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The role of time and storage conditions on the composition of hashish and marijuana samples: A four-year study

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ABSTRACT

The aim of this study was to investigate the role of time and different real-life storage conditions on the composition of different varieties of cannabis products (hashish and marijuana). Six high-potency cannabis products constituted by herbal and resin materials containing different initial concentrations of delta 9-Tetrahydrocannabinol (THC) were employed for this study. Four representative samples were collected from each study material and were maintained for a prolonged time (four years) under different controlled storage conditions: (A) light (24 h) and room temperature (22 °C); (B) darkness (24 h) and room temperature; (C) darkness and refrigeration (4 °C); (D) darkness and freezing (−20 °C). The concentration of the three main cannabinoids, i.e. THC, Cannabinol (CBN, produced from the degradation of THC), and Cannabidiol (CBD), were measured by GC-FID around every 100 days along the four-year study.

Significant changes in the THC (degradation) and CBN (formation) content were detected under storage conditions A and B, and almost 100% of THC was degraded after four years. A mono-exponential function was able to well fit both THC degradation and CBN formation, suggesting that these processes occur with a first order kinetics. Data treatment indicated that the storage temperature and light exposure had two different effects on the conversion of THC to CBN: temperature changed only the speed, light changed both the speed and the stoichiometry of this conversion.

Models were proposed which allow to predict the storage time, if unknown, and the initial content of THC (i.e. the concentration of THC at the starting storage time), from the measurement of THC and CBN content at any time under storage condition A. Values predicted are more uncertain at larger storage times and have an accuracy of around 5-10%. These models were also tested on data reported in the literature, and can represent a starting point for further improvements. Prediction models may be helpful for forensic purposes, if the initial concentration of THC or the approximate age of a degraded material need to be estimated, or to plan the storage of delicate samples which need to be re-examined over time.

1. Introduction

Cannabis samples (hashish and marijuana) deteriorate over time merely by standing in a safe at room temperature [1]. The main time-dependent change regards delta-9-tetrahydrocannabinol (Δ^9–THC, or commonly THC) content. In one of the first studies of this kind, Lerner showed that the THC content of marijuana at room temperature decreased at the rate of 3%–5% per month [2]. Also, it was found that the primary degradant of THC is Cannabinol (CBN) [3] and that UV light and heat accelerate THC degradation [4]. Coffman and Gentner studied the effect of temperature on the stability of THC and found that little decomposition occurred at 65 °C, but considerable losses occurred in the range 85–100 °C [5]. Turner and Elsohly reported that at 37 °C and 50 °C significant THC degradation occurred [6].

It was also observed that CBN formation is correlated to THC degradation. A study by Repka et al. [7] on the stability of THC in polymeric matrices reported that at 120 °C and 160 °C, 9.0% and 7.8%, respectively, of the total degraded THC appeared as CBN, and that at 200 °C the THC conversion to CBN was 29.1%. Turner and

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ElSohly proposed a possible pathway for the decomposition of THC to CBN mentioning the formation of epoxy and hydroxylated intermediates [6], and indicated that these compounds are susceptible to heat and acid, resulting CBN as final product.

In 1971, Fairbain et al. carried out experiments designed to test the effect of light, oxygen and temperature on the degradation of THC in herbal and resin materials, and found that the most important effect was due to light [8]. The effect of oxygen seemed much less significant; this may be due to the fact that the cannabinoids in the plant are stored in "well-closed containers", the glands, which protect the active ingredients [8]. Mechanical actions during sample pre-treatment might damage the glands releasing the active ingredients and facilitating exposition of THC to degradation.

Trofin et al. studied the influence of storage conditions on the cannabinoids content of different herbal samples which were stored in darkness at 4 °C and exposed to natural light at 22 °C for 4 years [9]. The content of THC and CBN was periodically determined and the degradation of THC and the increase of CBN was found to be faster in the first year than in subsequent years, and more pronounced for the samples exposed to light at 22 °C than those stored in darkness at 4 °C. Similar results were obtained for cannabis resin samples, although a steadily decay of THC over the entire storage period was rather found [10]. Lindholst investigated the stability of cannabinoids in cannabis resin slabs and cannabis extracts upon long-term storage [11]. The levels of major cannabinoids were periodically measured during storage at room temperature, 4 °C and −20 °C for up to 4 years. Cannabinoid stability in cannabis material was found to be influenced by light, temperature and possibly also oxygen availability.

