Review

Advanced sampling, sample preparation and combination of methods applicable in analysis of compounds in aged and deacidified papers. A minireview

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A R T I C L E   I N F O

A B S T R A C T

Determination of degradation compounds of aged and deacidified papers requires an application of several analytical methods, including chromatographic and electrophoretic ones. Paper and paper extracts are very complex samples. Therefore, application of sample preparation methods is mostly involved in process of analysis. Sampling and sample preparation techniques provide transfer of analytes from a solid sample or from the gas phase (vapour) that exists above a solid sample into the extraction medium. Many extraction techniques were introduced, including conventional and advanced extractions utilizing water or organic extraction solvents, sampling tubes with adsorbents or fibre, often with the preconcentration of analytes. Passive sampling and solid-phase microextraction approaches were introduced as non-invasive techniques in the analysis of historical books and monitoring of indoor air in libraries and archives. This mini-review summarizes the sampling and sample preparation methods as well as new trends applicable in the analysis of degradation compounds of aged and deacidified papers.

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1. Introduction

The scientific and lay communities are interested in the paper as a subject of cultural heritage (objects/artifacts), such as documents, books, works of art. Paper is a multi-component material consisting of cellulose fibres, the rest of lignins, hemicelluloses, sizing agents, fillers and colourants, including inks and colours used for pictures. A hierarchic structure of the paper is represented by: a paper sheet, cellulose fibres, macro fibrils, microfibrils and bunds of polymer cellulosic chains, which are kept together by hydrogen bonds. The object of interest for the evaluation of the degradation and stabilization of paper artefacts is cellulose, as a basic building block of paper fibres. Cellulosic bunds (elementary fibrils) have crystalline and amorphous parts, whereas amorphous parts are less stable than crystalline parts. The natural ageing process is typical with a large set of consecutive and parallel reactions leading to the change of paper properties (appearance and mechanical strength) and formation of many low molecular weight compounds, e.g. car-

bohydrates, volatile organic compounds (VOCs) [1,2]. Dominant is a cellulose degradation of polymer cellulosic chains. Chemical degradation (acid hydrolysis, enzymatic hydrolysis, alkaline degradation, and oxidative degradation), thermal degradation (effect of higher temperature), and radiation impact (exposure to UV/visible radiation or high-energy radiation) are processes responsible for the degradation [3–5].

Therefore, air quality monitoring, identification and determination of degradation compounds, their differences depending on the variation of storage conditions and conservation treatment can help to understand the mechanisms of degradation and consequently minimize the rate of this process. Many testing methods were introduced in the analysis of paper and other lignocellulose materials, mechanical tests, imaging methods, crystallinity measurements, separation methods. Currently, there is a tendency to utilize non-destructive or non-invasive analytical methods in the analysis of aged papers, but destructive testing methods are commonly used in research studies. An overview of current techniques utilized in the paper analysis is documented in Table 1.

Air sampling and/or monitoring of vapours, extraction and/or preconcentration of analytes play an important role in process of

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Table 1
Techniques applied for characterization of properties, stability and degradation of aged paper and other lignocellulose materials.

	Technique	Obtained information	Preparation of sample for analysis, Comment	Ref.
Imaging analysis	SEM	- surface characterization - morphology of the fibres - analysis of microstructure	- coating of sample with a vaporized metal (e.g., gold) or carbon, to made the samples conductive - the electron beam may damage the samples - additional methods appropriate: *drying:* freezing, freezing in liquid nitrogen *staining:* highlighting the different parts (e.g. with $KMnO_4$; used to highlight the location of the lignin within the cell wall	[9,10]
	SEM+EDS	- elemental composition - mapping of elements in the sample - characterization of paper origin - efficiency of paper modification/stabilization	- combination with SEM (1–3% accuracy) - sample preparation as for SEM - in the case fractured papers, rough and uneven sample from at least two different positions is necessary for analysis	[11]
	TEM	- visualization of the internal structure of the lignocelluloses	- stabilization of the biomass specimens in a resin, obtaining suitable thickness by sectioning	[12]
	AFM	- topographic, physical, and chemical properties of the material at nanometre resolution	- without the sample preparation, staining, dehydration, metal coating, freezing - *advantage*: low scanning speed	[13]
	fibre tester	- determination of fibres length, width, shape factor, fines content	- swelling of paper sample in water to complete pulping, dilution of suspension	[14]
Composition of surface, Crystallinity	XRD	- signals related to the crystalline unit cell distances (a non-crystalline part of the cellulose represents broader and weak signals in the diffraction pattern) - investigation the surface texture and orientation of crystalline materials - elemental characterization	- without sample preparation - analytical results are highly dependant on the crystallite size and cellulose polymorph (decreasing in the crystallite size results in errors)	[15]
	FTIR, ATR-IR, PAS	- identification of individual components/acids (characteristic groups in molecule), degradation compounds - kinetic of degradation compounds production - studies of binder migration - identification of contaminants present in paper - determination of changes in crystallinity - identification of the fibres origin	- minimal sample preparation - FTIR spectrum involve signals as contributions of both crystalline and amorphous regions - ART-IR spectra depend on pressure applied to the sample - PAS: without the sample preparation	[8,16]
	Raman spectroscopy	- study the vibration states of simple molecules - identification of fibres in cellulose - characterization of degradation products - sensitive for non-polar molecules	- without the sample preparation	[8,17]
	XPS	- information for all of the elements (except of H and He) - information about chemical environment of element (chemical state, bonding, etc.) - characterization of polymer surface	- without the sample preparation - high surface sensitive (top 2–10 nm of the surface) - process under a high vacuum	[9]
	SIMS Dynamic and static variations	- fragmentation of molecule on surface and their identification based on molecular mass in MS - information on functional groups and molecular fragments such as radicals - identification all elements (including H, He) at a low concentration levels	- without the sample preparation - mainly used for smaller samples (due to increased sensitivity of the SIMS) and for depth profiling	[9]
	UV–VIS	- determination of surface binder content of paper coating layers - characterization of degradation products based on UV–VIS spectra of chromophores (e.g. for ketonic groups in the range 230–440 nm)	- without the sample preparation	[9]
	NMR	- information on the ultrastructure of the cellulose, the ratio of the interior-to-surface of cellulose crystallites - evaluation of the state of conservation, information on deterioration processes	- solid state ^{13}C NMR - without sample preparation	[18,19]

Table 1 (*continued*)

