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Gellan residues on paper: quantification and implication for paper conservation

Ute Henniges[1*], Irene Brückle[1], Hajar Khaliliyan[2] and Stefan Böhmdorfer[2]

Abstract

Gels prepared from the polysaccharide gellan are used for aqueous poulticing treatments in paper conservation when the application of water must be restricted. Optimal use of the rigid, yet shapeable gel requires direct contact with the paper surface, which carries the risk of gel residues on the treated surface. We used acid methanolysis as a destructive analytical method to detect rhamnose as a component of gellan, which was undetectable with ATR-FTIR spectroscopy. We show that there is a significant probability of leaving gellan residues on the paper. Conservators should be aware of this potential side effect when considering the use of gellan poultices in direct contact with paper objects.

Keywords Gellan gel, Rigid gel, ATR-FTIR, Acid methanolysis, Residues, Paper conservation

Introduction

Gellan, a natural polysaccharide, forms rigid gels that are used for the aqueous poulticing treatments when the migration of water out of the immediate treatment area needs to be restricted. This is the case with paper objects that feature water-sensitive components, e.g., media. Gellan gels are very versatile. They can be prepared in different stiffnesses and concentrations and are adjustable in their shape. They have been studied for general cleaning [1], for swelling starch adhesive in preparation for its removal from the paper surface [2], which also involved the incorporation of enzymes into the gel [3], and have been used for bleaching and deacidification in overall treatments [4, 5]. Their internal networks retain water more effectively than cellulosic poulticing materials such as more porous blotting papers or microcrystalline cellulose. Gellan gels function in a similar way to Nanorestore® gels, which are used also as poulticing materials, e.g., for local stain removal [6, 7]. As with any conservation treatment, the use of gels requires knowledge of the associated benefits and risks, as discussed in a textbook [8] and a compendium of practice information [9].

Gellan is a linear anionic polymer with a tetrasaccharide repeating sequence consisting of two β-D-glucose monomers, a β-D-glucuronate and a α-L-rhamnose monomer [10, 11]. As an anionic polysaccharide, gellan interacts with alkali and alkaline earth metal cations that promote gelation and tailor the gel's stiffness. In conservation, calcium ions are typically used as aids for gel formation. Since the gel, which is prepared from the polysaccharide powder using boiling water, decomposes over time, it is inevitable that low molecular weight degradation products are formed. For this reason, the prepared gel is also susceptible to mold growth which limits its shelf life.

Conservators have been concerned that gellan could leave residues on the surface of a paper object following direct contact. This is because the gellan gel networks are physically cross-linked by ionic bonding forces, i.e., feature weaker bonding than chemically cross-linked

*Correspondence:
Ute Henniges
ute.henniges@abk-stuttgart.de
[1] Conservation of Works of Art on Paper, Archives and Library Materials, Stuttgart State Academy of Art and Design, Am Weißenhof 1, 70191 Stuttgart, Germany
[2] Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Straße 24, 3430 Tulln, Austria

networks such as they exist in Nanorestore® gels. Monitoring the removal of gellan as a foreign substance is therefore an integral part of research studies investigating possible uses of gellan gel poultices [12, 13]. Potential gel residues that can affect the ageing of paper are sugar monomers and oligomers that are low molecular weight products; gel residues may also be left on the paper in the form of high molecular weight polymeric deposits or debris of the gel pad that can alter the paper surface. Permeable barriers such as Japanese tissue mitigate the risk of residues, but they also tend to decrease the effectiveness and efficiency of the gel treatment [14].

It can be assumed that the gel residues after poulticing are very low, as the contact between the rigid gel and the substrate is limited in time and the gel is removed in one piece and usually without leaving any visible debris. Therefore, highly sensitive analytical methods are required to detect small amounts of gellan residues. In the destructive methods, highly sensitive and specific fluorescence labelling was able to detect residues on three different paper substrates [15], while scanning electron microscopy (SEM) [3, 5], which cannot detect monomeric or oligomeric residues, suggested that no gel residues remain on the paper. For non-destructive testing, Attenuated Total Reflection Fourier Transformation Infrared spectroscopy (ATR-FTIR) which is widely used in conservation science, is the most described method for monitoring paper substrates after gellan gel application [12, 13, 16]. In these studies, ATR-FTIR spectroscopy was chosen based on the visibility of characteristic gellan absorptions at 1605 cm^{-1} and 1414 cm^{-1}. This method suggests that gellan gel leaves no residue.

Acid methanolysis is a destructive, highly sensitive and selective method for the detection and quantification of individual sugars in the pulp and paper industry [17, 18]. We propose to use this method for the quantification of gellan residues using the gellan component rhamnose as a marker. To determine the viability of acid methanolysis as a method to quantify gellan residues, we used three representative paper types that we loaded with known amounts of gellan. For comparison, we also performed ATR-FTIR on these papers. In addition, the ability of the two analytical methods to detect potential residues was compared on papers that had undergone a simulated conservation poultice treatment with rigid gellan gel. Both analytical methods allowed us to focus on the surface of paper substrates. The quantitative data provide new insights into the risk of residues when treating paper objects with rigid gellan gel.

