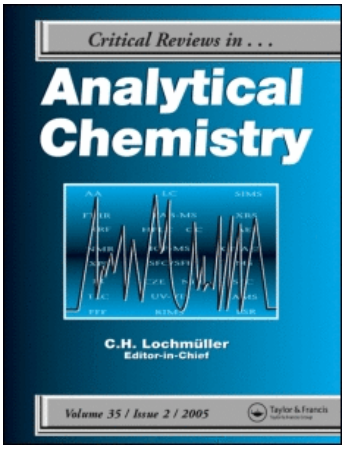

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PREPARATION OF CHEMICALLY MODIFIED CELLULOSE EXCHANGERS AND THEIR USE FOR THE PRECONCENTRATION OF TRACE ELEMENTS

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I. INTRODUCTION

Analytical chemistry at trace levels frequently requires special techniques and precautions to avoid systematic errors. Preconcentration of the analyte elements is one of these special steps that can be favorably applied to the sample prior to analysis.

The advantages of such a pretreatment are numerous:[1]

1. Increased sensitivity permitting the determination of very low concentrations
2. Reduced interelement effects by elimination of the original matrix
3. Easier handling because of reduced sample mass
4. Less danger for systematic errors due to adsorption and contamination after preconcentration
5. Sample easily stored for later use

There are, however, limitations to a preliminary separation step in trace analysis.[2] The most prominent of these limitations are the loss of trace elements and the contamination of the sample prior to or during the preconcentration procedure. Losses can be conveniently monitored using the radioactive tracer technique if it is possible to spike the sample with a tracer in the same chemical form as in the original sample. In practice this requirement can lead to difficulties, as very little may be known about the chemical state in natural water samples. Although a recovery of about 100% is advantageous, a known and constant recovery between several 10s and 100% is sometimes sufficient for the determination. Contamination of the sample with the analyte element is another very critical source of inaccurate results. Thus, it is crucial to use only the very purest reagents, to keep the time required for the separation to a minimum, and to work with vessels of only minimal surface area.

Different criteria can be employed to classify the large number of preconcentration procedures. One of the possibilities is characterized by the binding of dissolved trace ions onto solids. The support materials have to be chemically modified to achieve binding of trace ions by ionic or coordinative bonds. Cellulose from different sources offers a number of desirable properties for a support material. It can be obtained in very pure quality, has a very high specific surface area and, under certain conditions, has sufficient mechanical and chemical stability. Its hydrophilic character is a further advantage for the preconcentration from aqueous solutions. Depending on the natural source and the method of extraction from this natural source, cellulose can be obtained in a great variety of qualities, so that a more in depth discussion of its structure and properties is in order.

II. THE SUBSTRATE: CELLULOSE

Cellulose is a polymer built of glucose units that are linked by β-1,4-glycosidic bridges. With a degree of polymerization ranging from 2000 to 16,000, it occurs as a major constituent of the plant cell wall.[3] The glucose molecules are combined into chains of anhydro-β-glucopyranose units, with every second glucose moiety rotated 180° compared to its nearest neighbor.[4] These chains are associated into fibrils which have a high degree of order and crystallinity and are highly insoluble. The individual molecules can be part of crystalline and amorphous regions at the same time.[5] According to the "fringe micellar theory",[5,6] the crystalline regions alternate with less-ordered amorphous regions, and within broad limits there is no connection between the length of the crystalline region and the molecular chain length.[7] There are no sharply defined crystalline limits, but gradual transitions exist along the molecules from regions of high

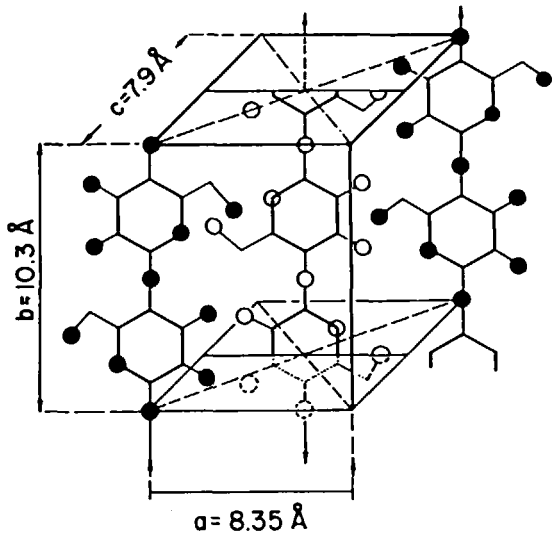


FIGURE 1. Schematic representation of the unit cell of native cellulose.

