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Mass Deacidification

The Efficacy of the Papersave Process

This paper discusses various questions regarding the efficacy of the Papersave mass-deacidification treatment based on laboratory investigations. The life of acid paper can, in principle, be prolonged by deacidification. However, further conservation treatments such as paper splitting are necessary for severely damaged paper. Introducing a high amount of alkaline reserve into already damaged paper can reduce its flexibility, rendering general minimal requirements for an alkaline reserve pointless from a conservator's point of view. Long-term investigations on deacidified test papers prove deacidification treatments to remain effective beyond a five year period.

An Hand von Laboruntersuchungen werden für das Papersave-Massenentsäuerungsverfahren verschiedene Fragen der Wirksamkeit und Effektivität einer Entsäuerungsbehandlung diskutiert. Zwar kann durch eine Entsäuerung die Lebensdauer von säurehaltigen Papieren prinzipiell verlängert werden, bei sehr stark vorgeschädigten Papieren sind jedoch weitergehende restauratorische Maßnahmen, wie z.B. die Papierspaltung, notwendig. Ein sehr hoher Eintrag von alkalischer Reserve kann bei bereits vorgeschädigten Papieren deren Flexibilität verringern, weswegen pauschale Mindestforderungen für alkalische Reserven konservatorisch nicht sinnvoll sind. Langzeituntersuchungen von entsäuerten Testpapieren belegen, daß eine Entsäuerungsbehandlung nach einem Zeitraum von fünf Jahren nichts von ihrer Wirksamkeit einbüßt.

With the beginning of industrial paper production more than 150 years ago and the acidic sizing connected with it, acids were brought into paper. These acids cause the catalytic degradation and oxidation of cellulose. Since cellulose is responsible for the mechanical stability of paper, it becomes brittle with the progress of the cellulose degradation and oxidation followed by cross linking reaction between the cellulose fibres. This process is auto-catalytic, i.e. the degradation process furthers the formation of new acids and thus, the reaction accelerates itself. The degradation process can be stopped effectively by neutralisation and the insertion of an alkaline buffer. Mass deacidification processes were developed in order to efficiently conserve books and archival material which contain acidic, industrially produced paper.

The Papersave mass deacidification process was developed within the framework of a research project of the Federal Ministry for Research commissioned to the Battelle Institute by the German Library (Liers, Vogelsanger 1997: 118-126).

Three different industrial plants currently operate on the basis of this process: ZFB Zentrum für Bucherhaltung GmbH (two systems in Germany: Leipzig and Frankfurt/Main [former Battelle Ingenieurtechnik GmbH]) and Nitrochemie Wimmis AG (Wimmis in Switzerland). The Leipzig plant has the longest operational experience: the plant being in operation since 1994 in the preservation department of the German Library. It has been operated commercially by ZFB since 1997. In 1998 the facility was completely rebuilt, introducing state-of-the art developments and adjusting its capacity to market demands by raising it to approximately 80 t per year. So far, nearly 300 t of books have been deacidified in this facility.

Our 7-year experience with the mass deacidification process has always been accompanied by intensive laboratory testing with not only the aim to optimise the process, but also to obtain guarantead data on the efficacy of the process.

Over and over again, questions are asked about the efficacy of deacidification, life-expectancy of deacidified books, deacidification results to be obtained or the kind of material to be treated—primarily in discussions with librarians, archivists, conservators and scientists.

The following questions are to be discussed on the basis of our numerous investigation results: What kind of material should be given priority for treatment? What are the results to be demanded of a deacidification treatment? How long does the success of a deacidification treatment last?

What kind of material should be given priority for mass deacidification?

This problem will be discussed using two different newspaper prints: "Deutscher Drucker" (1972) and "Handelsblatt" (1950). Both papers are of wood pulp with acid sizing. While the "Deutscher Drucker" retained sufficient stability, the "Handelsblatt" was found to be already brittle. Therefore, only the "Deutscher Drucker" was deacidified [1], while the samples of the "Handelsblatt" were deacidified or split (Wächter et al. 1997: 224-230) [2].

In order to investigate the ageing behaviour of the papers, the samples were aged artificially in a climate chamber at 80 °C and 65 % RH.