	Technique	Obtained information	Preparation of sample for analysis, Comment	Ref.
Degradation compounds	HPLC	- determination of compounds, carboxylic acids, carbohydrates	- solid-liquid extraction - solid-liquid extraction + SPE	[8]
	HPTLC	- determination of compounds, carbohydrates	- dilution of sample (e.g. samples from different pulping processes from softwoods and hardwoods)	[20]
	GC	- determination of compounds, VOCs	- SPME - HS-SPME - passive sampling	[8,21]
		- determination of monosaccharides	- solid-liquid extraction - derivatization (e.g. o-ethoximation or o-benzyloximation)	[22]
	CE	- determination of compounds, carboxylic acids, carbohydrates	- solid-liquid extraction	[8]
Degradation mechanisms	Viscosimetry	- determination of cellulose quality depending on fibre source and pulping - determination of degradation mechanism of cellulose	- dissolution in an iron (III) sodium tartaratecomplex (EWNN, FeTNa) and Cu cupriethylen diamine (Bis(ethane-1,2-diamine)copper(2+) CED) solution	[23]
	SEC	- characterization of the molar mass distribution - determination of the different molar mass averages, degree of polymerization - information about the degraded fractions	- derivatization of original sample - type and quality of the data, precision of M_r determination depend on the sensitivity of the detection method	[23,24]
	A4F-MALS	- characterization of the molar mass distribution - determination of the different molar mass averages, degree of polymerization - information about the degraded fractions	- preparation of cellulose tricarbanilates - separation of molecules occurs by flow in an empty channel, eliminating the undesirable phenomena related to the interaction of separated molecules with the column filling - reducing the possibility of shear degradation.	[25]

A4F-MALS - asymmetric flow field–flow fractionation in combination with multiangle light scattering, AFM - atomic force microscopy (or scanning force microscopy (SFM), ATR-IR - attenuated total reflectance IR, EDS - energy-dispersive spectroscopy, FTIR - fourier transform infrared spectroscopy, HPTLC - high performance thin-layer chromatography, HS-SPME - headspace-solid-phase microextraction, MS - mass spectrometry, NMR - nuclear magnetic resonance, PAS - photo acoustic spectroscopy, SEM - scanning electron microscopy, SIMS - secondary ion mass spectrometry, SPME - solid-phase microextraction, SPE - solid-phase extraction, TEM - transmission electron microscopy, XPS - X-ray photoelectron spectroscopy, XRD - X-ray diffraction.

analysis. Several publications and books are devoted to the issue of monitoring gaseous pollutants in indoor air [6,7]. Instrumental analytical methods utilized for the determination of degradation compounds of aged papers require sample preparation, mostly extraction of target compounds from the very complex matrix. Selection of sample preparation conditions depend on the nature of analyte/analytes to be determined, their concentrations, the nature of the sample, and on the desired parameters of analysis e.g. precision, accuracy and others requirements on analysis. The sample preparation procedure is often time-consuming and is the source of many errors. As discussed in the previous paper [8], advanced separation methods (liquid or gas chromatography, capillary electrophoresis) were involved in the paper analysis focused on the determination of degradation products, often on trace concentration levels. Sample preparation techniques provide transfer of target analytes into the extraction solvent (aqueous or organic solvent mixtures) by liquid extraction or into the gas phase (vapours) that exists above a solid or liquid sample. Extraction techniques involve conventional solvent extraction (mass of sample: 1–30 g, solvent volumes: 100–500 mL; extraction time: 1–48 h), advanced, e.g. microwave-assisted extraction, accelerated solvent extraction or supercritical fluid extraction (mass of sample: 1–30 g, solvent volumes: <50 mL; extraction time: <60 min) and micro-extraction, e.g. solid-phase microextraction, (mass of sample: <1 g or adsorption media placed in sampling area; solvent-free; extraction time: 10–60 min), often with the preconcentration of analytes. Even though the concentrations of analytes in the bulk of the sample are still mainly of interest, data on their distribution on the surface of the sample, in micro-regions, or phase boundaries, have become increasingly important particularly for monitoring of deacidification a preservation processes.

1.1. Research aim

This paper is focused on documentation of the role of sampling and sample preparation in analytical methods used for monitoring and determination of degradation compounds of aged and deacidified papers, mainly by chromatographic methods. New approaches in sample preparation, characterized by high selectivity and environmental friendliness, applicable in paper-based materials analysis will be also presented.

2. Techniques of extraction of VOCs and other low-molecular degradation compounds, sample introduction

The analysis of complex samples includes a combination of three major operations:

- sampling (the collection of solid or air samples)
- sample pretreatment (extraction and preconcentration techniques)
- detection and determination of target analytes (e. g. GC, HPLC or CE).

Sampling and sample preparation operations are focused on the isolation of analyte/analytes from the matrix components, reduction or elimination of interferences and/or analyte preconcentration in order to increase the sensitivity of the method. Some methods combine several steps into one (e.g. sampling and sample preparation/extraction) and thus reduce or eliminate the solvents or sample consumptions, minimize time consumption, as well as a decrease the amount of waste. Some of the methods also meet the requirements of "green analytical methods" [26]. While solid-liquid extraction can be used in methods for determination

of compounds in solid material, equilibrium techniques (e.g. HS-SPME, sorption tubes or solutions) are utilized in monitoring the compounds (volatiles) in a defined space of air to describe their emission from solid material or for monitoring of indoor air quality.

During degradation of paper-based materials (e.g. aged paper) volatile organic compounds (VOCs), mainly carboxylic acids, aldehydes, alcohols, aliphatic hydrocarbons, benzene and naphthalene derivatives, esters, PAH, are produced. These compounds are mostly detected as vapours in indoor air (room, closed box) or on the surface of pages of the book kept closed in the room. Methods of VOC sampling are used for the collection of air samples include both, active and passive (diffusive) sampling. An active sampling includes short-term (typically for several hours to a few days) or long-term (typically for 1–3 months) passing a defined volume of the air using a pump through an adsorbent with a constant flow rate (typically in the range of 10–100 mL/min). The active sampler can be a tube packed with a bed or multibed of adsorbents, for example, polyurethane foam, XAD resin, activated carbon, silica gel or other porous polymer materials. More complex and expensive equipment (includes pump and sorption unit; cost more than tens of thousands Eur) in comparison with passive samplers, the calibration of devices to obtain accurate results are factors affecting the utilization of active sampling technique. Samplers enable VOCs to be tracked at the sub-ppt ($<10^{-12}$) level. In a passive sampling technique, the air flowing spontaneously through the sampler results in a free flow of the analyte molecules from the air to a collecting media (media accumulate analyte) based on the difference in analyte concentration. Passive air samplers are usually small and simple devices that include tubes containing an adsorbent or reagent, coated fibres, impregnated paper strips, metal coupon and collect analytes via natural diffusion. They provide information on the long-term (from several hours to several days) average level of air contamination [27,28]. A passive sampling device can be direct-read, off-line or on-line connected to the instrumental analytical technique. After pre-concentration of analytes (VOCs) on adsorption media (e.g. packed tubes), they need to be desorbed for further analysis (GC or HPLC separation and determination of compounds). Desorption can be accomplished by many extraction techniques e.g. either by solvent or thermal desorption. During the last two decades, miniaturised air sampling techniques (Solid-phase microextraction, SPME; etc.) have been more frequently introduced because of reduction in sampling volume, organic solvent consumption, automation of operation, on-line coupling with analytical instruments [29,30]. A summary of sampling and sample preparation methods used in the aged paper analysis are summarized in Table 2.