lattice order to regions of low lattice order. In the cell wall, the crystalline structure fulfills, together with ligneous material, the need for rigidity and mechanical strength, while the amorphous regions provide binding sites for the other constituents of the cell wall, like hemicelluloses and lignin. Partly, these bonds appear to be of acetal- or hemiacetal nature.[8] The crystalline regions in native cellulose are made up of a unit cell with chains interconnected by molecular hydrogen bridges.[9] The work of Gardner and Blackwell[10] and Sarko and Muggli[11] provide strong evidence that in native cellulose these chains are parallel and are not, as previously debated, antiparallel. They are tightly associated into fibrils by hydrogen bonding; the so-called elementary fibrils[12] of approximately 3.5 μm in diameter containing about 32 chains associate further into microfibrils of varying size. The size of these microfibrils (and also of the larger macrofibrils) depends upon the origin of the cellulose and increases in the following order: wood < cotton < bacterial cellulose < animal cellulose < ramie.[13] (See Figure 1.)

An important aspect to consider for the present discussion is the ratio of crystalline to amorphous material, since the ratio is related to the reactivity of the cellulose. Without going into the different chemical and physical methods of determining this ratio, it should be stressed that the results are somewhat dependent on the method. A determination of the accessible hydroxyl groups by the diazomethane method gave results of only 0.4% for dry cotton, up to 9.5% for moist cotton, and up to 23% for mercerized cotton.[14] Another method to determine the accessible hydroxyls employing thallous ethylate in etheral solution gave a value of 27% of accessible material for mercerized linters.[15] Generally, the average ordered fraction as determined by X-ray diffraction or density measurements seems to be much lower than that determined by chemical methods (e.g., acid hydrolysis or periodate oxidation); the values for regenerated cellulose are approximately 30 and 70%, respectively.[16] This suggests that unordered regions also exist in substructures "entrapped" by crystalline regions emphasizing the strong influence of gross structure on reactivity.[17] In native cellulose, the only functional groups appear to be the three hydroxyl groups in position 2, 3, and 6. The dissociation constant of 8×10^{-8} suggests that no carboxylic groups are present.[18] Regenerated cellulose, however, has undergone changes in molecular and crystalline structure. The degree of polymerization has dropped to 500 to 2100,[19] the polymer chains

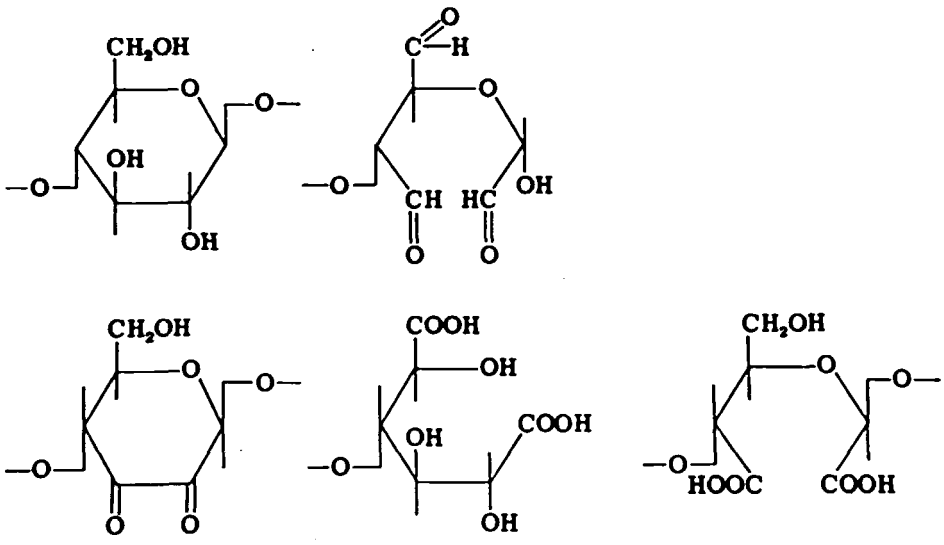


FIGURE 2. Functional groups in regenerated cellulose.

are rearranged in antiparallel orientation,[20] and additional functionalities are introduced.[21] A summary of the functional groups "generated" by the extraction of cellulose from native sources is given in Figure 2. Figure 3[22] shows the projection in the plane a-c of the elementary cell of native cellulose (cellulose I) and of mercerized cellulose (cellulose II). In cellulose II the molecules are displaced against each other along the a axis and are twisted 30° from the a-b plane.[23] From literature data, it is not always apparent what structure the substrate had when used for the production of chemically modified cellulose. Generally, however, better accessibility in subsequent substitutions can be expected from swollen cellulose or even gel-like structures, if the fibrous structure can be regenerated after substitution. Amines fulfill these requirements as swelling agents.[24] They act by increasing the distances a and c. The exact value of these distances depends on the nature of the amine: for ethylenediamine a is 12.2 Å and c is 12.3 Å; for octamethylenediamine a is increased to 19.1 Å, and c to 17.9 Å.[25] The fibrous structure is retained.