Fig. 1 illustrates the tensile strength after folding (in machine direction; Bansa, Hofer 1980: 348-355; DIN 63112 1981) of the untreated and deacidified samples of the newspaper "Deutscher Drucker". The tensile strength of the untreated sample was found to be 25 N after folding and was raised to 30 N by deacidification. The tensile strength of both papers decreased during artificial ageing. While the tensile strength after folding of the untreated paper was no longer detectable after 100 days of ageing, this state was reached by the deacidified sample after 400 days of ageing.

That is to say: considering the tensile strength after folding as a criterion of usability, the life expectancy of this paper is raised, under the conditions of artificial ageing, by a factor of 4 by the deacidification treatment.

Comparing the ageing curves of the treated and untreated samples, the results of the investigation for the "Handelsblatt" (fig. 2), show the ageing behaviour to be substantially improved. The remaining stability of the untreated samples is very low, however (9 N). This can only substantially be improved by a deacidification treatment. Due to this low mechanical paper stability, the papers suffer serious risks of mechanical damages, particularly during use. The total usability of this paper can only be re-established by an increase in paper stability. The tensile strength after folding was nearly quadrupled by paper splitting and thus corresponds with the mechanical stability of new newsprint.

In summary, it can be said that a deacidification treatment is very helpful for samples of the "Deutscher Drucker", while for the investigated copy of the "Handelsblatt" a deacidification treatment is possible, but paper splitting should be the chosen method.

Both examples clearly illustrate that all conservation treatments have their limits and should be used in dependence of the specific damage of the items. This means in practice that collections with extremely brittle paper are beyond the stage where a deacidification treatment would be beneficial. In contrast, items that are mechanically stable should undergo a deacidification treatment as soon as possible, as the remaining shelf life depends very much on the condition of the paper before treatment. If the original condition of the treated paper is good—as in our example of the "Deutscher Drucker"—the deacidification results are substantially better from a conservator's point of view than in already weakened paper. Unfortunately, this principle is often ignored in practice—possibly due to the urge to save what can still be saved.

What results are to be expected from a mass deacidification treatment?

It is generally known that the ageing resistance of paper depends more on the alkaline reserve than on the pH factor, since the alkaline reserve ensures the resistance of the paper against environmental effects and continuing degradation reaction caused by acids.

The question is; how high is the alkaline reserve that is to be introduced into the paper by a deacidification treatment? Different users have different demands in this respect. The Swiss National Library (Bern/Switzerland) requires an alkaline reserve between 0.5 and 2.0 wt.-% $MgCO_3$ (Schweizerische Landesbibliothek 1998). In the frame contract of the Federal Ministry of the Interior (Bonn/Germany) closed with ZFB, the minimal alkaline reserve is stipulated with 1.5 wt.-% $MgCO_3$ (Beschaffungsamt des Bundesministerium des Inneren 1999), while the Library of Congress (Washington/U.S.A.) demands an alkaline reserve of at least 1.5 wt.-% $CaCO_3$ (Harris 1999).

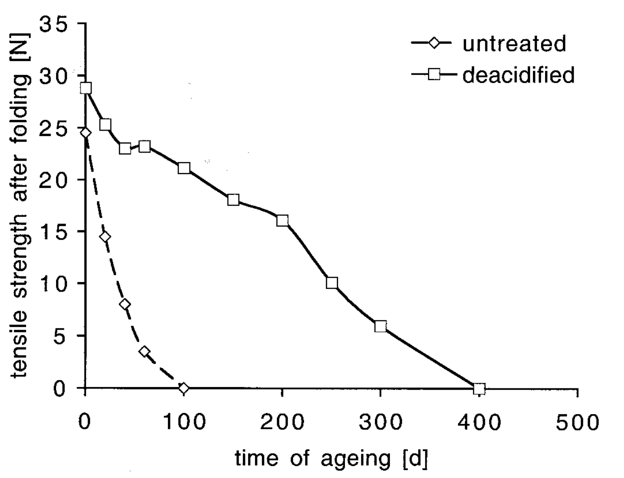
In the following, this problem will be discussed on the basis of a test series carried out on newsprint deacidified according to different processes. The test papers used were again the "Deutscher Drucker" of 1972 and the "Handelsblatt" of 1950. Both papers were subjected to three different deacidification treatments. By varying the concentration of the deacidification chemicals as well as by multiple drainings, a broad spectre of alkaline reserves (0.62-4.38 wt.-% $MgCO_3$) was introduced into the papers. Tab. 1 shows the pH factors (DIN 53124) and the alkaline reserves [3] (Liers 1999: 126-136) of the different paper samples.