Passive sampling was initially carried out with diffusion tubes, where which were impregnated with a suitable reagent ($20\mu l$ 1 M KOH and 10% glycerine on paper filters), and served to pre-concentration of carboxylic acids (acetic acid, formic acid). Paper support impregnated with derivatization reagent (an acidified solution of 2,4-dinitrophenylhydrazine) was applied for pre-concentration of carbonyl compounds in the air. Desorption of analytes was realised with water followed by HPLC-UV analysis or thermally (300 °C, 5 min) for GC–MS analysis (Table 2; [30–33]). The wide variability of sampling locations (air-filtered, non-ventilated, boxes, …) leads to different VOCs concentrations and thus sampling time varied, e.g. 1–28 days [34]. A passive sampler specifically designed for monitoring only one or few VOCs were developed by Huang or Canosa et al. [35,36]. Whereas passive sampling with pre-concentration of analytes by several extraction techniques is a non-invasive way to isolate VOCs, it can be applicable for sampling from archives, libraries, archival boxes. The limiting factor is a difficulty for analyte quantification. The passive sampling

method was repeatable and reproducible with RSD values below 7% for long-term exposures at low air velocities [31].

Miniaturised passive air sampling techniques include mainly diffusion-based systems, such as SPME on fibres. Emissive VOCs are sampled from indoor air (archives, libraries, archival boxes, closed chambers) or directly from paper in books (contact SPME; fibre is placed between two pages of the book kept closed in the room). The special copolymer matrixes for SPME are more sensitive and provide more information in a shorter sampling period. The studies show, that DVB/CAR/PDMS (divinylbenzene/carboxene/polydimethylsiloxane) is very useful for SPME of degradation compounds of aged paper. During air HS-SPME, the fibre is directly exposed to the air and VOCs are adsorbed on the SPME coating based on the partition of the target analytes between the sampling matrix and the fibre. The SPME fibre is then transferred into the GC inlet for thermal desorption [21,31–33,37,38]. For increasing sampling selectivity, SPME on derivatized DVB/PDMS (divinylbenzene/polydimethylsiloxane) fibres, e.g. o-(2,3,4,5,6-pentafluorobenzyl) hydroxyl–aminehydrochloride (PFBHA) were introduced. The results show, the derivatization with 1-pyrenyldiazomethane (PDAM) increases the molar mass of substances, and they are then more easily identified by GC/MS [39]. For purpose of the study of mechanisms and modelling of degradation processes, the paper samples or model paper samples were preconditioned (for 24 h to 23 °C and 50% RH; TAPPI T402sp-03, [40]). The contact SPME method can be used to provide information on the spatial distribution of emissions within a book. A cheaper alternative to the direct contact SPME fibre sampling is the use of PDMS (polydimethylsiloxane) strips [33]. To increase the concentration of VOCs determined, the strips could be placed inside the books for longer periods of time (2 days-5 months). VOCs trapped onto SPME fibres were thermally desorbed and directly analysed by GC–MS [31–33]. The efficiency of the method of capturing and enriching VOCs from naturally aged paper using contact SPME and headspace SPME was compared. The relative abundance obtained for the main classes of compounds showed that the contact method is more sensitive than the headspace method [37].

In the case of SPME methods, the ratios of the fibre/adsorbed analytes depend on the sampling time and the equilibrium is shifted towards the higher boiling components with increasing time. For these reasons, Hrivňák and co-workers introduced a non-destructive sampling technique called the headspace solid-phase microcolumn extraction (HS-SPMCE). In this method, a glass connector was inserted between two paper sheets and the end of the capillary was connected to a microcolumn containing adsorbent (Tenax TA, polymer sorbent recommended for retaining VOCs) whereas gaseous phase was aspirated through it. The advantage of HS-SPMCE lies in shorter sampling times (about 1 min) in comparison with the SPME (from tens of minutes to several days). Another advantage of a method operating up to the adsorbent packing breakthrough capacity is that the amount of analytes trapped in the microcolumn is comparable to the ratios in the aspirated gaseous phase [41,42].

An active sampling of indoor air in libraries during a period of 1 day was conducted to monitor the volatiles released from aged paper. Released VOCs were focused onto a Tenax TA tube cold trap held at a lower temperature (e.g. −30 °C). The desorption process involved a rapid heat of the cold trap to high temperature and desorbed analytes were passed directly into the GC–MS [33]. Limitations of Tenax TA occur for some low molecular weight compounds ≤C3, especially for polar substances, such as carboxylic acids (formic acid, acetic acid) and some aldehydes [43]. A much more precise determination of C1-C2 carboxylic acids in chamber air and indoor air were obtained by using silica gel tubes or by passing of air through a liquid absorber followed by liquid chro-

Table 2
Sampling and sample preparation methods used in analysis of aged papers and lignocellulose materials.