A high degree of swelling enhances the accessibility while drying the cellulose reduces it.[26,27] Therefore, a combined effect of accessibility and reactivity of the individual functional group has to be taken into consideration when carrying out substitution reactions; for example, the primary hydroxyl groups of cellulose are more reactive than the secondary hydroxyl groups in most cases, but secondary groups may react before the primary ones if the latter are rendered nonaccessible because of their steric relationships in the fine and gross structures of the cellulosic material. Cellulose enters into the usual reactions of organic chemistry (esterification, etherification, etc.), but in all cases in which cellulose remains as a solid phase in the reaction system, one must keep in mind that the extent of these reactions may be dictated by the morphology of the form in which the cellulose molecules are combined in the solid state.[16] A small percentage of the total hydroxyl groups react in normal production of the pure cellulose, particularly in oxidative bleaching; this "unsubstituted" cellulose exhibits ion-exchange properties.

III. ION-EXCHANGE CELLULOSES

Unsubstituted cellulose has a very low ion-exchange capacity. The greatest portion of

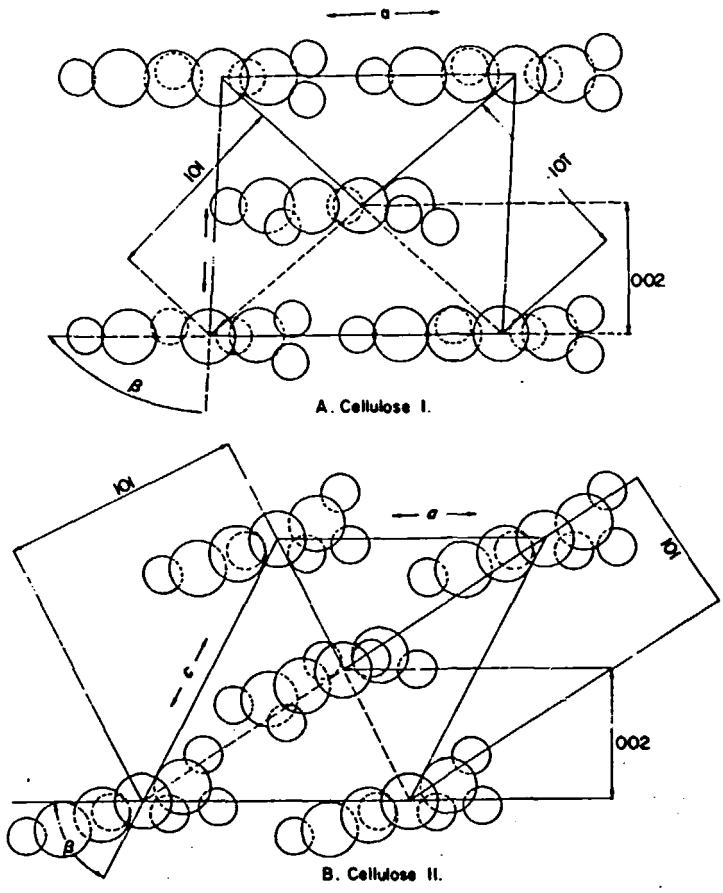


FIGURE 3. View in the direction of the b axis of the unit cell of (A) Cellulose I, native cellulose and (B) Cellulose II, mercerized cellulose. (A) a = 8.20 Å; b = 10.30 Å; c = 7.90 Å; β = 83.3°. (B) a = 8.14 Å; b = 10.30 Å; c = 9.13 Å; β = 62.8°.

the exchanging sites are attributed to the presence of acidic functional groups. These may be part of the cellulose in regenerated products or, in natural fibers, may be attached to materials associated with the cellulose (e.g., lignin, pectic substances, or hemicelluloses). These variations in the source of carboxyl groups reflect also upon the reported capacity data: Knight[28] gives a figure of 0.05 meq/g, while other values are on the order of 0.01 meq/g for filter paper[29] or depectinized cotton[30,31] and 0.022 meq/g for chromatographic cellulose powder.[32] The pK_a value of these metal uptake sites is approximately 4.4. Farrah and Pickering[32] have also presented evidence for the presence of a second type of adsorption site with a pK_a of 7.0 and a capacity of 0.015 meq/g, but little information was given as to the nature and origin of this second metal binding functional group. For the chromatographic cellulose studied, the relative affinity order is $H^+ > Pb^{2+} \approx Cu^{2+} > Zn^{2+} \approx Cd^{2+}$.