Materials and methods

Sample papers

The papers were a filter paper (Macherey–Nagel) from the stocks of the Stuttgart program, a modern gelatine-sized flax fibre paper made about 15 years ago (by Gangolf Ulbricht, Berlin), and a naturally aged, slightly yellowed, gelatine-sized rag paper of unknown date also from the Stuttgart program (Table 1). The papers represent a range of water absorbencies encountered in conservation treatment, from the highly absorbent filter paper to the rather water-repellent modern rag paper. Also, composition of the papers differs in that the filter paper contains only cotton linters, while the two rag papers are surface-sized with gelatine. Filter paper is the purest substrate; in addition to glucose, it also contains some arabinose and xylose. Modern and historic rag papers have a more complex sugar composition; their hemp and flax fibres contain mannose, xylose, galactose and, probably due to pectins, small amounts of rhamnose (Additional file 1: Table S1).

Sample paper preparations

For the determination of the detectable gellan

The procedure involved loading the sample papers with a known amount of gellan by immersing them in solutions of different concentration. All samples were cut to a size of 7 × 9 cm and weighed before further processing in order to accurately monitor the weight increase for each sample paper. To determine the detectable amount by ATR-FTIR and acid methanolysis, gellan solutions were prepared in seven concentrations (1.0%, 0.6%, 0.3%, 0.1%, 0.06%, 0.03%, and 0.01%). The gellan was prepared by dispersing an appropriate amount of gellan (Kelcogel GC-LA, purchased from Gaby Kleindorfer) in 50 mL of a cold calcium acetate solution (0.4% w/v, purchased from Sigma Aldrich) and heated to boiling to obtain a clear gellan solution. The papers were immersed into the heated solution to a depth of about 7 cm, leaving an untreated

Table 1 Description of the sample papers

Sample	Sample ID	Source	Composition	Grammage
Filter paper	Filter	Macherey–Nagel	Cotton linters, no additives, no sizing	120 g/m^2
Modern rag paper	Modern rag	Gangolf Ulbricht	Flax fibres, surface-sized with gelatine	100 g/m^2
Historical rag paper (naturally aged)	Historical rag	Study program Stuttgart	Rag fibres, surface-sized with gelatine with alum added	110 g/m^2

strip of 2 cm for handling (immersion area = 7 cm^2). Three specimens were prepared for each concentration and paper (Table 2). Two specimens were required for the destructive acid methanolysis and one for the non-destructive ATR-FTIR analysis where several spectra could be obtained per specimen thanks to the small measurement spot. The specimens were air-dried at ambient conditions (~ 22 °C and ~ 45% relative humidity, RH) by suspending them from the non-immersed part for several hours before storing them in the dark prior to analysis.

For the determination of gellan residues after poulticing treatment

Gellan gel of 3% concentration was applied in pieces of 0.5 mm thickness to one area of the paper to mimic a local aqueous treatment. The treatment was repeated on three different spots on each paper. The 3% gel represents an intermediate concentration between the 2–5% reported in literature, e.g., Delattre et al. [19] and Sullivan et al. [15]. To prepare the gel, a suspension of 3% (w/v) in calcium acetate (0.4%) was heated until boiling to obtain a clear solution as described in the previous section. The liquid was poured into a Petri dish and left to cool and solidify. After 24 h, pieces of 3.5 × 3.5 cm were removed and placed directly on each paper. Each gel was covered with polyester film to prevent it from drying and weighted with a small metal block to ensure even contact (210 *g*, corresponding to 17 g/cm^2) for 60 min. The gel was then removed, and the papers were air-dried and stored until sampling for methanolysis and ATR-FTIR. For ATR-FTIR, four replicate spectra were taken in four neighbouring locations.

Showing the visible poulticing effect

In addition, the gellan gel poulticing was compared with a poultice that consisted of a wet blotter placed in direct contact with the sample paper. This was done to highlight the properties of gellan as a poulticing medium with a low porosity and a high water retention. The blotting paper was soaked in demineralized water, excess water was blotted off, and the blotter was placed on the samples. These samples were evaluated for their appearance and their water response.

Weight increase

The weight increase was determined for the sample papers immersed in gellan with a Kern EMB 100–3 balance (d = 0.001g). The papers were weighed before immersion in the hot gellan gel solution (see Sect. "Sample papers"), dipped in gellan (see Sect. "For the determination of the detectable gellan"), left to dry for at least 24 h at ambient conditions (~ 22 °C and ~ 45% RH), and were weighed again. The weight increase was calculated according to Eq. (1).

$$\Delta = M_0 - M_1 \quad (1)$$

where M_0 is the weight of the air-dry paper before gellan immersion, M_1 is the weight of the paper after immersion and air-drying and Δ is the weight increase in mg.

ATR-FTIR

Samples loaded with known amounts of gellan to study the limits of spectroscopic detectability, papers after a mock-up gellan treatment, and the controls were analysed using an FTIR spectrometer (PerkinElmer) with UATR-accessory. Each spectrum consists of an average of 4 scans with a 4 cm^{-1} resolution from 4000 to 750 cm^{-1}. All spectra were baseline corrected and normalized at 1030 cm^{-1} to allow direct comparison between the individual spectra.