Sample	Sample preparation	Analyte	Method of analyte quantification	Notes	Ref.
Saccharides					
Paper from historical books	*Hydrolysis:* H_2SO_4 (72% w/w) s/l: 0.3 g/3 mL; incubation time: 60 min; temperature: 30 °C (water bath)	Xylose, galactose, arabinose, manose, glucose, holocelulose	HPLC-RI	*Analytes content:* glucose: 87–91% (books 18–19th centuries), 36–75% (books 20th centuries), 1–7% galactose, mannose, arabinose; no xylose	[47]
Newsprint paper	*Liquid extraction* s/l: 2 g/15 mL; extraction solvent: water; extraction time: 120 min; temperature: 25 °C	Celobiose, arabinose, fructose, galactose, glucose, manose, lactose, xylose	HPLC-RI HPLC-FLD (after derivatization)	*Total saccharides content:* 1.5 mg/g of non-impregnated paper 1.0 mg/g of paper impregnated by Bookkeeper suspension LOD(RI): 0.25 mg/L LOD(FLD): 0.01–0.04 mg/L	[52]
Lignocellulose biomass	*Dilution* in 0.05 mol/L sodium citrate buffer (3% w/v, pH 5.5), heat during 6 h *Enzymatic hydrolysis*	Xylose, galactose, arabinose, manose, glucose, fructose	HPLC-RI	*Analytes content:* glucose 22% v/v, mannose 34% v/v, fructose 13% v/v LOD: 0.04–0.35 mg/L	[53]
Papers from historical books	*Delignification* reaction mixture: distilled water, acetic acid, NaCl; reaction conditions: 70 °C, 3 or 6 h; reaction termination: cooling in ice bath	Glucose, arabinose, mannose, galactose, xylose	IC-EcD	*Analytes concentration in filtrates after 6 h of delignification:* glucose 0.12 mg/L, arabinose 1.16 mg/L, mannose nd, galactose and xylose <LOD LOD: 0.03–1 mg/L	[54]
Volatile organic compounds					
Vapours in museum cabinets	*Passive sampling* Sorption medium: filter paper disc impregnated with 0.02 mol KOH and 10% glycerine; extraction time: 1–14 days; elution solvent: water	Formic acid, acetic acid	IC-conductive detector	Detection of acetic and formic acids with vapour concentrations up to approximately 0.39 and 0.19 µg/L *Recovery:* 98% and 96% of acetic and formic acid (a sample spiked with a standard solution acetic and formic acid, 3 and 2 mg/L) LOD *of the passive sampler:* acetic acid 0.04 µg/L, 0.03 µg/L formic acid	[32]
Libraries and archives	*Passive sampling* Sorption medium: filter paper disc impregnated with 0.02 mol KOH and 10% (v/v) glycerine for sampling acids or a paper support impregnated with an acidified solution of 2,4-dinitrophenylhydrazine for sampling aldehydes; extraction temperature: 20 °C; extraction time: 24 h; desorption conditions: 5 min, 300 °C *Active sampling* sorption tubes filled with Tenax TA, preconditioned at 320 °C for 20 min; extraction temperature: 20 °C; sampling time: 24 h; sampling pump flow rate: 100 mL/min, desorption conditions: 5 min, 300 °C *Contact sampling* SPME DVB/CAR/PDMS fibre or PDMS strips (placed between pages of books); extraction conditions: 18–21 °C, 36.2–48.2% RH (depend on sampling site); extraction time: 2 days-5 months; desorption conditions: 3 h, 270 °C	Acetic acid, furfural, formaldehyde, trimethylbenzenes, decane, camphor, toluene, benzaldehyde, ethylhexanol, nonanal, decanal	GC–MS	*Analyte concentration in indoor air:* *Passive sampling:* Formaldehyde < 0.018 µg/L, acetic acid 0.036–0.348 µg/L, formic acid 0.022–0.310 µg/L. The method was repeatable and reproducible with RSD values below 7% for long-term exposures at low air velocities. *Active sampling:* Hexanal, furfural, heptanal and nonanal, with significantly higher concentrations were detected. Contamination of sampling air with petroleum based adhesives (the flooring of the hallway), cleaning fluid vapours (limonene), etc. *Advantage of Contact sampling:* determination of spatial distribution of emissions within a book	[31,33]

Table 2 (*continued*)

Sample	Sample preparation	Analyte	Method of analyte quantification	Notes	Ref.
Naturally aged paper, naturally aged wood, wood packaging used to transport and store heritage collections in storage buildings	*Active sampling* (sample conditioned at 23 °C, RH 20%) liquid absorber: 20 mL of 0.1 mol/L NaOH; sampling conditions: sample volume 75 L, flow rate 125 L/min; desorption: Na_2CO_3 solution	Acetic acid, formic acid and other VOCs	IC-EcD	The area-specific emission rates of formic acid and acetic acid from wood and paper ranged from 10 to 300 μg/m^2 h at normal indoor room conditions. Other VOCs can arise from multiple sources in the indoor environment (constructions materials and building Interior). LOQ: 0.005 µg/L	[44]
Ground wood pulp paper (historical books)	*HS-SPME* (sample conditioned at 23 °C, 50% RH) SPME fibre: DVB/CAR/PDMS; extraction temperature: 60 or 80 °C; extraction time: 60 min; desorption conditions: 10 min, 230 °C *Contact SPME* (book closed in room (23 °C, 50% RH)) SPME fibre: DVB/CAR/PDMS; extraction temperature: 23 °C; extraction time: 60 min; desorption conditions: 10 min, 230 °C	56 VOC (carboxylic acids, aldehydes, alcohols, aliphatic hydrocarbons, benzene and naphtalene derivatives, esters, PAH)	GC–MS	Contact method was more sensitive than the headspace method (except hydrocarbons).	[37]
Ground wood pulp paper (historical books)	*HS-SPME* (sample conditioned with Ar, 101.325 kPa, 20 °C) SPME fibre: DVB/CAR/PDMS; extraction temperature: 20 °C; extraction time: 24 h; desorption conditions: 240 °C *Contact SPME* SPME fibre: DVB/CAR/PDMS; extraction temperature: 21 °C; extraction time: 24 h; desorption conditions: 10 min, 230 °C	70 VOC (carboxylic acids, aldehydes, alcohols, aliphatic hydrocarbons, benzene and naphtalene derivatives, esters, BTEX)	GC–MS	Headspace method allowed identification of a wide range of organic compounds than contact method.	[38]
Different samples of historical books, newspaper, filter Whatman No.1 paper, softwood sulphate pulp	*Static HS-SPME* (sample conditioned at 80 °C for 18 h) SPME fibre: DVB/CAR/PDMS; extraction conditions: 40 °C; extraction time: 1 h; desorption conditions: - *Contact SPME* SPME fibre: DVB/CAR/PDMS; extraction temperature: 22 °C; extraction time: 24 h; desorption conditions: -	Acetic acid, furfural	GC–MS	The emissions of furfural correlate with pH of the paper. *Static HS-SPME*: destructive, requires about 100 mg of sample to be heated at higher temperature. *Contact SPME*: non-destructive	[21]

Table 2 (*continued*)