All three papers were subsequently subjected to an artificial ageing in a climate chamber (80 °C; 65 % rH).

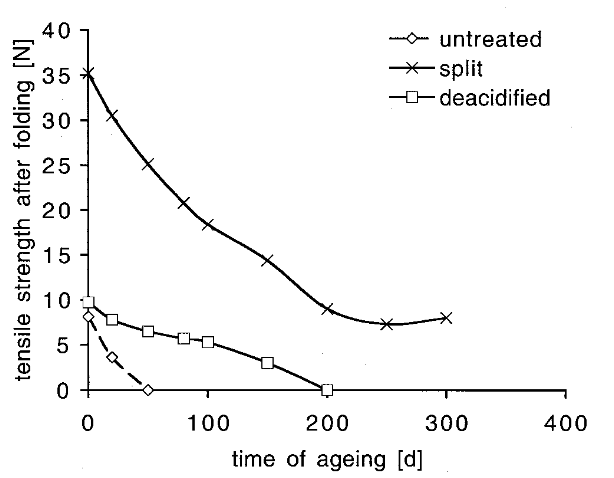
Fig. 3 and 4 show the tensile strength after folding in machine direction for the differently treated papers in correlation with the time of ageing. It is clearly to be seen that all deacidification treatments improve the ageing behaviour.

While no significant differences are to be detected in the ageing courses of the samples of the "Deutscher Drucker" with different alkaline reserves, the "Handelsblatt" shows clear differences. The stability of the paper after treatment 1 (containing the smallest alkaline reserve), remains significantly better over the entire ageing course when compared to the papers subjected to treatment 2 and 3.

This can be attributed to the above discussed considerable existing damages in the "Handelsblatt" when compared to "Deutscher Drucker". With the deacidification treatment, an additional solid substance is introduced into the paper fleece,



1 Tensile strength after folding (in machine direction) correlated with the time of ageing of the untreated and deacidified papers samples of "Deutscher Drucker".



2 Tensile strength after folding (in machine direction) correlated with the time of ageing of the untreated, split and deacidified samples of "Handelsblatt".

Tab. 1 pH factor and alkaline reserve of the untreated and deacidified paper samples.

	Journal "Handelsblatt"		Journal "Deutscher Drucker"	
	pH factor from the water extract	Alkaline buffer (wt.-% $MgCO_3$)	pH factor from the water extract	Alkaline buffer (wt.-% $MgCO_3$)
Untreated	4.5	−0.38	4.9	−0.13
After treatment 1	7.8	0.62	8.9	0.71
After treatment 2	9.3	1.73	9.4	2.95
After treatment 3	9.4	3.37	9.7	4.38

causing a slight stiffening. While this stiffening does not cause problems in mechanically intact papers, a higher concentration of solid substances decreases the flexibility in already damaged paper—e.g. measurable as a decrease of the tensile strength after folding. In extreme cases—i.e. very brittle paper—these stability losses are so substantial that the benefits of the deacidification treatments are neutralised by the worsening of the mechanical properties.

The following conclusions can be drawn from these results:

The introduction of too high alkaline reserves into the paper does not make sense, since this causes a decrease of the paper's flexibility, particularly in already damaged papers. In principle, all severely damaged papers—often displaying the highest acid content—should be subjected to a mild deacidification treatment, even though the alkaline reserve measured afterwards will be relatively low.

A general demand of a minimal alkaline reserve of 1.5 wt.-% $MgCO_3$ or $CaCO_3$ does not make sense in these cases. Similar to medicine, also in this field, the dose of the deacidification chemical should be adjusted to the overall condition of the patient (i.e. the paper). An individual treatment of single books is not possible with mass deacidification. But the introduction of a too high amount of deacidification agent can be avoided by applying variable demands with respect to the deacidification result, taking into account the degree of damage and acid contents of the original book. Therefore, it should be accepted that a paper with a high acid content will have a lower alkaline reserve after a deacidification treatment than a newer book with a lesser acid content. From that point of view, the variable demands stipulated by the Swiss National Library best reflect the conservational requirements.

How long does the effect of a mass deacidification treatment last?