In literature the term "ion-exchange cellulose" applies to substituted celluloses; the modification of cellulose is accomplished by oxidation, esterification, and etherification reactions under conditions that retain the fiber structure and that produce a product which does not dissolve or swell excessively in dilute aqueous acids or bases.[33] The ion-exchange properties are similar to those of ion-exchange resins, but some unique properties make cellulose ion exchangers particularly useful in certain applications: they

Table 1
RECENT IMPROVEMENTS OF CELLULOSE ION EXCHANGERS

Product	Goal of work	Main use of the product	Ref.
Phosphorylated cotton	Production of an ion exchanging cotton fabric	removal of Ca^{2+}	36
Sulfate cellulose cross-linked with epichlorohydrine	Optimization of reaction degree-of-substitution 0.8—0.9 capacity, 1.9—2.2 meq/g	—	37
Copolymer of cellulose and methacrylic acid	Studies of pH and temperature dependence of ion exchange process, 15% COOH groups	water purification	38
Copolymer of cellulose and acrylic acid	1.25 meq/g	purification of waste water from dyeing and metalization	39
Cross-linked carboxymethyl cellulose	Cross-linking the CM-cellulose after preparation as thin film on a glass plate; 3.2 meq/g	—	40
Amphoteric cellulose	Optimization of exchange capacity	—	41
Copolymer of cellulose, poly(acrylic acid) and quaternary ammonium groups	Optimization of exchange capacity and affinity studies	purification of waste water from dyeing	42—44
Borate cellulose	Preparation of borate cellulose	sorbent for blood stabilization	45
Carboxymethyl and DEAE cellulose	Synthesis in one reaction vessel, reduced reagent consumption, improved flow properties	—	46
Sulfonated cellulose	Increased capacity	—	47

are much finer than ordinary resins, present a larger surface and because of their porous structure, permit the entrance or attachment of larger molecules which are not readily adsorbed by the resins. The rate of exchange is very rapid so that methods used to measure exchange rates of the resins are not even applicable. In general, the capacities of the cellulose ion exchangers are lower than the capacities of ion-exchange resins. Cation exchangers on a cellulose basis offer a wide range of acidic strength as measured by their pH at half capacity which is an approximation of their pK_a values. The anion exchange celluloses are considerably more basic than weakly basic anion exchange resins, but are less basic than strong base resins.

A great number of routes have been taken to prepare ion-exchange materials on a cellulose base; a good review of these has been given by Guthrie.[33] Little fundamental progress in preparative work has been reported since. The claimed improvements are mostly related to less reagent consumption, higher stability, higher degrees of substitution, and shorter reaction times. A summary of the relevant recent literature is compiled in Table 1.

With the exception of phosphorylated cellulose, the major limitation in obtaining even higher capacity celluloses has been the loss of the original physical properties that parallels high degrees of substitutions; excess swelling occurs which interferes with column operation in chromatography or causes fiber structure to be lost so that the product becomes a soluble polyelectrolyte without any value as ion-exchange material. By subsequent cross-linking, such materials can be converted to insoluble, granular ion exchangers of high capacity, but with loss of the fiber structure.[34] However, if the cellulose is cross-linked by a difunctional reagent before introduction of the ionic group,

fiber structure is retained and a much higher capacity may be reached. Guthrie and Bullock[35] have tested about 30 potential cross-linking agents and found di(2-sulfatoethyl)amine, 1,4-disulfatobutane, 1,3-dichloro-2-propanol, divinylsulfone, and formaldehyde to be very suitable for this purpose.

In special instances, cross-linking and introduction of ionic groups may be accomplished with a single reactive compound. For example, dichloroacetic acid can be used with sodium hydroxide to attach carboxyl groups and cross-link at the same time. The resulting cation exchange cellulose has a capacity of 1.4 meq/g.[35]

The bulk of analytical chemistry performed with ion-exchange celluloses appears to be in the field of affinity chromatography.[48] Work done in the field of inorganic chromatography has been reviewed by Muzzarelli[49] and will only be considered if it applies to our present problem, the concentration of trace ion species. Of all ion-exchange celluloses that have been synthesized, only carboxycellulose (oxycellulose), carboxymethyl cellulose, diethylaminoethyl (DEAE) cellulose, and phosphorylated and sulfonated cellulose have been studied as support for trace ion preconcentration. Except for changes in selectivity, no fundamental differences in preconcentration capability exist for those celluloses not discussed in this paper.