Sample	Sample preparation	Analyte	Method of analyte quantification	Notes	Ref.
Whatman No.1, P1, bleached sulphite softwood cellulose, cotton linters with traces of softwood cellulose, groundwood pulp, bleached sulphite softwood pulp	*SPME on derivatized fibre* (paper samples conditioned for 24 h to 23 °C and 50% RH) A) Derivatization reagent for carbonyls: PFBHA: loading of the derivatization reagent on the DVB/PDMS fibre (5 min, 23 °C); exposure of the fibre to the sample (2 h, 23 °C); exposure of the fibre to the internal standard (isobutyraldehyde; 2 min, 23 °C) - desorption conditions: 1 min, 270 °C B) Derivatization reagent for carboxylic acids: PDAM: loading of the derivatization reagent on the PA fibre (15 min, 23 °C); exposure of the fibre to the sample (1 h, 23 °C); exposure of the fibre to the internal standard (valeric acid; 2 min, 23 °C); desorption conditions: 1 min, 270 °C	Formaldehyde, acetaldehyde, acetone, hexanal, furfural, formic acid, acetic acid	GC–MS	Specific extraction of carbonyls and carboxylic acids by SPME on-fibre derivatization. LOD(carbonyls): 0.57–90 nmol/L LOD(carboxyls): 14–560 nmol/L RSD: 10–23%	[39]
Newsprint paper	*Dynamic HS-SPMCE* (sample conditioned at 23 °C for 24 h, RH 50%; accelerated temperature ageing) SPMCE adsorbent: Tenax TA (30 mg); sampling conditions: sample volume 5–10 mL, flow rate 1 mL/min, temperature of 23 °C; desorption conditions: 230–250 °C, 1 min	VOCs including acetic acid, furfural	GC–MS	Shorter sampling time in comparison with HS-SPME on fibre. *Analytes content:* acetic acid 2.6 µg/L, furfural 0,8 µg/L LOD(acetic acid): 0.03 µg/L LOD(furfural): 0.01 µg/L RSD: 1.7–2.8%	[41,42]
Paper from historical books	*Solid-liquid extraction* s/l: 2 g/15 mL; extraction solvent: water; extraction time: 120 min; temperature: 25 °C	Formic acid, acetic acid (free acids , water soluble salts)	HPLC-RI	*Analytes content:* acetic acid to 5.8 mg/g, formic acid 3.8 mg/g	[47]
Newsprint paper	*Solid-liquid extraction* s/l: 2 g/15 mL; extraction solvent: water; extraction time: 120 min; temperature: 25 °C	Formic acid, acetic acid	HPLC-UV(210 nm)	*Analytes content:* acetic acid 0.4-, 4.8 mg/g, formic acid 0.2–3.3 mg/g (content depend on type of paper deacidification) LOD(acetic acid): 18 mg/L LOD(formic acid): 11 mg/L RSD: < 4%	[47–50]
Paper from historical book (very, slightly and no degraded leaves)	*Solid-liquid extraction* s/l: -; extraction solvent: water; initial temperature: 50 °C; extraction time: until the water temperature decreased to room temperature; extracts stored in the freezer (−20 °C); for the analyses, small frozen amounts were melted and then quickly freeze-dried to obtain powders (around 25 mg of powder can be obtained from 1 g of paper for the sample solution)	Acetic acid, formic acid, succinic acid, glycolic acid, lactic acid	CE-DAD	*Analytes content:* acetic acid 4.2–6.3 µg/g; formic acid 2.2–4.0 µg/g; succinic acid 5.3–8.2 µg/g; glycolic acid 0.6–1.6 µg/g; lactic acid 2.9–4.6 µg/g (content depend on paper origin)	[55]

Table 2 (*continued*)

Sample	Sample preparation	Analyte	Method of analyte quantification	Notes	Ref.
Whatman No. 1 paper or tidelines formed on paper	*Solid-liquid extraction* extraction solvent: water or methanol; extraction time: 6 h; temperature: 23 °C *Modified CRI method* (treatment of paper with a Lewis acid (boron trifluoride acetic acid complex) containing a sodium sulphide, followed with phases separation in presence tocopherol-dichloromethane) extraction solvent: dichloromethane; extraction time: 48 h; temperature: 23 °C	20 low molecular weight compounds (carboxylic acids, furanic compounds, anhydrocarbohydrate derivatives)	GC–MS	CRI method is more complex. It led to the formation of more intensively coloured extracts indicating improved efficiency of extraction.	[51]

CRI - chromophore release and identification technique, DVB/CAR/PDMS - divinylbenzene/carboxene/polydimethylsiloxane, DVB/PDMS - divinylbenzene/polydimethylsiloxane, ELSD - evaporative light scattering detector, FLD - fluorescence detector, HS-SPMCE - headspace solid-phase microcolumn extraction, HS-SPME - headspace solid-phase microextraction, IC - ion chromatography, IC/EcD - ion chromatography with electrochemical detection, nd - not detected, LOD - limit of detection, PA - polyacrylate, PAH - polycyclic aromatic hydrocarbons, PDAM - 1-pyrenyldiazomethane, PFBHA - o-(2,3,4,5,6-pentafluorobenzyl)hydroxylaminehydrochloride, RI - refractive index detector, RH - relative humidity, SAX - strong anion exchanger, SPE - solid phase extraction.

matography separation of analytes on an anion-exchange separation column coupled with a conductivity detector [44].

In addition to previously mentioned methods, a solid-liquid extraction (SLE) of degradation compounds is applicable for aged paper analysis. The SLE is a process of solute component removal from the solid sample utilizing a liquid solvent. The method most often used is a maceration which can be supported by shaking [45]. Advanced and environmentally friendly solvent-based extraction techniques, providing higher yields, better penetration ability and a selective extraction, include ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), pressurized liquid extraction (PLE), supercritical fluid extraction (SFE). Liquid extraction with water or methanol as extraction solvents, and SPE-mixed mode (RP, SAX sorbents) for extract cleaning and analytes (free carboxylic acids, water-soluble salts, furanic compounds, saccharides) preconcentration were off-line coupled with HPLC (Table 2, [46–51]). However, these techniques are destructive, not applicable for analysis of historical papers, but they are convenient in the study of mechanisms of paper ageing and effects of deacidification/preservation procedures.