In a forensic context such degradative processes can have relevant consequences especially when illegal cannabis products are seized during law enforcement activities. Prolonged storage may alter the chemical composition of cannabis products, and this may become relevant when results from analyses are used to determine if a criminal offence has been committed. Hashish and marijuana samples are usually analyzed by forensic-toxicology laboratories adopting well established methods [12], and a variable amount of time may elapse between the date of seizure and analysis. During this period, the integrity of the collected samples should be granted, otherwise the validity of analytical results may be contested in court. Furthermore, the judge and the prosecutors may be interested in tracing back to the original state and chemical composition of the materials. This calls for reliable quantitative models describing the degradative process of cannabis products in realistic storage situations. In particular, the potency of cannabis products is nowadays extremely different [13–15] than those considered in older studies [1–6], most of which have been carried out decades ago. By employing high-potency cannabis products, concentration-related effects may become more evident and materials can be studied for longer periods before they are totally degraded. Therefore, results from these studies better reflect real storage situations occurring nowadays.

The aim of this study was to investigate the role of time and different real-life storage conditions on the chemical composition of different varieties of high-potency cannabis products. In particular, the effect of temperature and light on samples stored for prolonged time have been studied, and kinetic models describing such degradative processes have been developed. Concentrations of THC, Cannabidiol (CBD) and CBN were considered as they are relevant for forensic purposes and requested in court, e.g. for evaluating the toxicological properties of a seized material, or for comparing amounts of psychoactive ingredients with fixed thresholds established by law (as those for defining personal use or the number of "average daily doses" obtainable from a seizure, depending on the specific national legislation) or to discriminate among different cannabis phenotypes.

In this paper, a model is presented which allows to estimate the initial concentration of THC (i.e. at the start of the storage period), or the approximate age of a degraded material, both of which are useful for forensic purposes, or to plan the storage of delicate samples which need to be re-examined over time. Results of this investigation can be useful to expand knowledge about quantitative degradation of cannabinoids.

2. Materials and methods

Six high-potency cannabis products constituted by herbal and resin materials containing different initial concentrations of THC (ranging from 9.8 to 18.9% in herbal materials, and from 18.1 to 53% in resins) were employed for this study. The characteristics of such materials are summarized in Table 1. All materials were seized by the law enforcement in the two weeks before the commencement of the study period. Materials 1, 2 and 5 were derived from resins of different quality (e.g. dark brown hashish eggs or agglomerates). Materials 3, 4 and 6 were buds derived from cannabis plants of different origins. To prepare representative study samples from these materials, the herbal cannabis were dehydrated, homogenized and reduced to fine powder with mortar, then filtered through a sieve, providing particles mostly distributed in the range 20–200 μm [16]. The resins were reduced into granules and fragments with an average size of about 2 mm were produced. Material 5 was not treated like the others as it was highly oily and not reducible.

Four representative primary samples were collected from each study materials (n = 24 primary samples) and kept for a prolonged time (4 years) under 4 different storage conditions. About every 100 days, two individual test samples were collected from the 24 study samples and analyzed in duplicates. The concentration of THC, CBD and CBN were determined for each of them and a dataset of about 4000 analytical records was produced. Detailed information on the method used for the analytical determinations carried

Table 1
Summary of materials used in the study. Standard uncertainties associated to concentration values are expressed with one significant figure and concentration values are rounded accordingly.