Acid methanolysis: choice of method, technique, sample paper preparation

Choice of method: Acid methanolysis is used to break down accessible regions of polysaccharides into their monosaccharide components to determine the monomeric sugars that make up the sample. Of the three monomers of gellan—glucose, glucuronic acid, and rhamnose—that can be detected with methanolysis, rhamnose was chosen as a marker compound for the following reasons. Glucose was ruled out because its increase is likely too low and could therefore easily be masked by the amorphous cellulose also present in the papers. Glucuronic acid, which was not present in the three papers, would have been a clearly identifiable marker for gellan residues but is far less stable than rhamnose under acid methanolysis conditions [20],

Table 2 Number of samples for the determination of detection limits

Sample paper ID	Immersion in hot, liquid gellan solution						
	1.0%	0.6%	0.3%	0.1%	0.06%	0.03%	0.01%
Filter	3	3	3	3	3	3	3
Modern rag	3	3	3	3	3	3	3
Historical rag	3	3	3	3	3	3	3

which is why rhamnose was the better choice. However, rhamnose not only accounts for about 25% of the characteristic gellan tetrasaccharide repeating unit, but it is also a natural component of pectins and/or hemicelluloses in paper-making fibres and can therefore be present in paper [21]. Thus, to use it as a marker, its content in the sample papers before and after gellan treatment had to be determined. Within our sample papers, it was detected in the historical rag paper and was present in barely detectable amounts in the modern rag paper. For this reason, a qualitative check for rhamnose content or setting a typical background value would not have been sufficient.

Technique: In acid methanolysis, sampled solids are depolymerized, derivatized, and analysed. A few milligrams of the solid sample are mixed with hydrochloric acid in methanol (2 M, 2 mL), the mixture is heated (100 ℃, 3 h) and mixed repeatedly. Since the reaction is carried out in methanol and not in water, only hemicelluloses, pectins, and the more easily accessible parts of cellulose are broken down, while the more crystalline cellulose remains intact. Uronic acids can also be detected after acid methanolysis, while they would be degraded in hydrolysis based on sulfuric acid [18]. The released monomers are dissolved in the methanol. After completion of the reaction, the solution is neutralized with pyridine, the methanol is evaporated, and the mixture is further treated to allow analysis of the monomer composition. Since we used gas chromatography, in which the target compounds must be volatile, the monomers must be derivatized to make them volatile. To do this, the released monomers are dissolved again and derivatized with trimethylsilyl groups to increase their volatility. The derivatized monosaccharides are then separated by gas chromatography using a HP1-type column (internal coating of 100% dimethylpolysiloxane) with a temperature gradient. For detection, a flame-ionization detector is used to detect compounds containing organic carbon. The quantification of the individual monosaccharides is based on the integrated areas of a specific peak per monosaccharide. This peak area is related to the peak area of an internal standard (sorbitol, 100 µg), of which a known amount was added after depolymerization and before evaporation of the methanol. This area ratio is then converted into mass per sample using calibrations that have been previously established. For details of the method, we refer the reader to the original publication and our recent work [17, 18].

Sample paper preparation: Acid methanolysis was performed on two papers of each gellan preparation and untreated controls for comparison. All samples were prepared by scraping off the surface of paper with a scalpel in the area where the paper had been in contact with gellan gel or had been left untreated. The paper material was removed within a 3.5 × 3.5 cm window opening of a cardboard template that was placed on top of the paper. Approximately 20 mg of the paper was removed and transferred to an appropriately sized Eppendorf tube.

Accelerated ageing

The sample papers poulticed with gellan to simulate a conservation treatment (see Sect. "For the determination of gellan residues after poulticing treatment") and with blotting paper for comparison (see Sect. "Showing the visible poulticing effect") were aged for 21 days at 80 ℃ and 65% RH (Vötsch Heraeus VC0020) in accordance with ISO 5630–3:1996 [22]. In the chamber, the individual samples were suspended from a metal clip.

Evaluation of the appearance and water response of the papers after poulticing and accelerated ageing

In addition to instrumental analytical methods such as ATR-FTIR and acid methanolysis as the key to quantifying the effects of conservation treatments, visual testing methods that can be easily integrated into the conservation process are also essential for developing and monitoring a suitable treatment procedure. Objects undergoing treatment are usually assessed repeatedly in visible light (VIS) and also under UV-A radiation. In addition, it is common practice to test the wetting properties and water absorbency of paper using a water droplet test [23]; the common conservation procedure involves the application of a water droplet to the paper surface with a pipette and observe its interaction with the paper with the naked eye. Both assessment methods were used here to identify visible effects of the gellan poulticing treatment, also in comparison with the results of wet-blotter poultice. The results are discussed in their relation to the results of the instrumental analyses.