3. Sample preparation for SEC methods

The size-exclusion chromatography (SEC) [56] analysis requires the sample to be dissolved in an appropriate solvent (ideally, in the mobile phase). Sample preparation for the SEC analysis includes dissolution of cellulose in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) or derivatization of the original sample (dried sample cut into little pieces (the area of a few mm^2)) using phenyl isocyanate to obtain cellulose tricarbanilates (CTC) which are subsequently dissolved in tetrahydrofuran. The derivatization conditions, temperature, and time vary in intervals 70–110 °C and 6–72 h, respectively (Table 3). To terminate the reaction, methanol is added into the reaction mixture and the mixture is cooled to room temperature [61–63]. SEC of cellulose in LiCl/DMAc provided higher Mr values in comparison with SEC of CTC. These differences were more or less pronounced depending on the initial degradation state of the paper [23,57].

The carbonyl content of polysaccharides can be investigated using several different carbonyl labelling strategies combined with

SEC-MALLS (multi-angle laser light scattering), RI, fluorescence detection or off-line tritium detection. An analytical approach for the determination of carboxyl groups in cellulosics has been developed by Bohrn and Henniges [58,59]. This employs COOH-selective fluorescence labelling with 9H-fluoren-2-yl-diazomethane (FDAM) to convert carboxyl structures into fluorescent fluoren-2-yl methyl esters. The fluorescence label FDAM did not interfere with the MALLS detection and was sufficiently stable. The COOH labelling neither changed the solution state of the pulp nor caused cellulose degradation.

Other fluorescence labels introduced in the detection of carbonyl groups/reducing ends of oligosaccharides include, e.g. carbazole carbonyl oxyamine (CCOA; carbazole-9-carboxylic acid [2-(2-aminooxy-ethoxy)ethoxy]amide) or 2-aminobenzamide (2-AB). These labels allow the detection of carbonyl functionalities in cellulose at the picomolar level. One of the most common strategies for carbonyl detection in oligosaccharides is the incorporation of tritium utilizing NaB_3H_4 reduction [60].

4. Trends in sample preparation applicable in analysis of paper-based materials

Innovations in sample preparation are focused on increasing selectivity towards target analytes and improvement in environmental friendliness (Table 4).

Molecular imprinting technology allows preparing polymeric materials with predetermined selectivity and high affinity applicable for various analytical targets, solid adsorbent for SPE, stationary phase for chromatographic separation, chemical/biosensors, and others. The process is based on the creation of template-shaped binding sites (cavities) in polymer matrices, which allow selective recognition of the imprint species or structurally related compounds. The molecularly imprinted polymer (MIP) preparation process involves the formation of a complex between a target molecule (template) and functional monomer through covalent or non-covalent interactions, afterwards polymerized to form an imprinted matrix. Finally, the template is removed, leaving behind a cavity complementary in size and shape to the template molecule [64].

Table 3

Sample preparation for SEC analysis of aged papers and lignocellulose materials.

Sample	Sample preparation	Parameter	Method of separation	Ref.
Whatman No. 1 filter paper (pure cellulose)	*Derivatization* - 200 mg of sample, 30 mL dimethylsulfoxide, 10 mL of phenyl isocyanate - reaction conditions: 70 °C at 48 h - reaction termination: 20 mL of acetone, precipitation in ethanol - dilution with tetrahydrofuran *Dissolution in LiCl/DMAc* - 50 mg of sample, 8 mL anhydrous DMAc (23 °C, 12 h), filtration - addition of 8% LiCl/DMAc (5 mL, 23 °C, 4 h)	Mass distribution parameters	SEC-LALS (633 nm) SEC-MALLS	[23]
Newsprint paper	*Derivatization* - 50 mg of sample, 8 mL of pyridine, 1 mL of phenyl isocyanate - reaction conditions: 70 °C, 72 h - reaction termination: 2 mL of methanol, 23 °C - addition of methanol:water (7:3, 150 mL) - dilution with tetrahydrofuran	Degree of polymerization	SEC-DAD (240 nm) SEC-MALLS A4F-MALLS	[25]
Papers from historical books	*Derivatization* - 3 mg of sample, 1 mL of pyridine, 0.1 mL of phenyl isocyanate - reaction conditions: 80 °C, 48 h - reaction termination: 0.1 mL of methanol, 23 °C - dilution with tetrahydrofuran	Mass distribution parameters	SEC-UV (235 nm, 210 nm)[a]	[54]
Laboratory prepared paper from pine pulps; accelerated ageing;	*Derivatization* - 5 mg of sample, 1 mL of pyridine, 0.1 mL of phenyl isocyanate - reaction conditions: 80 °C, 48 h	Degree of polymerization	SEC-UV (254 nm) MALLS (658 nm)	[61]
Whatman No. 1, an additive-free bleached sulfite softwood cellulose paper, regular copy paper and recorder paper, rag papers dating from 1796 and from the 19th century	- reaction termination: 0.1 mL of methanol, 23 °C - dilution with tetrahydrofuran (1:10)	Mass distribution parameters	SEEC-UV	[62]
Newsprint paper	*Derivatization* - 20 mg of sample, 6 mL of pyridine, 1 mL of phenyl isocyanate - reaction conditions: 110 °C, 6 h - reaction termination: 2 mL of methanol, 23 °C - addition methanol:water (7:3, 150 mL) - dilution with tetrahydrofuran	Degree of polymerization	SEC-DAD (240 nm)	[63]
Pulp	*Pulp preconditioning* - 20 mg of dry pulp suspended with 0.1 mol/L HCl, agitation for 20 s - washing of pulp with 0.1 mol/L HCl, 96% ethanol, and DMAc *Derivatization* - suspensions of pulp in 3 mL of DMAc and 1 mL of FDAM (0.125 mol/L in DMAc) - reaction conditions: 40 °C, 7 day - filtration, washing with DMAc - dissolution of the cellulose: 1.6 mL of DMAc/LiCl 9% (m/v)	Evaluation of carboxyl profiles, molecular weight distribution	GPC-FLD (252/323 nm)	[58]

A4F - asymmetric flow field–flow fractionation, DAD - diode array detector, DMAc - N,N-dimethylacetamide, FDAM - 9H-fluoren-2-yl-diazomethane, FLD - fluorescence detection, LALS - low-angle light scattering, MALLS - multi angle light scattering, SEEC - size exclusion electrochromatography.

[a] 235 nm for the determination of cellulose tricarbanilates and 210 nm for the determination of polystyrene standards.

MIPs find application as the molecular recognition element in sensors, including electrochemical sensors (EIS) (electrochemical impedance spectroscopy). The preparation of the sensor can be realised by: i) depositing the film of MIP on a solid support of electrode by surface grafting using e.g. chemical, UV, or thermal initiation [65], ii) applying of a potential (or the exposition to UV light) in situ on the detector surface, coated with a mixture of the monomer in an appropriate solvent [66].