Material #	1	2	3	4	5	6
Cannabis product type	Hashish	Hashish	Marijuana	Marijuana	Hashish	Marijuana
Material description	Brown dark hard 10-grams eggs	Brown dark malleable 10-grams eggs	Compressed buds (1-kg blocks)	Loose buds	Dark oily small agglomerates	Compressed buds (2-kg blocks)
Initial THC (%)	26 ± 1	18.1 ± 0.7	9.8 ± 0.4	18.9 ± 0.8	53 ± 2	12.7 ± 0.5
Initial CBD (%)	4.2 ± 0.2	6.2 ± 0.2	1.0 ± 0.1	n.d.	n.d.	n.d.
Initial CBN (%)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Study samples (n)	4	4	4	4	4	4

n.d. = not detected (value below the detection limit); THC = delta-9-tetrahydrocannabinol; CBD = cannabidiol; CBN = cannabinol.

Table 2
Storage conditions for the study samples listed in Table 1.

Storage condition	Light exposure (24 h)	Temperature (°C)	Notes
A	yes	22 ± 2 (room)	closed with transpiring gauze
B	no	22 ± 2 (room)	closed with transpiring gauze and completely covered with dark fabric
C	no	4 ± 1 (refrigerator)	closed with screw cap
D	no	−20 ± 1 (freezer)	closed with screw cap

out on cannabis products has been previously reported [14–16]. The storage conditions differed mainly by 24-h light exposure (yes or no) and by storage temperature (from about +22° to −20 °C). Storage conditions are marked with letters A, B, C, D and are resumed in Table 2.

Along the 4-year study period (starting in March 2014) 14 analytical rounds were carried out. For practical reasons, analysis of materials 5 and 6 started at the second scheduled round, and the analyses of materials 3, 4 and 6 were not performed at the scheduled 5th round. From the 8th rounds on, all the study samples were analyzed on the same date. About once a month all the samples were accurately mixed. Data analysis and statistical processing were performed by the software ORIGIN (OriginPro 9.0 64Bit). Data were statistically compared by means of *t*-test analyses performed at the 95% confidence level. Significance level was set at $p \leq 0.05$. Correlations were obtained with the Pearson method.

3. Results and discussion

3.1. THC degradation and CBN formation

Fig. 1 shows the experimental concentrations of THC and CBN obtained from the analyses of the study samples kept under the 4 storage conditions (A–D). For comparison purposes, all concentrations have been normalized by dividing the experimental concentration of THC and CBN by the initial concentration of THC:

$$C_{THC} = \frac{[THC]}{[THC]_0} \quad (1)$$

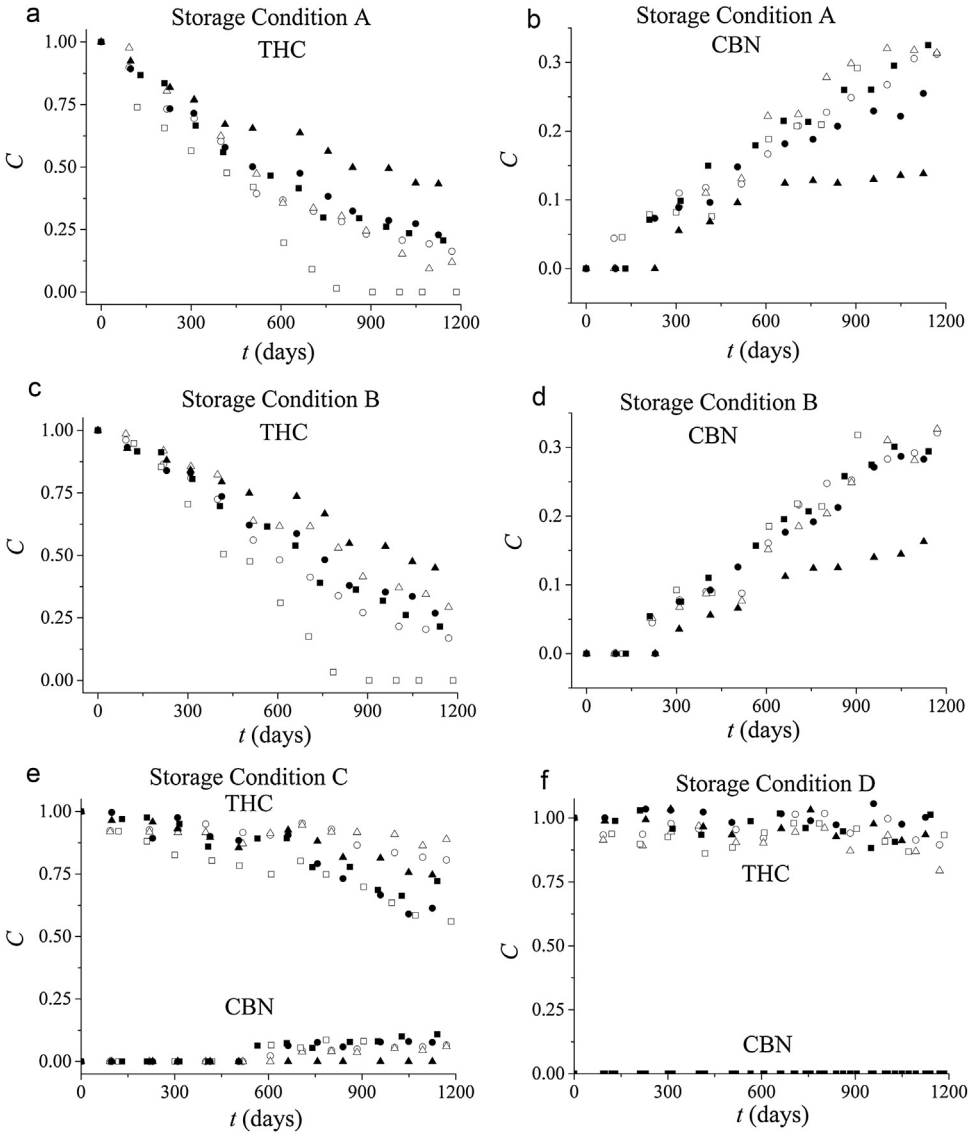

Fig. 1. Normalized concentration values ($C = C_{THC}$ or C_{CBN}, see Eqs. (1) and (2) as a function of time (*t*, days) obtained from the analyses of the samples collected from the six study materials (1(○), 2(Δ), 3(●), 4(▲), 5(□), 6(■)) stored in the conditions A, B, C, D.

$$C_{CBN} = \frac{[CBN]}{[THC]_0} \quad (2)$$

where [THC] and [CBN] are concentration values at storage time t, and $[THC]_0$ is the concentration of THC at time zero (t_0; the starting storage time). Non-normalized graphs are shown in Fig. S1 (Supporting information).

As expected, it was observed that THC is constantly decreasing, and CBN is constantly increasing, for all the samples kept at room temperature (storage conditions A and B). The average THC degradation in the first 100 days was about 13% and 11%, in storage conditions A and B, respectively. All the samples kept at 4 °C (storage condition C) demonstrated a less pronounced variation in THC and CBN contents over time. When samples were stored at −20 °C (storage condition D), no significant changes were observed either for THC or for CBN concentration values.

The normalized concentration profiles for THC and CBN were statistically equivalent for the samples derived from materials 1, 2, 3 and 6. Samples derived from materials 4 and 5 diverged in some cases from the others, but only after about 600 days. No clear assumption can be made about the different behavior of such samples. It should be noted that these samples had the highest $[THC]_0$ values in the herbal and resin material groups, respectively, and material 5 had clear physical differences compared to the others as it was highly oily.

In order to obtain quantitative estimates of the THC degradation and CBN formation rates, the experimental points of Fig. 1 have been fitted assuming a first-order mechanism. In particular, the degradation of THC was modeled by Eq. (3):

$$C_{THC} = e^{-k_{THC}t} \quad (3)$$

whereas the formation of CBN was modeled by Eq. (4):

$$C_{CBN} = a\left(1 - e^{-k_{CBN}t}\right) \quad (4)$$

where k_{THC} and k_{CBN} are the kinetic constant of THC degradation and CBN formation, respectively, and a represents the value of C_{CBN} at plateau (when THC is totally degraded and no more CBN is formed).