Results

Weight increase of papers after immersion in gellan

The papers absorbed between 3 and 41 mg gellan, resulting in a weight increase of 0.53–7.61% (Fig. 1). Between 0.06 and 0.84 mg/cm^2 of gellan was deposited, calculated for a paper sample area of about 7 cm^2.

The filter paper showed the highest weight increase, followed by the modern and the historical gelatine-sized papers. In terms of gellan concentrations, the weight increase was most significant for concentrations of 0.3% and above. Below 0.3% gellan concentration, the weight increase was between 3 and 8 mg, close to the limits of reliable weighing. This corresponds to 0.53–1.33% or 0.06–0.16 mg/cm^2. It could now be argued that the weight increase of the samples is due to hysteresis-induced water gain after aqueous treatment and not due to the gellan treatment. With the average weight of our

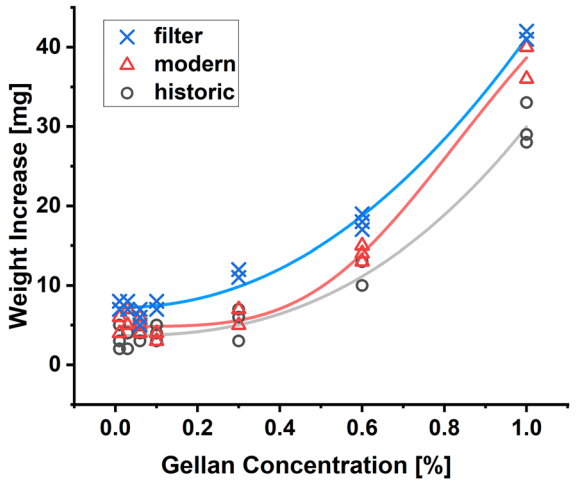

Fig. 1 Weight increase [mg] of papers (7 cm^2) after immersion in 0.01–1.0% concentrations of gellan (3 samples for each gellan concentration, see Table 2). The weight increase was modelled with a logistic function for illustration purposes

paper samples of 0.5 *g*, all of them preconditioned at about 50% RH, a hysteresis-related weight increase after dehumidification from 100 to 50% RH for never-dried pure cellulose would amount to approximately 5 mg. This means that, at gellan concentrations of 0.3% and below, the weight increase is not clearly attributable, but at higher gellan concentrations, the potential effects of cellulosic hysteresis are negligible compared to the gellan-related weight increase.

Detectable amount of gellan: ATR-FTIR on sample papers immersed in gellan

The ATR-FTIR spectra show clear absorption maxima at 1603–1606 cm^{-1} and 1411–1414 cm^{-1} for all of the three sample papers immersed in a 1% gellan solution, which differ significantly from the spectra of the untreated papers (Fig. 2; full spectra available as Additional file 1: Fig. S1). However, the ability of ATR-FTIR to detect gellan residues is limited to high gellan concentrations. Below a gellan concentration of 0.3%, the spectral differences are very small for all papers. On the historical rag paper, the ATR-FTIR spectra showed no visible evidence of gellan below 0.6% (Fig. 2c), which is most likely due to the larger amount of degradation products in this older paper. This means that a gellan uptake of 0.1–0.2 mg/cm^2 or 0.2–0.4 mg/cm^2, depending on weight of the paper tested, was not detectable. For illustration purposes: Relating these values to a letter-sized paper (624 cm^2), 62.4 to 249.6 mg of gellan residues would go unnoticed in ATR-FTIR spectra. Overall, the results indicate that the ATR-FTIR spectra have the same limitations as weight determination when checking for small amounts of gellan residues.

Detectable amount of gellan: methanolysis of sample papers immersed in gellan

As with ATR-FTIR, the sensitivity of methanolysis was determined by analysing samples that had been immersed in gellan solutions of different concentrations. We define detectability based on the visibility of a peak associated with rhamnose in the GC chromatograms (Additional file 1: Fig. S2). The observed amounts of monosaccharides were expressed as mass fraction of the sampled paper powder. For the filter paper—the paper that was free of detectable amounts of rhamnose—the lowest detectable amount was 40 ng/mg after immersion in a 0.06% gellan solution. This makes methanolysis ten times more sensitive than ATR-FTIR, with which gellan residues can only be detected from an immersion concentration of 0.6% and above.

We applied a one-sided t-test to compare the increase of rhamnose in treated papers with its concentration in untreated papers. The probability that the rhamnose content was indeed not equal exceeded 95% ($\alpha = 0.05$) at around 30 ng/mg, which is in good agreement with the first estimate of 40 ng/mg. This confirmed the higher sensitivity of methanolysis compared to ATR-FTIR.

Detection of gellan residues after poulticing: ATR-FTIR

The ATR-FTIR spectra of three sample papers, each of which received poulticing treatments from which four measurements on different locations were recorded, do not show any visible differences in comparison to the spectra of the untreated control (Fig. 3). As discussed in chapter 3.2 that—depending on the paper substrate—between 0.1 and 0.4 mg/cm^2 of gellan are not detectable by ATR-FTIR, the analyst must falsely conclude that no gellan residues remain on the paper. In other words, ATR-FTIR's insensitivity leads the analyst to believe that gellan treatments do not leave any residues on an item.