In 1955 a preliminary communication by Kember and Wells[50] marked the first analytical use of phosphorylated cellulose. In a subsequent study the same group prepared cellulose phosphate with 9.7% phosphorus.[51] The best product was produced by steeping 9 g of wood-pulp cellulose in a solution of urea (50% w/w) and orthophosphoric acid (18% w/w/), so that a weight ratio of liquor to cellulose of 3 was obtained. The cellulose strips were electrically heated ("cured") to 130°C in an oven (30-cm cube), through which air preheated to the same temperature was vigorously forced (22 air changes per minute). The maximum capacity was reached after curing for 1 hr and was as high as 10 meq/g cellulose. The principle product is believed to be monoammonium monocellulose hydrogen phosphate. The claim that part of the phosphoric acid groups are diesterified thereby cross-linking the cellulose has led to some controversy,[52] and some of the commercially available high-capacity phosphate cellulose seems to contain a certain portion of unbound phosphate.[53] Nevertheless, the most remarkable quality of this type of material is the high density of ionized groups that can be achieved without destroying the fibrous structure. In their studies, Head and co-workers[51] found a high affinity for Th^{4+}, Ti^{4+}, U^{4+}, Ce^{4+}, Fe^{3+}, ZrO^{2+}, and UO_2^{2+} which are adsorbed from 4 *N* acid. Kember[54] used the ion-exchange cellulose from filter paper prepared in the same manner to enhance the sensitivity of spot tests for copper and iron in water. The detection limits were 20 ng Cu and 100 ng Fe in a 50-mℓ sample of water. The application of this concentration procedure to the determination of Cu in hard tap water was unsuccessful because of the calcium competition for exchange sites. Iron is preconcentrated from acidified solutions (1% v/v HCl) without interference from Ca^{2+}.

The high affinity of phosphorylated cellulose for uranyl and ferric ions was utilized later for matrix separation[55] in the analysis of high purity uranium; the determination of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} by square wave polarography is hampered by UO_2^{2+} and Fe^{3+}. The latter two are separated from the analyte ions on an ion exchange column in 1 *N* HCl. Repeated evaporation to dryness was necessary resulting in a somewhat lengthy procedure, but detection limits of 0.25 μg for Cd^{2+}, and Pb^{2+} and 0.5 μg for Cu^{2+}, and Zn^{2+} were claimed.

In a series of papers, Schulek and co-workers studied the trace ion retention on carboxycellulose[56-61] prepared by hypobromite treatment as given by Birtwell and co-workers.[62] A two-step preparation with periodate and chlorous acid yielded dicarboxy-cellulose containing 10% carboxyl.[59] The pK_a of the carboxycellulose used in these studies was 3.46 ± 0.05, and the maximum exchange capacity was 0.22 meq/g. This maximum can only be reached if the liberated H^+-ions are buffered. The uptake of Ni(II)

Table 2
OPTIMAL pH VALUES FOR THE COLLECTION OF INDIVIDUAL METAL IONS ON CARBOXYMETHYL-CELLULOSE

pH	Ions
3	Bi^{3+}, Fe^{3+}
5	Al^{3+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+} Fe^{2+}, Mn^{2+}, UO_2^{2+}, VO^{2+}
6	Pb^{2+}
8	Co^{2+}, Ni^{2+}, Zn^{2+}
9	Ag^{+}, B^{3+}, Hg^{2+}

(milliequivalent per gram of C cell) from 0.005 *M* solution of nickel salts is 0.206 for the acetate and 0.076, 0.077, and 0.068 for the chloride, nitrate, and sulfate, respectively. In qualitative work, 3 to 5 mg carboxycellulose were suspended in volumes up to 10 ℓ, and as little as 10 μg of metal ions were collected. The pH optima for concentration are given in Table 2. Moderate concentrations of the metal-cyanide complexes corresponding to microgram per millimeter quantities of Cu, Ni, and Zn were also retained by carboxycellulose.[58] The concentration factor for a 100-mℓ solution can reach 30,000 and more. Quantitative results have also been published[60] for carboxycellulose. Traces of Cu^{2+}, Fe^{3+}, Zn^{2+}, and Co^{2+} were determined in high-purity water and ethanol, and good agreement with neutron activation analysis is claimed. If carboxycellulose is used as a column filling, traces of Cu^{2+}, Zn^{2+}, and Co^{2+} can be removed from high-purity water, with residual concentrations below the nanogram per milliliter range. Fe^{3+} is retained quantitatively on a mixed bed column (carboxycellulose/DEAE cellulose). The flow rates in these experiments were about 28 mℓ/min cm^2. For quantitative sorption of trace ions from ethanol, the flow rates have to be reduced to approximately 12 to 15 mℓ/min cm^2. Close to the break-through capacity, the metal ions appear in the effluent in the order Zn, Ni, Cu, and Pb from an H^+- or Na^+-form carboxycellulose column.[59]