By comparing the obtained values for the kinetic constants (k_{THC} and k_{CBN} values obtained under different storage conditions are shown in Fig. S2 — Supporting information) it was observed that k_{THC} was significantly larger than k_{CBN} for all the samples and storage conditions, and they were highly correlated each other (Pearson's coefficient $R = 0.82$).

In particular, with regards to THC degradation, the mean kinetic constant k_{THC} for storage condition A (0.00143 $days^{-1}$) was found to be significantly higher ($p = 0.004$) than the kinetic constant for storage condition B (0.00105 $days^{-1}$), indicating that light had a significant effect on the degradation of THC (samples derived from materials 4 and 5 were excluded from the means). This significant difference confirms that cannabis materials stored in dark environments experience slower THC degradation. However, the mean k_{CBN} value for storage condition A (0.000275 $days^{-1}$) was not statistically different ($p = 0.27$) from that obtained for storage condition B (0.000265 $days^{-1}$). This unexpected result may have relevant consequences: as light was found to increase the speed of THC degradation but not that of CBN formation, whereas temperature affected both the kinetic constants (all kinetic constants for C and D were significantly smaller than those obtained for A and B), it is reasonable to assume that light and temperature mediate different mechanisms for the degradation of THC.

This hypothesis was further investigated by defining a stoichiometric conversion factor, *SCF*, defined as the ratio between the concentration of residual THC and that of formed CBN:

$$SCF = \frac{[THC]_0 - [THC]}{[CBN]} \quad (5)$$

SCF is the number of degrading molecules of THC forming one molecule of CBN. An average value of *SCF* was calculated for each sample and under each storage conditions A, B and C (the kinetic constants for D were not statistically different from zero, and they were not considered). Weighted *SCF* average values were 3.2 ± 0.1, 2.7 ± 0.1, and 2.9 ± 0.2 for storage condition A, B and C, respectively. *t*-tests indicate that stoichiometric conversion factors obtained for B and C were statistically equivalent, whereas that obtained for A was statistically larger than the other two (values for each samples are shown in Fig. S3 — Supporting information). Storage condition A was the only one in which samples were stored under light and not in the dark (see Table 2): the presence of light significantly modify the stoichiometry of the conversion of THC to CBN. The temperature change, on the other hand, had no statistically relevant effect on the stoichiometric conversion factor, and it significantly changed only the speed of the conversion of THC to CBN, as seen above. To our knowledge such quantitative aspects about THC conversion to CBN were not previously described.

3.2. The degradation and seasonal fluctuations of CBD

CBD was present from the beginning only in samples derived from materials 1, 2 and 3. The highest initial CBD content ($6.2 \pm 0.2\%$) was observed in samples collected from material 2. For comparison purposes, CBD concentrations have been normalized by dividing the experimental concentration of CBD by the initial concentration of THC:

$$C_{CBD} = \frac{[CBD]}{[THC]_0} \quad (6)$$

where [CBD] is the concentration value at the storage time t. Fig. 2 shows normalized CBD concentrations for samples derived from materials 1–3 and kept under storage conditions A–D, as a function of time.

Interestingly, the observed fluctuations are well fitted by a model combining an exponential decay function and a sinusoidal function, as follows:

$$C_{CBD} = \frac{[CBD]}{[THC]_0} e^{-k_{CBD}t} + b\sin\left(\frac{2\pi(t - t_m)}{P}\right) \quad (7)$$

where k_{CBD} is the kinetic constant ($months^{-1}$) for the degradation of CBD, t_m is the phase shift (months), P is the period (months) and b is the amplitude of the experimental fluctuations.