Detection of gellan residues after poulticing: methanolysis

Methanolysis revealed an increase in rhamnose content in all three paper types after gellan poulticing (Fig. 4). That the presence of rhamnose is due to the gellan treatment is obvious in the case of the filter paper, which was originally free from rhamnose. The observed concentration is well within the detectable range, and the probability that the increase in rhamnose content is due to a random fluctuation and not to the gellan treatment is negligible at 0.061%. The case is not so clear for the other two papers. In the control of the modern rag paper (untreated), some rhamnose is detected; however, in one sample no rhamnose was detected and in the other

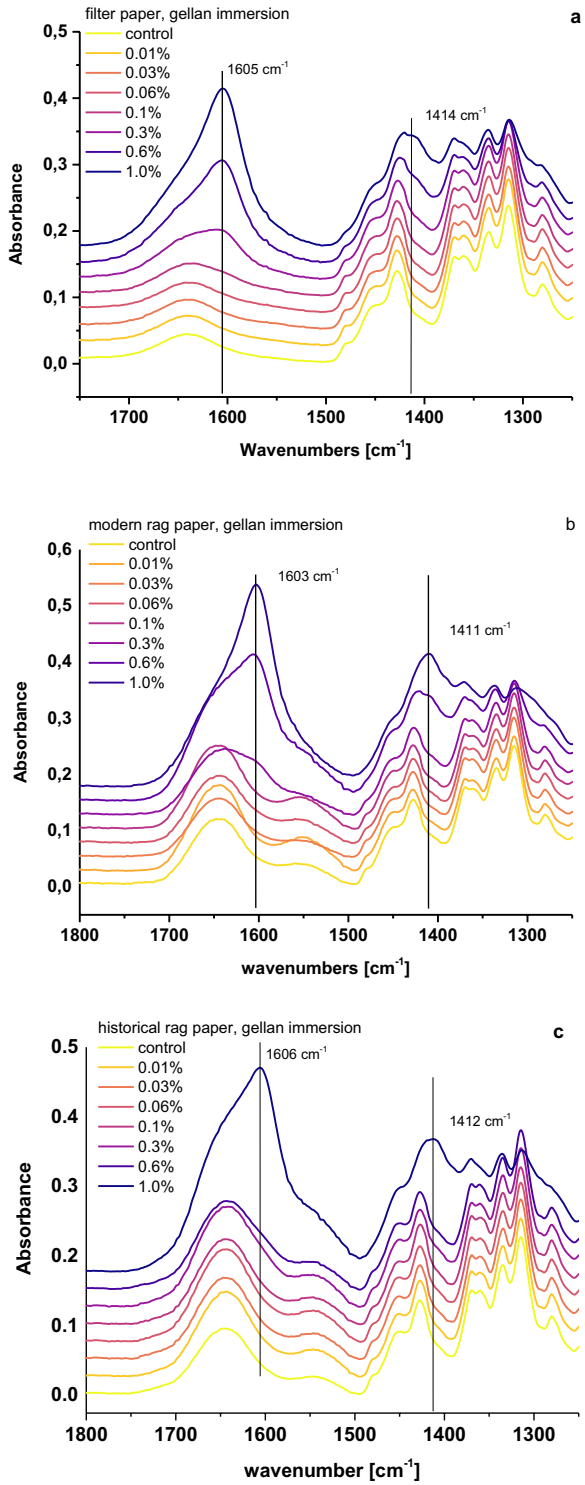

Fig. 2 ATR-FTIR spectra (the relevant section is shown) of filter paper (**a**), modern rag paper (**b**), and historical rag paper (**c**) immersed in different concentrations of gellan; the peaks at the wavenumbers 1606 cm^{-1} and 1412 $cm.^{-1}$ (indicated by vertical lines) show the presence of gellan, most clearly for 1% gellan compared to the untreated control. The spectra are stacked to make the regions of interest more visible. Full spectra are provided in supplementary information (Additional file 1: Fig. S1)

sample the rhamnose concentration was at the detection limit. As a result, the reference point for the t-test is poorly defined. In addition, the increase is close to 30 ng/mg, the smallest discernible difference. This increases the probability that the observed increase in rhamnose after treatment is due to chance and not a treatment outcome to 7.2%, which still makes it unlikely. In the historical rag paper, the initial rhamnose content is much higher and can therefore also be detected in the untreated control. The increase in gellan content after the treatment is comparatively small; the probability that it is due to chance increases to 11%.

An increase in rhamnose was observed in all three papers, which we can attribute to the gellan treatment with absolute (filter paper) and relative certainty (two rag papers). All three tested sample papers confirm the hypothesis that gellan gels do indeed leave residues on treated paper.