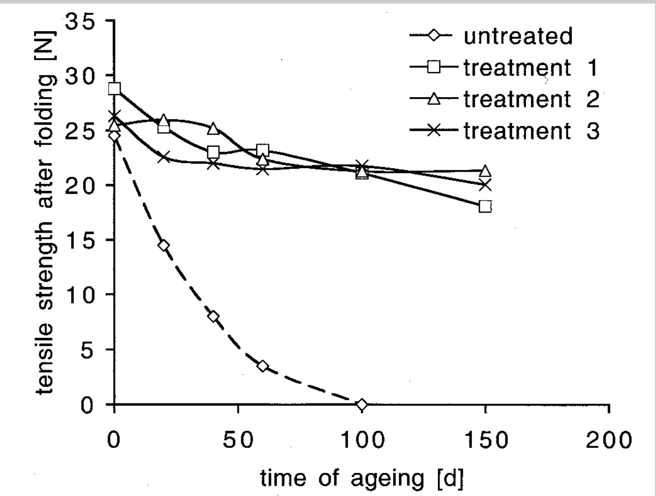
This question will be discussed on the basis of the conduct of deacidified paper samples under normal storage conditions.

Five different sample books were deacidified in 1995 and subsequently stored in a standard climate (20 °C; 50 % rH). Samples were taken in 1995, 1998 and 2000 for testing. The long term test is to be continued.

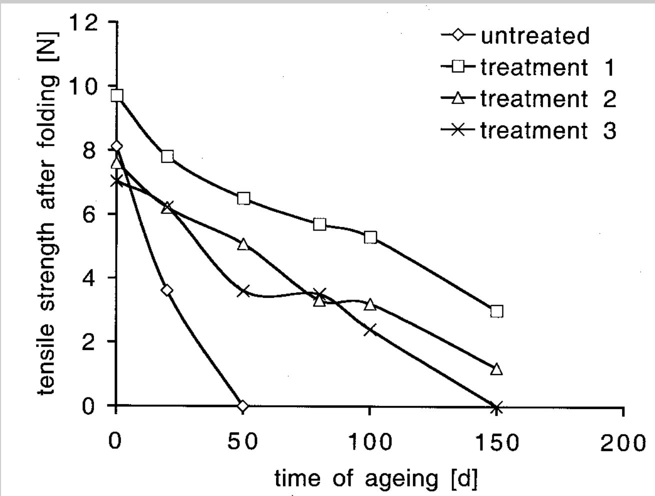
Three test books are to be discussed: "Bibliographie" ("Bibliographie der Deutschen Zeitschriftenliteratur" 1954, wood-free paper with acid sizing), "Einheit" ("Einheit" 1975, wood-pulp paper with acid sizing, already brittle) and "Deutscher Drucker" ("Deutscher Drucker" 1972, wood-pulp paper with acid sizing). The remaining two test books displayed the same behavioural tendencies.

Fig. 5 shows the extract pH factor for these papers before and immediately after deacidification and, at sample-taking in 1998 and 2000. The original pH factor was found to range between 3.9 and 4.9. This was raised to values between 7.5 and 8.9 through deacidification. During ageing, the extract pH factor decreased only slightly and all papers were clearly alkaline after five years.

Fig. 6 shows the surface pH factor of the papers before and immediately after deacidification as well as at sample-taking in 1998 and 2000. The original pH factor was found to range



3 Tensile strength after folding (in machine direction) correlated with time of ageing of the untreated paper samples and those subjected to different deacidification treatments of "Deutscher Drucker".



4 Tensile strength after folding (in machine direction) correlated with time of ageing of untreated paper samples of the "Handelsblatt" and those subjected to various deacidification treatments.

between 3.3 and 4.3 and was raised to 7.6 to 8.9 by deacidification. In the course of ageing the pH factor decreased slightly, but all papers proved to have an alkaline or neutral pH factor after five years. However, the surface pH factor decreased a little faster than the extract pH factor during these five years.

Fig. 7 shows the alkaline reserve of the tested papers before and immediately after deacidification, as well as at sample-taking in 1998 and 2000. The acid content of the untreated samples was determined with –0.59 wt.-% and –0.3 wt.-% $MgCO_3$. After deacidification, an alkaline reserve of 0.21 and 0.9 wt.-% $MgCO_3$ was measured in the samples (according to the quality requirements valid in 1995, a considerably lower alkaline reserve was introduced at that time). During the next five years, a slight decrease of the alkaline reserve was only observed in "Einheit". No significant change in the alkaline reserve was observed in the other papers.