When Eq. (7) was used to fit the experimental data, the fitted curves shown in Fig. 2 and the optimized parameters in Table S1 (Supporting information) were obtained. The most important result is that CBD was found to be relatively constant over time in all the considered samples (the average values are shown in Fig. S4 — Supporting information). The period of the fluctuations P resulted to be around 12 months: maximum and minimum peaks were observed in May and November, respectively. A small sinusoidal behavior was observed for THC and CBN also, however, due to the relative stability of CBD over time, the observation of such fluctuations in the analyzed materials was much clearer for CBD. These fluctuations may indicate the contribution of the environment (*e.g.* temperature and relative humidity) on the measurement process. Usually, the variability associated to environmental parameters is included in the estimation of intra-laboratory long-term precision, which is studied through the analysis of homogeneous and stable samples which are periodically re-analyzed over a long period of time. The contribution of the intra-laboratory long-term precision is therefore included in the overall measurement uncertainty associated to analytical results. In this case, the herbal and resin materials were not stored in climatic chambers, and refrigerated

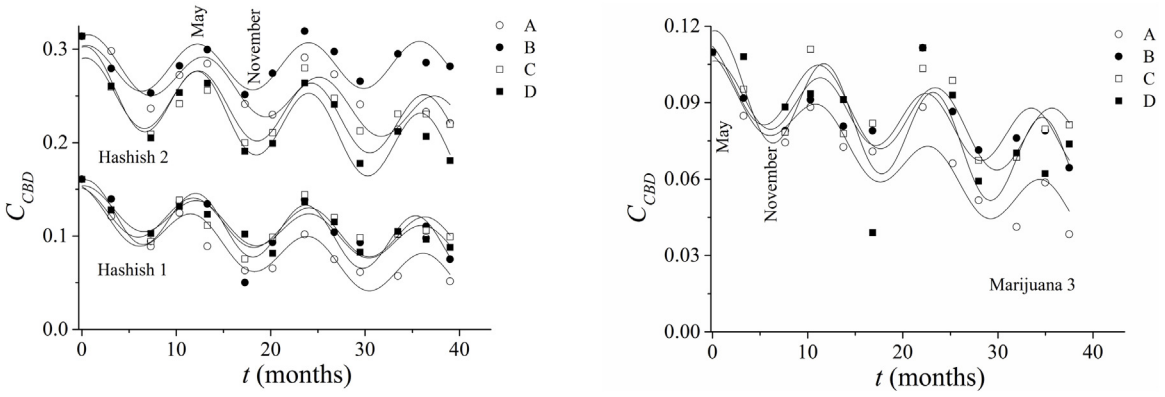

Fig. 2. Normalized concentration values (C_{CBD}, see Eq. (6)) as a function of time (t, months) obtained in the analyses of the samples derived from three CBD containing materials stored at the conditions A–D. Lines represent the fitting obtained through Eq. (7).

samples were allowed to equilibrate before processing. It is reasonable to assume that they were affected by the fluctuation of the indoor relative humidity and temperature along the year: the materials might then have absorbed or released a variable quote of humidity according to the environmental conditions. However, no specific measurements were conducted to determine the relative humidity inside the building along the four years study, and a definite correlation can not be demonstrated.

3.3. Prediction of the storage time

The obtained experimental data can allow to set up a model to predict how much time elapsed since the start of the storage period (*i.e.* to approximate the age of the material). To this aim, Eqs. (3) and (4) can be used. In particular, the storage time t can be calculated from the experimental values of C_{THC} or C_{CBN} and from the fitted parameters k_{THC},k_{CBN} and a. If both experimental results, C_{THC} and C_{CBN}, are taken into account, for example as a ratio C_{CBN}/C_{THC}, better prediction results are expected. However, the ratio calculated from Eqs. (3) and (4) is a complicated expression which is not suitable to perform fittings, as the parameters k_{THC}, k_{CBN} and a are correlated to each other and the statistical treatment to estimate the uncertainty of the results is complex. Nevertheless, a more simple empirical equation was found to properly describe the observed kinetic behavior of the CBN/THC ratio over time:

$$F = \frac{C_{CBN}}{C_{THC}} = \frac{[CBN]}{[THC]} = F_0\left(1 - e^{-k_F t}\right) \quad (8)$$

where F is the ratio between C_{CBN} and $C_{THC,}$ which can be determined experimentally at a certain time (the time of analysis), t is the storage time (to be predicted), and F_0 and k_F are two parameters which can be obtained by fitting the dataset of the study.