Assessment of the appearance and water response of the papers after poulticing and accelerated ageing

Visual evaluation in VIS and under UV-A: Overall, the composition of the paper impacted the results as discussed in the following. The highly absorbent filter paper wetted quickly and evenly after both, the gellan gel and the water-soaked blotters. The water migrated beyond the treatment area into the paper plane, which indicates that even gellan gel cannot restrict water migration beyond the contact area when the paper is highly absorbent, and consequently may alter the paper also outside the treatment area (Additional file 1: Fig. S3a). The modern rag paper lightened only slightly in the area poulticed with gellan (Additional file 1: Fig. S3b). In VIS, it shows almost no colour change; this is probably due to its barely aged state, which is practically free of coloured water-soluble degradation products. However, the treatment area fluoresces under UV-A, especially along the edge of the wetted area. This can be attributed to the partial removal of the gelatine sizing that is a known consequence of exposure to liquid water [8]. It is possible that the treatment edge areas, so far invisible in VIS, will become visibly discoloured in the course of future natural ageing. The historical rag paper, which contains water-soluble coloured degradation products in the surface sizing and from cellulose degradation products, lightened visibly with the gellan poultice due to the removal of coloured products. Also, the gellan-poulticed paper was lighter than the blotter-treated paper and remained lighter after accelerated ageing (Fig. 5).

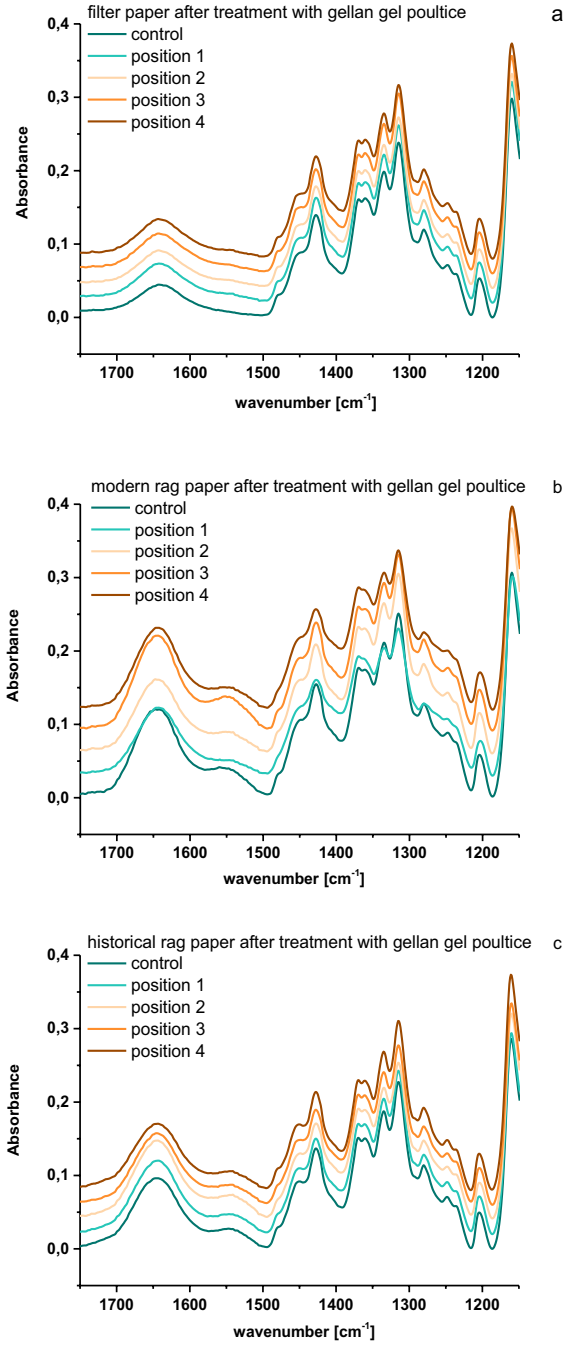

Fig. 3 ATR-FTIR spectra (the relevant section is shown) of filter paper (**a**), modern rag paper (**b**), and historical rag paper (**c**) after poulticing with 3% gellan gel compared to a control; the baseline is corrected and normalized to 1030 cm^{-1}. The spectra are stacked to make the regions of interest more visible

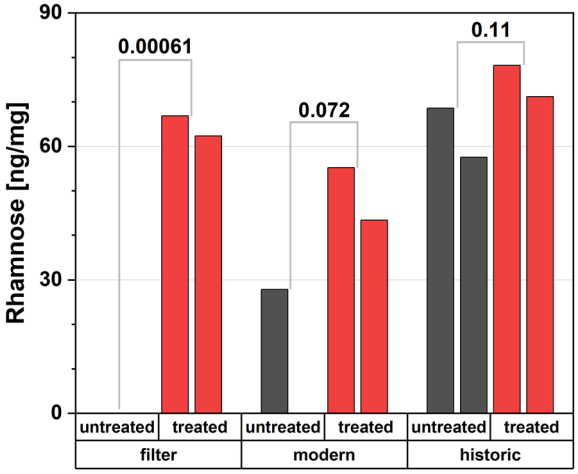

Fig. 4 Rhamnose concentrations in the three sample papers before and after poultice application of gellan gel according to methanolysis (duplicate analyses). The brackets are the p-values obtained with a one-sided t-test, which evaluates the probability of equality between untreated and treated samples; the smaller the number, the more certain the presence of gellan residues

The treated areas were easily distinguishable from the untreated paper under UV-A due to their altered fluorescence; this effect decreased with accelerated ageing. This also applies to the weakly fluorescent edge around the area that was poulticed with gellan. Overall, VIS and UV-A showed a significant difference between the treated and untreated paper area and some difference between the gellan and the wet blotter applications.