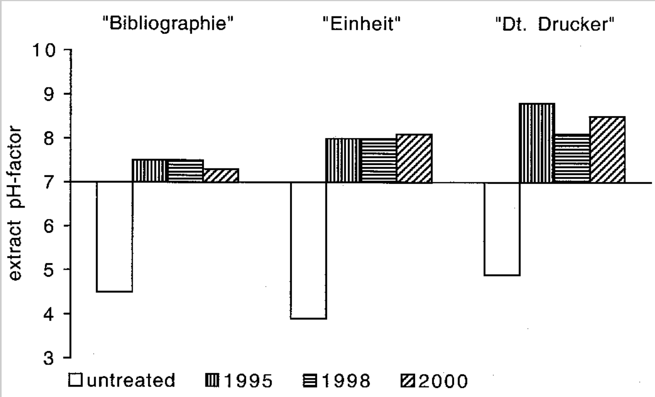
Fig. 8 shows the tensile strength after folding in machine direction for the samples before and immediately after deacidification, as well as at sample-taking in 1998 and 2000. While an increase of the tensile strength could be measured in "Bibliographie" and "Deutscher Drucker", the tensile strength of "Einheit" was slightly lower after deacidification. During the following five years, no significant changes in paper stability were observed.

In summary, all papers proved to have an alkaline pH factor and an alkaline reserve after five years of ageing under standard conditions. While the alkaline reserve did not change in the course of five years, the pH factor decreased slightly. These changes can be attributed to the transformation of the deacidification chemicals: magnesium hydroxide transforms to magnesium carbonate. These reactions take place primarily on the surface, explaining the stronger change in the surface pH factor than in the extract pH factor. Similarly, the paper surface is the first to suffer the introduction of hazardous substances contained in the air. This explains that the surface pH is sometimes considerably lower than the extract pH factor. The surface pH factor therefore, has only limited validity from a conservational point-of-view.

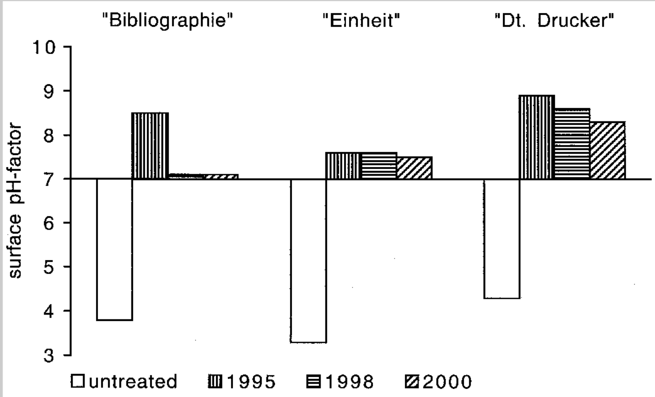
Summarising, it can be said that despite of partly milder deacidification conditions, the effects of the treatments are undiminished after five years.

Conclusion

The results of our investigation proved very clearly that mass deacidification is an effective means to stop the acid degradation of paper. Under the conditions of artificial ageing the life expectancy of deacidified paper was shown to increase 4-fold. The papers to be subjected to deacidification, however, still need sufficient stability. Otherwise, stabilisation measures

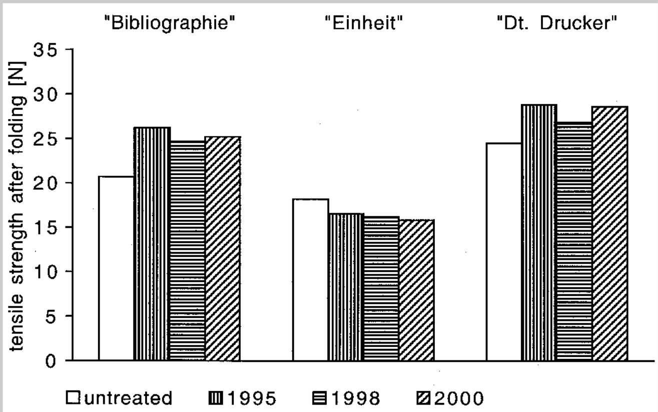


5 Extract pH factor of the untreated paper samples, those deacidified in 1995 immediately after treatment (1995) and at sample-taking in 1998 and 2000.



6 Surface pH factor of the untreated paper samples, those deacidified in 1995 immediately after treatment as well as at sample-taking in 1998 and 2000.