While these applications had preconcentration of trace ions as the primary goal, a considerable number of contributions in inorganic chromatography were mainly concerned with separations. Although the potential for preconcentration is not rigorously explored in these chromatographic studies, some of the results suggest that successful adaptation to this end may be possible. Most workers in the field have investigated cation as well as anion exchange cellulose. The latter are found useful for metals forming anionic complexes. Cobalt, for example, in the microgram per milliliter range could be retained quantitatively from ethyl ether and ethyl etheric/nitric acid solutions on a wide variety of substituted celluloses;[63] the celluloses studied include unsubstituted Whatman® CF II, DEAE cellulose Whatman® DE II, aminoethyl cellulose Whatman® AE 50, phosphate cellulose Whatman® P II, and carboxymethyl cellulose Whatman® CM II, all in powder form. A mixture of methane/ethyl ether (20:80), containing 5 g of NH_4CNS or similar solutions can be used for quantitative recovery of Co, as well. A similar behavior was found for Cd and Zn; a quantitative separation of these two ions from mercury[64] was achieved on several substituted celluloses. Bismuth nitrate is retained quantitatively on natural cellulose Whatman® CF II, DEAE cellulose Whatman® DE II, sulfoethyl cellulose Bio-Rad® SE, and *p*-amino-benzyl cellulose Bio-Rad® PAB. Natural cellulose was also used to separate traces of Hg

from large quantities of Bi.[65] Antimony is strongly absorbed by natural and substituted celluloses and can be easily separated from manganese, iron, and other metals.[66] Quantitative elution could be achieved from natural cellulose and cellobiose, only. Common to all these absorption studies is that the ions were dissolved in pure etheral solution or in etheral/HNO_3.

Kuroda and co-workers[67] studied the sorption of Hg^{2+} on weakly basic cellulose ion exchanger. DEAE cellulose retains traces of Hg from a solution 0.01 *M* in ammonium thiocyanate and 0.1 *M* in hydrochloric acid and separated them from large excess of other ions. The potential of DEAE cellulose ion exchanger for the concentration of platinum and paladium from base metals has been demonstrated by the same group.[68] Unlike ion exchange resins, DEAE cellulose does not prevent complete elution of the noble metals after sorption; 0.05 *M* thiourea solution is used to recover Pt and Pd in 30-mℓ volume. Later, the sorption of Cu^{2+}, Zn^{2+}, Cd^{2+}, In^{3+}, Bi^{3+}, and U^{6+} by DEAE cellulose from a methanolthiocyanate-hydrochloric acid medium was accomplished. The sharp decrease of distribution coefficients at increased, but still moderate loadings (0.03 mmol/g), however, makes a general use questionable.[69]

Au^{3+} is also adsorbed on DEAE cellulose under conditions that facilitate its separation from Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Se^{4+}, and Cd^{2+}. A dilute chloride medium with a concentration of hydrochloric acid of 0.05 *M* or less gave the highest distribution coefficients. Au^{3+} is stripped by elution with 40 mℓ of 1 *M* hydrochloric acid.[70] If acetic acid is mixed in the sample solution, an initial concentration of 0.5 *M* HCl can be tolerated. Such a mixture of acetic acid/0.5 *M* hydrochloric acid (9:1) was used in the analysis of anode slime for gold.[71]

Trace elements analysis by X-ray fluorescence spectrometry is frequently limited by the insensitivity of this technique. Particularly, aqueous solutions cannot be analyzed to the low microgram per gram or even nanogram per gram ranges unless the water matrix is removed.[1] Rabe[72] has recently employed sulfoethyl cellulose (0.2 meq/g capacity) for the concentration of cations and DEAE cellulose (0.85 meq/g capacity) for anions. After separating the finest cellulose particles by sedimentation, the cellulose was packed in a column. The flow rate was about 300 mℓ/hr. The column filling was dried, disintegrated in a mixer, and pressed to a tablet. The relative SD was less than 10%, and the recovery of cations from artificial solutions was good. No data for reference analyses were given, however, and it must be expected that the low capacity and relatively low selectivity of the ion-exchange material will not permit accurate analyses of natural water samples.

Generally, the low selectivity of the ion-exchange materials will, in spite of the good technological potential for water treatment, prevent its widespread use as preconcentration media. Even though the distribution coefficients are quite large in a number of cases, ion-exchange celluloses do not give good recoveries in those situations where preconcentration and separation of the analyte species from the matrix are most urgently needed, i.e., for the determinations of trace ions in presence of large excess of concomitant material.

IV. CHELATING CELLULOSES

The relatively low specificity of ion-exchange celluloses has prompted the search for new and improved ways of modifying cellulose. Celluloses with immobilized chelating agents open up new possibilities for trace ion preconcentration. Although a very high capacity is advantageous to avoid displacement effects, the same level of capacity required for ion-exchange celluloses is not mandatory for chelating celluloses if it is possible to select the proper selectivity. No one functional group can be expected to span the entire region of analytically important element combinations, as these combinations

are frequently determined by the required information that can be deduced from the analytical results and/or by the selectivity of the analytical method following the concentration step. For good economy of analytical measurements, it is therefore indispensable to immobilize "group reagents" on cellulose and perform the determination of several elements simultaneously. Modern instrumental techniques generally have enough selectivity to permit successive or simultaneous multielement determinations following a single preconcentration procedure. Frequently, this also simplifies the sampling step by combining preconcentration and sampling.

