right)_{g,\ vapor}$), the water condensed at the sample surface ($\left(\frac{T}{H}\right)_{l,\ cond}$) and the exchangeable organically bound tritium of the sample ($\left(\frac{T}{H}\right)_{s,\ E-OBT}$), which can be described by Equation 2:

$$\left(\frac{T}{H}\right)_{l,\ bath} = \left(\frac{T}{H}\right)_{g,\ vapor} = \left(\frac{T}{H}\right)_{l,\ cond} = \left(\frac{T}{H}\right)_{s,\ E-OBT} \quad (2)$$

Isotopic exchanges were conducted on native celluloses following four tritium-enrichment experiments with tritium-rich baths (HTO = 120, 300, 500 and 700 $Bq.L^{-1}$). After 2 days of solid-gas contact time, the steady state was assumed to be reached, and solid samples were recovered at days 2, 3 and 4 to ensure the reproducibility and steady state of the system. Three baths aliquots were also collected at the steady state and kept at a temperature below 5°C prior to distillation. After liquid nitrogen immersion and freeze-drying, the solid samples were heat-treated in a tubular furnace (Eraly, France), where the organic matter was transformed into carbon dioxide and combustion water. Liquid samples (combustion waters and baths aliquots) were purified by distillation under atmospheric pressure after pH adjustment with sodium peroxide (Na_2O_2) as needed. The tritium activities were measured by means of liquid scintillation counting (PerkinElmer Wallac Quantulus 1220 model) using an Ultima Gold LLT cocktail. The detection limit was estimated at below 1 $Bq.L^{-1}$ for a counting time of 24 hours and a blank value of 0.7 counts per minute. A quench correction was applied for each measurement according to a quenching curve calculated after calibration with laboratory-prepared quenched standards.

155 At each steady state, a mean value of the combustion water from each matrix sample $\left(\frac{T}{H}\right)_{s,\ OBT}$

156 was obtained by averaging the measured sample values forming the plateau. A mean value of each

157 saline solution $\left(\frac{T}{H}\right)_{l,\ bath}$ was also obtained by averaging the three measured bath aliquot values.

158 The (α_{iso}) parameter could thus be determined as the slope of the plot of $\left(\frac{T}{H}\right)_{s,\ OBT}$ versus

159 $\left(\frac{T}{H}\right)_{l,\ bath}$, in accordance with the description provided in Equation 3:

$$\alpha_{\mathrm{iso}} = \frac{\Delta\left(\frac{\mathrm{T}}{\mathrm{H}}\right)_{\mathrm{s,\ OBT}}}{\Delta\left(\frac{\mathrm{T}}{\mathrm{H}}\right)_{\mathrm{l,\ bath}}} \qquad \text{Eq. 3}$$

160

161

3. Results and discussion

3.1. Crystallinity Index (CrI) determination

The XRD patterns for the series of native celluloses are shown in Figure 1. All celluloses in the series exhibited crystalline peaks attributed to the typical structure of cellulose I at: 2θ = 16.1° (110), 22° (200) and 34.7° (004) (Johar et al.,2012; Melikoğlu et al., 2019). Cellulose I is one of the four allomorphic forms of crystalline cellulose (I to IV) and the most common form in a natural source (Chen et al., 2011; Lu et al., 2013). CrI values for celluloses A, B, C, D and E were calculated at 13, 34, 46, 55 and 62%, respectively. From celluloses E and C, the crystallinity ratio decreases as expected due to the partial destruction of crystalline regions during the ball-milling process (Sun and Cheng, 2002).