Today, attention is focused on the development of sensitive, specific, cheap, and reliable sensors for real-time monitoring of analytes concentration. The optical chemical sensors can be effective, reproducible, fast, and low-cost devices for the detection of degradation compounds of aged paper, e.g. furfurals, glucose, formaldehyde [67–70]. The optical chemical sensors based on a

PET (polyethylene terephthalate) substrate combined with a MIP layer for 2-furfuralaldehyde (2-FAL) were prepared by Cennano and coworkers [64]. The PET optical waveguides, covered by MIP, used two plastic optical fibres to connect with a light source and with a spectrometer. This simple sensor was suitable for the determination of 2-FAL in water samples even at low concentrations, LOD ≈ 0.03 mg/L. The detection is based on the MIP receptor combined with the optical sensor, through measurement of intensity at a fixed wavelength (intensity-based configuration).

A potentiometric MIP sensor for glucose was synthesized by bulk polymerization using glucose as a template and methacrylic acid as a functional monomer. The potential responses of the MIP-based electrode depend on the concentration of glucose. For glucose concentration up to 7 mmol/L, the measured potential was

Table 4

Applications of MIP based sensors, MIP adsorbents and LTTM solvents in analysis of selected compounds.

Analytes	Application	Sample	Advantages	Ref.
Molecularly imprinted polymers				
Furfural	*Optical chemical sensors based on PET substrate and MIP* Thermal polymerization of MIP: 16 h, 80 °C Polymeric mixture: DVB - cross linker, MAA - functional monomer, 2-FAL – template, AIBN - radical initiator; (2-FAL:MAA:DVB 1:4:40, mol/mol)	Water	Selective detection based on MIP receptor. LOD: 0.03 mg/L	[67]
Furfural	*SPR-MIP electrochemical sensor based on a D-shaped POF, combined with a biomimetic receptor (MIP)* Thermal polymerization of MIP: 16 h, 80 °C Polymeric mixture: DVB - cross linker, MAA - functional monomer, 2-FAL – template, AIBN - radical initiator; (2-FAL:MAA:DVB 1:4:40, mol/mol)	Aqueous solutions	Miniaturization - MIP can be easily deposited over the chip LOD: 6×10^{-6} mol/L	[68]
Glucose	*MIP-glucose potentiometric sensor* Thermal polymerization of MIP: 21 h, 60 °C Polymeric mixture: EGDMA - cross linker, MAA - functional monomer, glucose - template, AIBN - radical initiator, DMSO - porogen, BPO- additive	–	–	[69]
Glucose, mannose, galactose, sucrose	*MIP-galactose adsorbent* Thermal polymerization of MIP: 12 h, 50 °C Polymeric mixture: EGDMA - cross linker, AA - functional monomer, galactose - template, AIBN - radical initiator, chloroform - porogen; (galactose:AA:EGDMA 1:4:20, mol/mol)	Synthetic or biological samples	Separation of saccharides.Ads orbent for extraction techniques.	[71]
Formaldehyde, VOCs	*PPy-based MIP/TiO$_2$-NTA sensor; MIP-formaldehyde sensor on a TiO$_2$ NTA* TiO$_2$-NTA preparation PPy-based MIP synthesis by electropolymerization Electrode patterning	–	Stable over one year	[70]
Green extraction solvents				
Furfural	*HDES based solid-liquid extraction* HDES: camphor (HBA) : 1-decanol, decanoic acid or 3,4-xylenol (HBD) (1:2, mol/mol)	Lignocellulose hydrolysates	Extraction efficiency higher than 80%	[75]
Furfural	*HDES based liquid-liquid extraction* HDES: decanoic or dodecanoic acid: N4444Br or N8888Br (1:3, mol/mol)	Water, aqueous solutions	LOD: 0.1%	[76]

DVB - divinylbenzene, 2-FAL - 2-furfural aldehyde, HBA - hydrogen bond acceptor, HBD - hydrogen bond donor, HDES - hydrophobic deep eutectics solvent, LOD – limit of detection, MIP - molecularly imprinted polymer, NTA - nanotube array, PET - polyethylene terephthalate, POF - plastic optical fibre, molecularly imprinted polymer for formaldehyde on a TiO$_2$ nanotube array, PPy – polypyrrole, SPC - screen printed cell.

within the range of 72.5 up to 295.8 mV. The potential response was linearly correlated to glucose concentration within the range of 0.02 mmol/L up to 5 mmol/L [69]. Tang and coworkers present a chemical sensor for detecting formaldehyde, based on polypyrrole-MIP employed as the sensing recognition layer. MIP was synthesized on a titanium dioxide nanotube array for increasing its surface-to-volume ratio and improving the sensor performance. The sensor has shown long-term stability and sensitivity to detect formaldehyde at ppm range [70].

Solid-phase extraction (SPE) is commonly used for sample pre-treatment since it has many advantages, such as high efficiency, simple operation, less time-consuming, and good compatibility with different analytical methods. It uses a solid adsorbent to adsorb the target analytes from the sample solution/primary extract, and thus type of adsorbent is the key parameter affecting the efficiency of extraction. Adsorbents often used (e.g. C18 type, silica) are usually nonspecific for a target analyte and limit its application for analysis of complex samples. MIPs as SPE adsorbents (MISPE) specifically recognize and effectively adsorb target analytes. Therefore, MISPE is extensively used for the selective clean-up and enrichment of trace amounts of analyte in complex samples. In addition to the conventional SPE, it can be realized in several modes:

- dispersive SPE (DSPE)
- magnetic SPE (MSPE)
- matrix solid-phase dispersion (MSPD)
- solid-phase microextraction (SPME)
- stir-bar sorptive extráction (SBSE)
- pipette-tip SPE (PT-SPE).

MIP based extraction adsorbent selective for several saccharides, glucose, mannose, fructose, maltose, lactose, sucrose and raffinose was prepared by Okutucu and coworkers [71] utilizing ethylene glycol dimethacrylate as a crosslinking agent, acrylamide as a functional monomer and galactose as a template molecule. MIP has shown application potential for the recognition of different saccharides. The results indicated that the orientation of the functional groups in saccharide molecules was the dominating factor for the selectivity of galactose imprinted polymer.