7 Alkaline reserve of the untreated samples, those deacidified in 1995 immediately after treatment and at sample-taking in 1998 and 2000.



8 Tensile strength after folding (in machine direction) of the untreated samples, immediately after deacidification in 1995 and at sample-taking in 1998 and 2000.

such as paper splitting are more suitable. In extreme cases, i.e. very brittle paper, the introduction of too high an alkaline reserve can neutralise the benefits of the deacidification by reducing the paper's flexibility. Therefore, the requirements concerning the results of the deacidification treatment should not be established generally but depending on the material to be treated.

The monitoring of deacidified papers over a five years period showed that the effects of the treatment did not diminish during this period. Even objects subjected to a mild deacidification did not show any signs of a renewed acidification. Problematic is the fact that the only property that can be measured non-invasively, the surface pH factor, has the lowest relevance. If measurements such as these are to be taken, they should be carried out using surface electrodes and not indicator pens or strips, since the values obtained by those carry the risk of measurement deviation in addition to the difficult interpretation of surface pH factors.

The aim of future research should therefore be the development of non-invasive tests for the evaluation of the paper condition. This would enable fast and reliable statements on the necessity, as well as the probable success, of conservation and preservation measures. Two interesting research projects presently are carried out in this field: one project that is supported by the Deutsche Forschungsgemeinschaft is carried out at the Academy of Fine Arts in Stuttgart and the Stuttgart University and will contribute some interesting insights (Binder et al. 2000: 45-47). Aim of the other international project called "MICROPAP" is the development of micro-analytical methodologies for the characterisation of the condition of paper (Pedersoli 1999).

Annotations

[1] The Papersave deacidification process comprises three steps. The first step is the pre-drying of the books, which remain in a closed treatment chamber during the entire process. The normal moisture content of 5–7 % is decreased temporarily to less than 1 %. The drying process takes place under vacuum conditions, accompanied by a mild heating to not more than 50 °C. Due to optimisation of the drying technology, the previously used microwave technology has been replaced by a more favourable method. Drying is followed by deacidification. The books are impregnated with an alkali solution. The treatment chamber is flooded completely with the treatment chemical. The deacidification chemicals are alcoholates of magnesium and titanium dissolved in a volatile silicone oil. Due to the previous drying, the closed books within in the chamber absorb the solution like a sponge. After the treatment solution has been drained, the books are dried once again. The solvent absorbed during impregnation dries away, whereas the actual deacidifying chemicals (magnesium and titanium compounds) remain in the paper. The entire process takes two to three days. After the books have been removed from the chamber, they regain lost humidity and return to their normal moisture content. The books exude alcohol due to the reaction of the treatment chemicals with water and the treated books are stored in a ventilated room for approx. 3 weeks before being returned to the client.

[2] Since paper splitting is a single sheet treatment, the books or files have to be disbound before treatment. The process of paper splitting is a part of a complete paper conservation process which includes as well as splitting, wet treatment and leaf casting. In practice, the decision regarding which of the individual processes to be used depends on the specific damage of the objects. In our case the leafs were washed in warm water and then split. During paper splitting, the damaged object is sandwiched between two support papers by means of gelatin glue and subsequently split in its cross-section when the two support papers are torn apart. Then, a very thin but sturdy core paper is inserted between the front and reverse sheet. Since the core adhesive and the core paper contain an alkaline buffer, a level of deacidification is achieved during the splitting process. Subsequently, the support papers are removed. According to the damage and format of the object to be treated, paper splitting is carried out manually or mechanically. In our example the paper splitting process was done by machine.

[3] For determination of acids or alkaline in paper the following analytical method was used. At first the test paper is conditioned at 23 °C and 50 % r.h. Then one gram of the chipped paper is extracted in 50 ml distilled water for 12 hours at room temperature. During extraction the jar used is closed by a tube filled with CaO. Finally the pH value of the extract, still containing the paper fibre, is measured. Depending on the pH value, 10 ml decinormal H_2SO_4 (for a pH value ≥7) or 0.05 g $CaCO_3$ (for a pH value <7) are added and the extraction is continued for one hour. The extract which contains the neutral or alkaline paper is then back-titrated with decinormal NaOH. 20 ml decinormal H_2SO_4 is added to the extract which contains acid paper. This mixture is shaken for 1 hour, then back-titrated with decinormal NaOH.

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