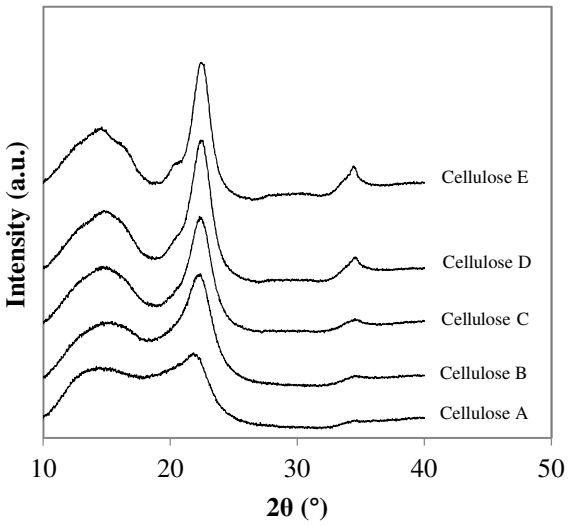


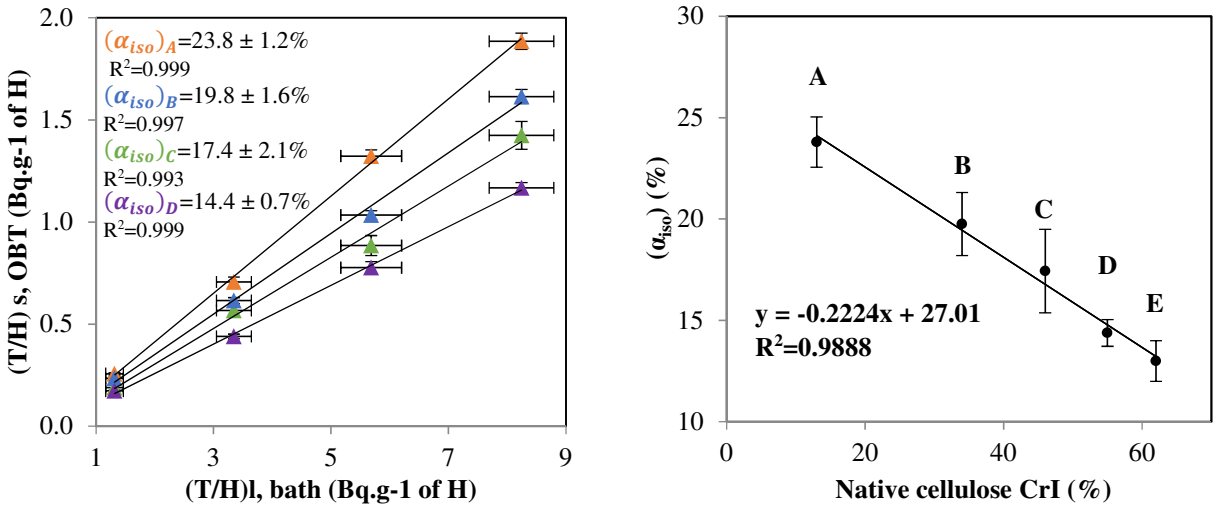
Fig. 1: XRD patterns for the series of five native celluloses from cellulose A through cellulose E

In order to assess the potential impact of the vapor phase contact during the gas-solid isotopic exchange procedure onto the crystalline structure of the series of native celluloses, X-ray diffraction analysis were conducted before and after the isotopic exchange step. Modifications on

both the intensity data of the XRD peaks (for the CrI calculation) and the allomorphic attribution (cellulose I allomorphic form) were thus established to be negligible as no significant change was observed on any of the samples.

3.2. Linear experimental model for the cellulose accessibility determination

Isotopic exchanges were conducted on native celluloses to assess their exchangeable parameter (α_{iso}). Accurate values of (α_{iso}) equal to 23.8 ± 1.2% (R^2 = 0.999), 19.8 ± 1.6% (R^2 = 0.997), 17.4 ± 2.1% (R^2 = 0.993), 14.4 ± 0.7% (R^2 = 0.999) and 13 ± 1% (R^2 = 0.990) were obtained for celluloses A through E, respectively (Fig. 2). The results on cellulose E exchangeable parameter (α_{iso}) were previously presented in Péron et al., (2018).



(a) (b)

Fig. 2: (a) (T/H) of celluloses A through D in the steady state after freeze-drying vs. measured set (T/H) of saline solutions and their associated exchangeable parameter (α_{iso}). (b) Exchangeable parameter (α_{iso}) vs. Crystallinity Index (CrI) for the series of five native celluloses from A through E.

From these findings, an experimental model based on (α_{iso}) vs. CrI was obtained for the series of native celluloses (Fig. 2). A decrease in the exchangeability parameter (α_{iso}) can be observed as the degree of crystallinity in the cellulose molecule increases. The crystalline structure of cellulose is represented by an orderly arrangement of D-glucose chains generated by hydrogen bonds. The (1→4)-beta-D-glycosidic bonds and monomer arrangements oriented at 180° are thus responsible for a three-dimensional network (see SI-1). Hence, hydroxyl groups of D-glucose units behave like hydrogen-bound donors at both the intra-molecular and intra-strand levels to provide a stabilized structure to cellulose (Jarvis, 2003; Nishiyama et al., 2003, 2002). As such, a larger proportion of the hydrogen atoms is made inaccessible for isotopic exchange and behaves as non-exchangeable hydrogen, while the degree of crystallinity in the cellulose is increasing.