Water droplet testing: On the historical paper, the water droplet test showed interesting effects after the gellan treatment (Fig. 6): While the unaged, untreated paper absorbed the water droplets after a few seconds, the water droplets applied on the treated area remained on the paper surface for longer (Fig. 6a). After accelerated ageing (80 ℃ and 65% RH), the untreated paper absorbs the water droplets quickly (Fig. 6b and c, untreated areas), which indicates a degradation of the gelatine surface sizing. The results are similar for the paper area contacted by a wet blotting paper where the water droplets are also absorbed quickly, indicating that any remaining gelatine sizing has degraded (Fig. 6b, treated area). In the area poulticed with gellan gel, however, the water droplets remained on the surface for longer (Fig. 6c, treated area). Apparently, gellan residues remaining on the paper can delay water absorption for some time, which is explained by the presence of its many hydroxyl groups that greatly diminish water movement. In principle, gellan here showed an effect that is reminiscent to surface sizing, comparable to cooked starch, a polysaccharide like gellan, that was used in Arabic papermaking for the surface sizing of paper. This suggests that the presence of gellan residues, however minute, can diminish the wettability of the paper before and more so after ageing.

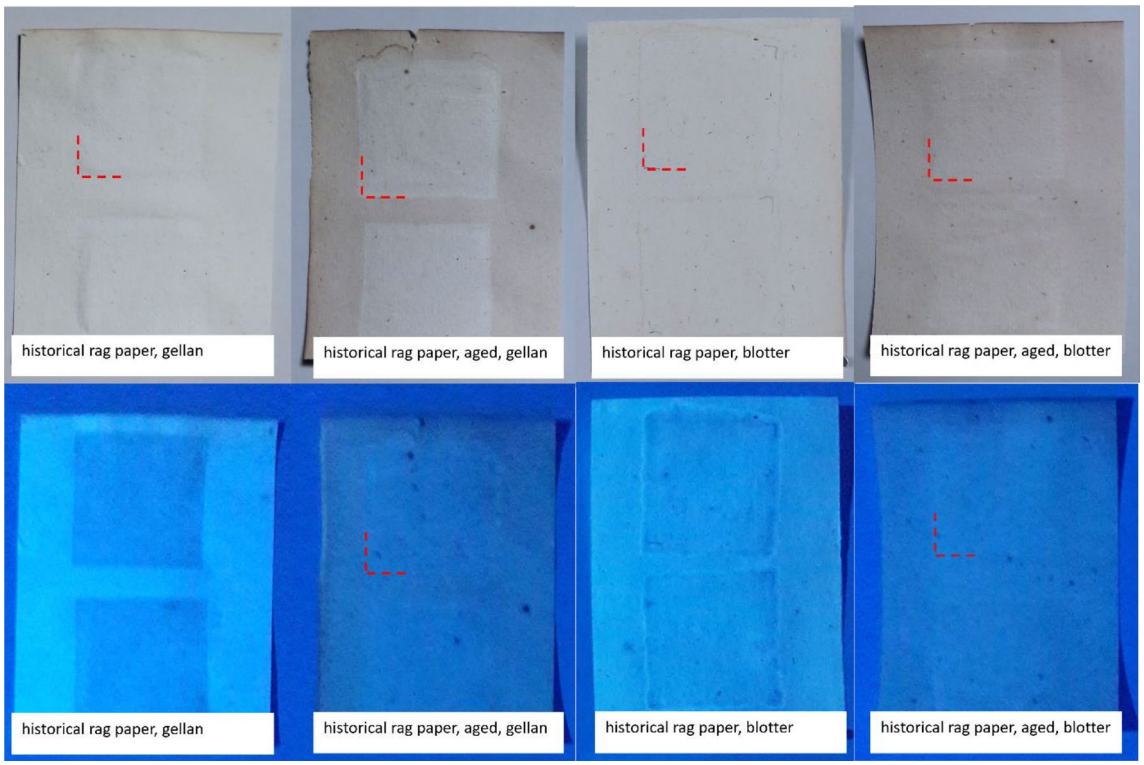

Fig. 5 Gelatine-sized historical rag papers seen in visible light (top) and under UV-A radiation (bottom) after gellan or blotter poulticing, before and after accelerated ageing (21 days at 80 ℃ and 65% RH). Both poulticing methods remove discoloured products from the papers (indicated by red line) detectable under both illumination conditions