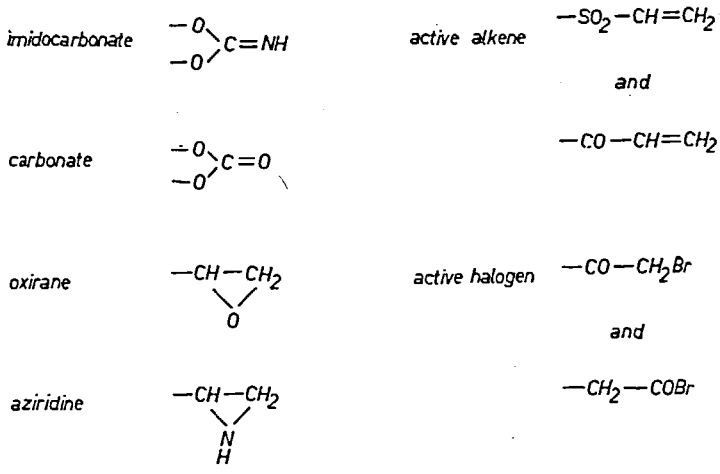
A fair number of chelating agents fulfill these requirements, but they all have one common property that complicates the synthesis: they are fairly complex organic molecules that disintegrate under the severe reaction conditions frequently employed for the preparation of ion-exchange cellulose. For this reason immobilization is generally accomplished by a reaction scheme involving more than one step, so that the "activation" of the cellulose can be separated from the actual immobilization of the ligand. It is also possible to insert "spacer" atoms between the solid support and the ligand to enhance the accessibility of the ligand. In such a synthesis, two distinct approaches can be adopted.[73] The space-arm-ligand assembly can be synthesized in free solution by orthodox organic chemistry, purified, and the entire preassembled complex then coupled to the cellulose matrix in one final step. Alternatively, a modular solid-phase approach can be adopted in which the spacer-ligand assembly is built up in stages on the cellulose matrix. Technically, the latter approach is almost always easier than the preassembly approach, especially for workers who are not accomplished synthetic chemists. Problems associated with the protection and deprotection of the group to be linked directly to the matrix are eliminated. At each stage in the synthesis, excess amounts of reactants and soluble side products can be removed simply by washing the cellulose, whereas the preassembly approach involves complex fractionation and purification steps at each stage in the synthesis.[73] For glass and silica substrates, Leyden and co-workers[74-76] have chosen an analogous modular solid-phase approach. They modified the surfaces first with a silanization reaction, introducing a diamine functional group that was later reacted to give a material with strong chelating properties for heavy metals.

Among the drawbacks are the introduction of incomplete assemblies that frequently contain ionic groups with low specificity towards metal ions and the relative instability of the cellulose that may cause a loss of the fibrous structure. Both of these disadvantages are unlikely to seriously affect the properties of the modified cellulose. The introduction of ionic groups will reduce the usefulness of the substituted cellulose for the concentration of ions only marginally as the overall degree of substitution tends to be much lower than one. As for the loss of fibrous structure, a variation of reaction conditions will frequently prevent this loss or if the molecular order is not completely destroyed, a reconstitution of the fibers with their good mechanical and low properties may be possible.

Most of the fundamental work in activating polysaccharide matrices has been performed in the field of affinity chromatography, particularly on agarose supports. The objectives are somewhat different than in preconcentration work, but the common problems suffice to warrant a discussion of the most relevant results.

A. Activation of the Cellulose

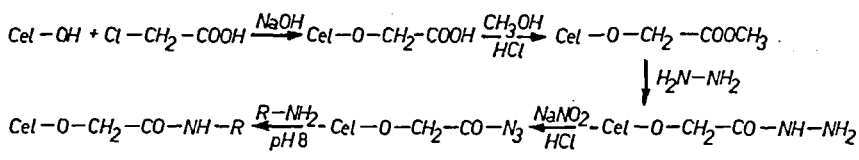
There are two approaches to the attachment of ligands to the polysaccharide matrix.[77,78] These are derivatization of hydroxyl groups and partial degradation of the matrix thereby introducing reactive functional groups. Ligand attachment via the hydroxyl groups involves first the attachment of residues susceptible to electrophilic attack. These include



The electrophilic groups primarily react with amino and thiol groups, but may also be attacked by weaker nucleophiles such as phenolic hydroxyls.