The experimental model constructed with the series of native celluloses exhibits a linear tendency, with a correlation coefficient equal to 0.9888. Hence, the suggestion of a proportionality ratio is entirely noticeable between the decreases in hydrogen atom accessibility and the extent of the crystalline phase in native cellulose. This dependency can therefore be described as linear (Equation 4):

$$\left(\alpha_{iso_{celluloses}}\right) = -0.2224 \times (\mathrm{CrI}) + 27.01 \qquad \text{Eq. 4}$$

where $\left(\alpha_{iso_{celluloses}}\right)$ is the exchangeable hydrogen atom ratio of the native celluloses series, in %, and (CrI) the crystallinity index from 13 to 62 %.

Equation 4 can thus serve to deduce the ratio of exchangeable hydrogen atoms in native cellulose molecules merely from information on the degree of crystallinity. Hence, these findings could give access to the tritium under the form of NE-OBT storage capacities of native cellulose molecules from a single XRD analysis.

3.3. Environmental matrices applications and limits

Investigations on organically bound tritium distribution and speciation towards cellulose pertain to environmental cellulosic organic matter (Nivesse et al., 2021a; Péron et al., 2018). Consequently, the linear model method established to determine cellulose accessibility requires applicability to cellulosic materials from direct environmental matrices CrI measurements. In environmental matrices, native cellulose may display a wide range of crystallinity rates and is always found in combination with other amorphous to semi-amorphous compounds. An XRD analysis on the entire environmental sample might therefore detect the attributed peak at 22° for the cellulose needed for a CrI calculation, yet with a significant impact lowering its intensity in proportion with the amorphous compound content. At some point, the presence of this amorphous phase, provided by the other constituents, may become too great compared to the crystalline phase of the cellulose, making the cellulose peak at 22° undetectable by means of XRD analysis. Nevertheless, it is important to recall here that the main point of this study was to provide reliable information on the accessibility of cellulose OH group from a very simplified and unique sample characterization, as XRD measurements. In order to assess the applicability of the linear experimental model to cellulosic materials from direct measurements in environmental matrices, a study of the significant limits of the CrI parameter determination from XRD analysis was thus carried out. For this purpose, each native cellulose of the series was mixed in different ratios with SiO_2 amorphous compounds to simulate other non-crystalline fractions of environmental matrices and then analyzed by XRD. CrI (%) values for the modified sequences of increasing cellulose content samples are presented in Table 1. From these results and the cellulose content (in % by weight) of each sample, theoretical CrI values could be calculated and attributed to each of the studied native celluloses (calculated native cellulose CrI (%)) and compared to their actual CrI values (actual native cellulose CrI (%)) (Table 1). For each modified sequence, the cellulose contents were

adapted in each sample to achieve the minimum content of cellulose needed to reach the actual calculated CrI value.

Native cellulose sequence	Sample	Native cellulose ratio (in % by weight)	Sample CrI (%)	Calculated native cellulose CrI (%)	Actual native cellulose CrI (%)
Cellulose A	A-1	60,3	-	-	13
	A-2	70,2	-	-	
	A-3	80,0	4	5	
	A-4	90,4	8	10	
	A-5	94,8	**12**	**13**	
Cellulose B	B-1	20,2	4	18	34
	B-2	30,0	9	30	
	B-3	35,6	**12**	**34**	
	B-4	40,1	14	34	
	B-5	50,1	17	34	
Cellulose C	C-1	15,5	4	26	46
	C-2	20,3	8	40	
	C-3	26,1	**12**	**46**	
	C-4	30,3	14	46	
	C-5	40,1	18	46	
Cellulose D	D-1	15,0	8	50	55
	D-2	19,6	11	54	
	D-3	23,2	**13**	**55**	
	D-4	30,3	17	55	
	D-5	40,3	22	55	
Cellulose E	E-1	10,2	6	56	62
	E-2	14,5	9	60	
	E-3	20,4	**13**	**62**	
	E-4	25,3	16	62	
	E-5	30,1	19	62	

Table 1: Results on modified sequences of increasing cellulose content samples from celluloses A through E, along with their respective native cellulose ratio (% by weight), obtained sample CrI (%) and the resulting calculated native cellulose CrI (%) compared to the actual native cellulose CrI (%).

Results obtained on the minimum content in % by weight of native celluloses A through E needed to effectively reach an XRD analysis peak at 22° for the correct calculation of their respective CrI values are presented in Figure 3. For medium to highly crystalline cellulose (i.e. celluloses B through E), the minimum cellulose content needed in samples was found to lie around 20% to 35% by weight. These values are by far lower than the minimum content of cellulose in natural cellulosic sources like trees or cotton, yet which does approximately correspond to that found in green cellulosic plants like grass or tree leaves (Sun and Cheng, 2002). For very weak crystalline cellulose (cellulose A), only a very high cellulose content was found to be acceptable for an accurate cellulose CrI determination from XRD analysis.