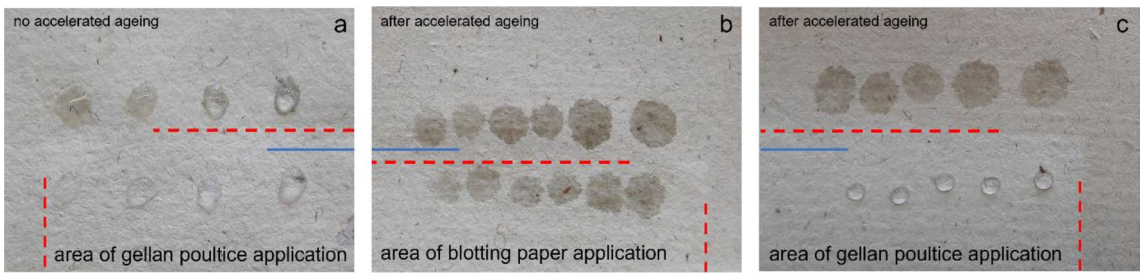

Fig. 6 Historical rag paper after the application of several water droplets to the untreated (outside the red line) and treated (within red line) areas. The papers were photographed immediately after the application of all water droplets, starting on the non-treated area. Please note that the images are not colour-corrected. The blue line corresponds to 1 cm

Discussion

The results of this study for conservation treatments in which gellan gels come into direct contact with a paper object are relevant for several reasons:

1. We have shown that acid methanolysis analysis using rhamnose as a marker is more sensitive than ATR-FTIR for checking gellan residues on paper. The difference in sensitivity was evaluated on three different paper substrates loaded with known gellan concentrations. While analysis of the filter paper, which initially contained no rhamnose, clearly showed the presence of rhamnose as a marker for gellan residues after poulticing, both the modern and the historical rag paper contained rhamnose. However, the statistical analysis of the acid methanolysis showed a significant probability that gellan gel residues are also present on these two papers.

2. Since rhamnose makes up only about 25% of gellan's composition, the actual amount of gellan left on the paper may be up to four times higher than what was

detected by acid methanolysis. These residues could not be detected by ATR-FTIR.

3. Acid methanolysis cannot reveal the exact structure of gellan residues remaining on the paper because the acid-catalysed destruction of the polymeric substance and cannot distinguish between polymeric or monomeric residues. However, the decreased wettability of the gellan-treated area of the historical paper suggests that the gellan residues may not be in the form of monomeric or oligomeric degradation products but consist of polymeric structures that diminish water absorption.

4. In principle, gellan, like any other local aqueous treatment, carries the risk of undesirable changes occurring beyond the treatment objective. This applies to immediately visible side effects such as cracking in the albumen layers on photographs [24] or tide lines that only appear after the paper has aged [25, 26]. In this study, we observed an increased, yet unexplained hydrophobicity of the treated paper areas (see Sect. "Assessment of the appearance and water response of the papers after poulticing and accelerated ageing"), which must be considered another possible side effect of the gellan gel application.

Conclusion

When making decisions about conservation treatments, all stakeholders involved should be aware of the risks and discuss ways to minimize them. This also applies to the use of gellan poultices where, apart from the benefits of the treatment, there may be potential side effects on hygroscopic substrates. Furthermore, we note that the small amounts of gellan residues that may remain on a paper object can only be detected by highly sensitive and specific analysis. Whether these residues are then acceptable as a side effect of a treatment is to be assessed by the parties involved. Residues of treatment substances are acceptable in some cases; for example, residues of methylcellulose might be accepted in some cases after the application of a poultice [15]. Overall, gellan gels are valuable as a versatile tool for some conservation treatments, but they are not necessarily the only or the best choice for all aqueous treatment objectives, especially if any residues are to be avoided. Gellan gels should be considered as one option within the wide range of other effective aqueous treatment methods.

Supplementary Information

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Additional file 1: Table S1. Monosaccharides from paper substrates and gellan analyzed by acid methanolysis in µg/mg dry matter (averaged; recovery included). **Fig. S1.** ATR-FTIR spectra of filter paper (**a**), modern rag paper (**b**), and historic gelatin-sized paper (**c**), baseline corrected and normalized at 1030 cm^{-1}. The paper was dipped in gellan solutions of different concentrations; for each type, blank paper without gellan is included. Spectra are stacked for better visualization of the areas of interest. **Fig. S2.** Area of interest of FID data of filter paper (W), modern rag paper (F), and historical gelatin-sized paper (H), showing the control papers (R; blue and green lines) and those papers that have been treated with a mock-up gellan gel treatment (B; red and black lines). **Fig. S3. a** Filter papers seen in visible light (top) and under UV-A radiation (bottom) after gellan or blotter poulticing, before and after accelerated ageing (21 days at 80 ℃ and 65% relative humidity). **b** Modern rag papers seen in visible light (top) and under UV-A radiation (bottom) after gellan or blotter poulticing, before and after accelerated ageing (21 days at 80 ℃ and 65% relative humidity).

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Author contributions
UH developed the experimental design, prepared the samples, performed and interpreted the ATR-FTIR data, sampled the papers and drafted the manuscript. HK analysed the paper samples by acid methanolysis and evaluated the data. SB developed the experimental design, evaluated the methanolysis data, performed statistical analysis and was a major contributor in writing the manuscript. IB was instrumental in improving the data interpretation and was a major contributor in writing the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare that they have no competing interests.

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