Many analytical methods, including extraction procedures based on principles of "green" analytical chemistry, have been developed or transferred for mass application [46]. Thus, the preparation and application of environmentally friendly extraction agents are acceptable alternatives. Low transition temperature mixtures (LTTMs) including deep eutectic solvents (DESs) or natural deep-eutectic solvents (NADESs) represent a new generation of fluids. They are typical as a mixture of two or more compounds; the hydrogen bond acceptor (HBA; e.g. quaternary ammonium salt) and the hydrogen bond donor (HBD; e.g. organic acid, alcohol), which can interact with each other through hydrogen bonds, to form a liquid mixture with the melting point lower than that of the individual constituents [72]. The main advantages of LTTMs over traditionally used organic solvents are their good salvation properties, reusability, biodegradability and biocompatibility, easy preparation with a broad scale of polarities [73,74]. The DES-based on camphor (HBA) and 1-decanol, decanoic acid or 3,4-xylenol (HBD) (1:2) were applied for extraction of furfural (FF) and 5-hydroxymethylfurfural (HMF) from lignocellulose hydrolysates. The experimental studies

revealed high extraction efficiency resulting in 79.2% and 87.9% removal of FF and HMF, respectively, from model hydrolysates and in the range of 74.2–76.1% and 87.8–82.3% from real samples in one-step extraction [75,76].

5. Assessment of method greenness

Practically applied analytical methods should meet some requirements, e.g.:

- a short time of analysis
- low or reduced amount of reagents and solvents
- no or minimal sample handling, avoiding or reducing the waste
- utilization of low energy consumption instrumentation.

Eco-approaches applicable in analytical methods used for the analysis of aged papers include mainly the use of:

 i) methods without or with minimal sample preparation (e.g. microscopy, XRD, FTIR, …)
 ii) sensors for monitoring of degradation compounds (VOCs, others);
 iii) miniaturization in sampling and sample treatment methods (SPME);
 iv) increase of sample handing selectivity (the use of selective extraction adsorbents and materials);
 v) on-line coupling extraction and separation/determination techniques (extraction technique on-line coupled to chromatography).

Several approaches were introduced for the evaluation of the green character of analytical methods. Galuzska et al. developed a quantitative criterion named Eco-scale based on the application of penalty points concerning the number of reagents, hazards related to reagents and solvents, energy consumption and wastes [77]. The GAPI (Green Analytical Procedure Index) [78] used the pentagrams approach, which includes the evaluation of the green property of sample preparation and analytes determination.

HPLC and CE methods applied for the determination of carboxylic acids and sugars in aged paper treated by SLE, hydrolysis or passive sampling [32,46,47,55] are characterised by low hazard chemicals, waste and energy instrumentation. Calculated Eco-scale total penalty points were more than 80 (calculated based on experiments presented in listed publications; 100 mark present the ideal green method). The SEC-DAD or SEC-MALLS [25] methods for determination of the degree of polymerization and mass distribution, based on derivatization procedure for obtaining cellulose tricarbanilates, used more hazardous chemicals resulting in lower Eco-scale score (total penalty points 52).

6. Conclusion

Description, evaluation of sample preparation for analysis of degradation compounds from aged and deacidified/preserved books can help researchers and library specialists to choose a proper procedure for quantification of chemical changes in studied objects. Organization of methods to Tables gives the reader a faster orientation and comparison of what method is suitable for. The advanced and innovative analytical methods contribute to understanding the mechanisms of paper degradation and evaluating the chemical stability of paper and the efficiency of preservation procedures. In this paper, we present techniques that precede the quantification step of the main degradation compounds of paper. Sampling, sample preparation and/or extraction of degradation compounds, eventually, their pre-concentration, are an important part of the process of chemical analysis. Although the combining of several steps into one and non-destructive methods are currently introduced (e.g. SPME-GC/MS for VOCs determination; sensors for

analytes monitoring), sampling and analysis with destructive techniques are still mostly used procedures (SEC for determination of the molar mass distribution; solid-liquid extraction of sugars and VOCs).

Many papers documented a wide range of VOCs detected and determined (many of them at high concentration levels) in the indoor air of selected locations in libraries and archives where the large volume of paper-based materials was stored. The type of identified compounds and their concentrations vary considerably depending on sampling location. Several approaches of sampling and sample preparation were applicable in the monitoring degradation compounds:

 I) non-destructive techniques
  - Studies show that it is appropriate to combine multidimensional sampling approaches to evaluate analytes emitted by naturally aged papers, e.g. active or passive sampling of indoor air, contact sampling the emissions of whole books or small paper samples, generally placed in vials (headspace SPME) or directly between pages of books (contact SPME using fibres and strips, or SPMCE). VOCs emitted directly from books were also found in the indoor air and were identified as emissive by-products from paper [31,42].
  - The relative abundance obtained for the main classes of compounds shows that the contact method is more sensitive and selective than the headspace method [37].
  - The application of direct contact SPME fibre sampling proved to be a more sensitive sampling method and provided more information in a shorter sampling period (mostly 1–24 h in comparison to 1–14 days for passive sampling). PDMS strips are cheaper (each strip costs approximately 0.30 Eur, compared to an SPME fibre at approximately 100 Eur) and simpler alternative (ease to place between book pages; longer time of emission collection for analytes at trace concentration levels).
  - Contact studies may also show an increased tendency toward early fibre saturation by the major VOCs (e.g. acetic acid, formaldehyde) which easily desorb from the book. Finally, the thin polymeric coating of the fibres are easily damaged or stripped from repeated contact, particularly considering the mass of a closed volume on the fibre [38].
  - The methods used for sampling of indoor air (on fibres, passive sampling - cost approximately 300 Eur/kit consists of adsorbing cartridges and barcode labels, diffusive body, support plate) are often unspecific and result in the extraction of a wide range of compounds, including contaminants present in the atmosphere or compounds emitted by other materials in the immediate vicinity of the sample (e.g. cleaning products, building materials, furniture).
  - An increase in selectivity of sample preparation, separation and detection as well as increasing of method "greenness" leads to the application of environmentally friendly extraction agents (e.g. besides water, alcohols also LTTMs as extraction solvents; MIP based adsorbents, SPME on derivatized fibres).
 II) destructive techniques
  - Solid-liquid extraction for the extraction of nonvolatile degradation compounds, assisted by shaking or ultrasound are characterized by high extraction yields, good penetration ability, selectivity and experimental simplicity. However, this technique is destructive, applicable in the analysis focused on the study of mechanisms of paper ageing through accelerated ageing processes.
  - The SEC separation requires the sample to be dissolved in an appropriate solvent compatible with mobile phase and/or derivatization.

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