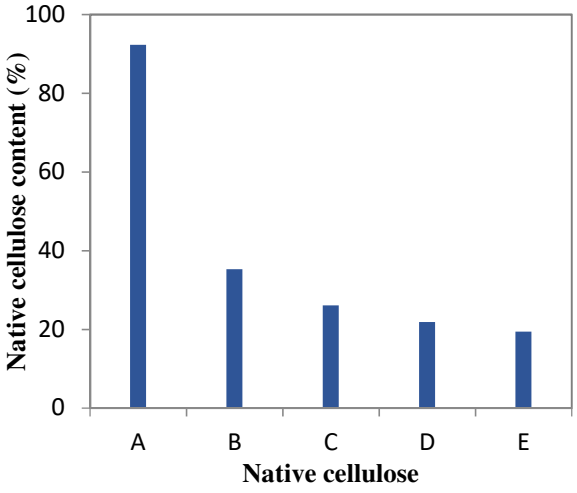


Fig. 3: Minimum content (% by weight) of native celluloses A through E needed to effectively reach an XRD analysis peak at 22° for the accurate calculation of their respective CrI (%)

For each of the native cellulose results, it was then estimated that the minimum CrI value calculated from XRD analysis was acceptable as of 12% in an environmental sample to produce an accurate cellulose CrI deduction. Nevertheless, this value remains dependent on the typical internal parameters used in a cellulose analysis of the XRD equipment and could thus be further

improved, as needed. Similarly, this information proves to be relevant when cellulose is the only constituent of the studied matrix whose crystallinity is directly related to the XRD analysis peak at 22°. The linear model is therefore applicable to environmental matrices for cellulose accessibility determination under this condition whenever the CrI value obtained from the matrix sample XRD analysis exceeds 12%. A complementary analysis of the sample composition in cellulose is then needed to deduce the CrI and, hence, the accessibility of the studied cellulose to the main radionuclide released by nuclear power plants, tritium. A fast and efficient analytical process is therefore available for further investigations on organic tritium retention capacities of cellulosic environmental matrices and should also be of great interest to understanding tritium behavior into other major constituents in food chain samples like proteins.

Besides radioactive pollution concerns, the exchange capacities of OH group hydrogen atoms in native cellulose are also important in other hydrogen isotope-related topics, such as investigations on cellulosic material origins within protium and deuterium ratios, to the same extent as in the field of nuclear forensics and retrospective studies on tritium releases into the environment. Most of the functional properties of the cellulose polymer derives from its hydroxyl groups since its chemical reactivity is mainly a function of the high donor reactivity of its OH groups (Klemm et al., 2005; O'Connell et al., 2008). The hydrogen exchange properties of these OH groups are then heavily involved in the binding processes of metal ions into cellulose fibers, from sorption supported by a hydrated shell exchange with OH groups or electrostatic interactions with carboxyl groups (Kongdee and Bechtold, 2009; Öztürk et al., 2009). As such, the established linear model could also find an interest to estimate the complexing capacities of cellulose with transition metals and actinides in its natural state in environmental samples.

4. Conclusion

To improve the scientific knowledge on tritium behavior prediction in the environment, hydroxyl reactivity has been investigated in a series of native celluloses with an increasing degree of crystallinity using a robust and reliable T/H gas-solid isotopic exchange procedure. A linear relationship was derived between OH group accessibility to tritium and the Crystallinity Index (CrI) of native celluloses. Since the purpose of this study relies on natural cellulose sources, the applicability of the linear model from direct measurements on environmental matrices was investigated with samples of increasing cellulose content at various crystallinity rates. An acceptable minimum value of 12% for the CrI parameter on environmental matrices could thus be established for the direct deduction of an accurate cellulose content CrI and OH accessibility. These findings then make it possible to determine efficiently, by means of a single and fast XRD analysis, the accessibility of the entire cellulose hydroxyl group pool to tritium bound into environmental matrices. This information can subsequently be used not only to highlight the hydrogen isotopes including tritium storage capacities in cellulosic environmental matrices, but also to evaluate the contribution of other complex compounds involved with structures difficult to characterize, like proteins. Applications to investigations on cellulosic material origins could emerge, to the same extent as retrospective studies of tritium releases and nuclear forensics. In a more fundamental manner, this method of determining hydroxyl group accessibility on native cellulose also provides much relevance in understanding the involvement of the polymer in environmental matrices accessibility to deuterium and tritium, as well as in grasping complexing capacities with metals in the environment.

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