If F is measured for a given sample at any time, the predicted value of the storage time, $t_{(p)}$, can be computed by writing Eq. (8) as a function of t, as follows:

$$t_{(p)} = -\frac{1}{k_F}\ln\left(1 - \frac{F}{F_0}\right) \quad (9)$$

The uncertainty associated to $t_{(p)}$, $s_{t(p)}$, can be estimated by the law of error propagation, and the corresponding equation is reported in the Eq. S1 (Supporting information). The value of $s_{t(p)}$ becomes larger at larger t values due to the increase of the uncertainty of F. This means that the storage time prediction is increasingly less precise at larger storage times.

As an example, from the experimental F values (CBN/THC ratios) obtained for material 1 stored under condition A (Fig. S5 — Supporting information) the corresponding fitting parameters were obtained:

$$F_0 = -0.17 \pm 0.01$$

$$k_F = -0.00215 \pm 0.00007 \text{ days}^{-1} \quad (10)$$

By applying such fitting values into Eq. (9) it is possible to derive estimates of storage time $t_{(p)}$ (and its uncertainty $\pm s_{t(p)}$) for each THC and CBN concentration value determined at a certain time (the time of analysis). Table 3 resumes some examples of storage time predictions obtained by applying Eq. (9) and Eq. S1 (Supporting information).

The accuracy of the prediction can be defined as the difference between the real and the predicted value divided by the real value (Eq. S2— Supporting information). Time accuracy was estimated by applying a cross-validation technique, *i.e.* by excluding one experimental point and by calculating the predicted values from the remaining ones (leave-one-out method). Differences mostly below 5% were found if only results of one sample (sample 1) were considered (Fig. S6 — Supporting Information). This model (Eq. (9) and fitting parameters 10) was also applied on other experimental data available in the literature. In particular, concentration values of THC and CBN determined by Trofin et al. [9] from the analysis of 3 cannabis resins stored for four years in the light and at room temperature (the same storage condition as A in the present paper) were input in the present model to predict the storage time. It was observed that the predicted storage time agreed very well (maximum differences of about 6% at the 4th year of storage) with the experimental storage time reported by Trofin for sample

Table 3
Examples for the prediction of the storage time ($t_{(p)}$) and its uncertainty ($\pm s_{t(p)}$) for samples stored at room temperature and under light, as a function of the experimentally determined values of [CBN] and [THC] (F = [CBN]/[THC]).

F	$t_{(p)}$ (days)	$\pm s_{t(p}$ (days)
0.02	52	15
0.05	120	16
0.1	215	17
0.25	421	24
0.5	638	41
1	897	94
1.5	1060	170
2	1180	280

Table 4
Examples for the prediction of the initial content of THC for samples stored at room temperature and under light, depending on the known storage time, and assuming that the experimentally determined THC content was 5% ($k_{THC} = 0.00157 \pm 0.00003\ days^{-1}$ obtained from Fig. S5).

Storage time t (days)	$[THC]_{0(p)}$ (%)	$\pm s_{[THC]0(p)}$ (%)
30	5.24	0.42
90	5.76	0.46
180	6.63	0.53
365	8.87	0.72
500	10.96	0.89
730	15.7	1.3
1100	28.1	2.4

Table 5
Examples for the prediction of storage time and initial content of THC for samples stored under condition A, as a function of experimentally determined values of [CBN] and [THC] (F = [CBN]/[THC]), and assuming that the experimentally determined THC content was 5% ($k_{THC} = 0.00157 \pm 0.00003\ days^{-1}$ obtained from Fig. S5).

F	$t_{(p)}$ (days)	$\pm s_{t(p)}$ (days)	$[THC]_{0(p)}$ (%)	$\pm s_{[THC]0(p)}$ (%)
0.02	52	15	5.42	0.30
0.05	120	16	6.03	0.34
0.1	215	17	7.01	0.40
0.25	421	24	9.68	0.61
0.5	638	41	13.6	1.1
1	897	94	20.5	3.2
1.5	1060	170	26.5	7.3
2	1180	280	32	14

R2, whereas larger differences (up to 37% and 26% for R1 and R3, respectively) were observed for the other two samples (results are shown in Table S2 — Supporting information).

3.4. Prediction of the initial concentrations of THC

By considering the THC concentration measured at any time, it is also possible to predict how much THC was present in the material at the start of the storage period, *i.e.* at time zero. In particular, the predicted value of the initial amount of THC, $[THC]_{0(p)}$, can be obtained by merging Eqs. (1) and (3), as follows:

$$[THC]_{0(p)} = [THC]e^{k_{THC}t} \quad (11)$$

where k_{THC} is the kinetic constant for THC degradation determined from the dataset of this study; and t is the known storage time.

Table 4 reports some estimation examples obtained by applying Eq. (11) to samples stored under condition A, by assuming a known storage time (from 30 to 1100 days) and a THC content equal to 5% (at the time of analysis). The error propagation law gives the uncertainty ($s_{[THC]0(p)}$) associated to $[THC]_{0(p)}$ (Eq. S3 — Supporting information).

It is also possible to predict simultaneously both the initial content of THC ($[THC]_{0(p)}$) and the storage time ($t_{(p)}$) if [THC] and [CBN] are measured at any time. The storage time is predicted by Eq. (9), and then its value is used as input to predict the initial content of THC through Eq. (11) (uncertainties $s_{t(p)}$ and $s_{[THC]0(p)}$ are determined by Eqs. S1 and S3 — Supporting information). Table 5 reports some prediction examples obtained for samples stored under condition A, assuming that the experimental THC content ([THC]) was 5%. The predicted values become more imprecise for larger storage times.

The accuracy of the prediction of $[THC]_0$ (Eq. S4 — Supporting information) was estimated by applying a cross-validation technique, and differences mostly below the ±5% range were found even when data from all six materials were considered (results reported in Fig. S6 and Fig. S7 — Supporting information). Larger differences (up to ±10%) were observed only for some analyses of samples derived from material 3, which had a low initial content of THC, and from material 5.

Again, this model was applied on the experimental data by Trofin et al. [9] and prediction values of $[THC]_0$ were found to be more accurate for shorter storage times (differences as small as 1%), whereas they increase at larger storage times (results are shown in Table S3 — Supporting information).

With a similar treatment it is possible to predict the plateau content of CBN ($[CBN]_{\infty(p)}$). The relevant equations (S7–S9) are reported in the Supporting information.

4. Conclusions

The contents of THC and CBN in cannabis products (hashish and marijuana) were found to significantly depend on the storage time, unless samples are stored at −20 °C, indicating that freezing is the best storage condition to avoid the reduction of the cannabinoids content over time. Under the other considered storage conditions (light and dark storage at room temperature and refrigeration), THC content showed a significant reduction over time, whereas CBN content significantly increased. The degradation process which consume THC and produce CBN were found to be highly correlated and dependent on the storage temperature. The presence of light was found to have a significant effect on the kinetic constants and also on the stoichiometry of the degradation processes. A stoichiometric conversion factor was introduced to discuss quantitative aspects of THC conversion to CBN which were not previously described. The contents of CBD, on the other hand, were found to be mostly independent by storage conditions and time. Models were evaluated assuming a first-order type kinetics which allow to predict the storage time and/or the starting content of THC, from the measurement of THC and CBN concentration at any time. Cross-validation techniques were applied to estimate the accuracy of the predicted values and deviations from the expected were mostly in the ± 5% range. The defined models were also applied to experimental data obtained by other authors showing more accurate estimates for shorter storage times. Although the present models were derived from a limited number of materials, results of this study should be considered a starting point for further improvements which can be extremely relevant for forensic proposes. Accurate models quantitatively describing the degradation processes affecting cannabis products are necessary if the initial concentration of THC or the approximate age of a degraded material need to be estimated, or to plan the storage of delicate samples which need to be re-examined over time.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.forsciint.2019.02.058.

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