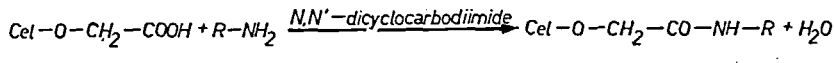
The side reactions occurring in such activation reactions are cross-linking reactions; these can be suppressed, but not completely avoided by a proper choice of reaction conditions. The problem is to find the optimum conditions for the introduction of a maximum number of electrophilic groups such that the product is suitable for the following chelate coupling step. Thus each attachment method must be optimized with respect to activation as well as subsequent coupling. To date very little systematic work has been done. In fact, only very few of the suggested activation procedures have actually been applied for the immobilization of chelates onto cellulose.

Binding a substance with a free amino group onto cellulose is easily accomplished by the Curtius azide method:[79]

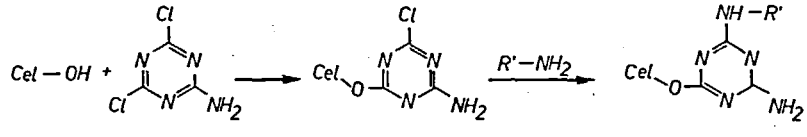


After preparation of carboxymethylcellulose azide by Curtius rearrangement, an isocyanate is formed on to which an amino group of the reagent can be bound.

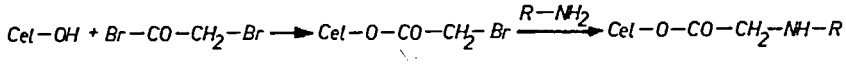
Reagents with basic amino groups can be coupled to the carboxyl-groups of carboxycellulose in the presence of carbodiimide:[80]



Kay and Lilly[81] developed the triazine methode. 2-Amino-4,6-dichloro-s-triazine is bound to the hydroxyl group of cellulose and reacts further with an amino group:

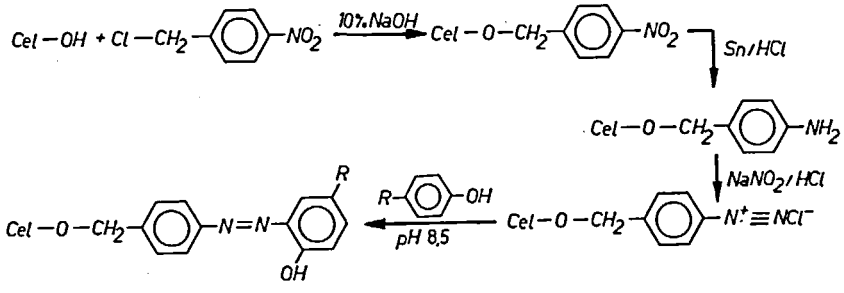


Jagendorf et al.[82] developed a method of protein binding based on the acylation of the hydroxyl group in cellulose with bromoacetyl bromide and subsequent alkylation of the amino group of the protein:

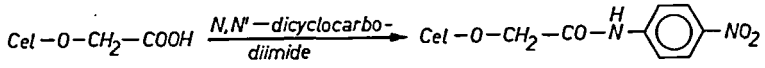


The same reaction can probably be employed for other reagents as long as they contain an amino group.

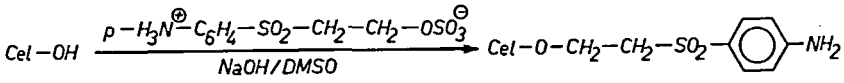
Diazonium groups open up still another possibility to attach chelating agents. Campbell et al.[83] have used the following route to obtain diazonium substituted cellulose:



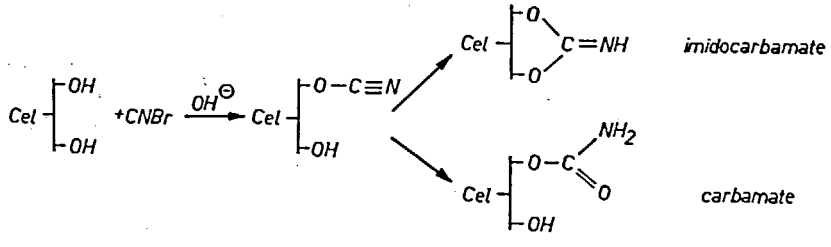
Another reaction to produce diazonium cellulose has carboxymethylcellulose as an intermediate and uses the carbodiimide reaction in presence of benzidine:[84]



or, ethylsulfonyl (aniline)-cellulose as intermediate[85]



The activation by cyanogen bromide, though very common in ligand immobilization for affinity chromatography,[86-88] has not been used extensively for cellulose. Gstrein et al. have demonstrated the potential of this activation procedure for cellulose,[89] but more work needs to be done before the merits are fully exploited. The general reaction can be written as:

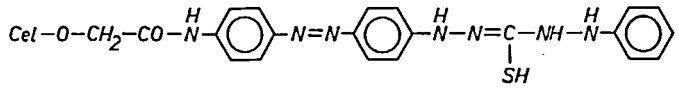


From this scheme it is obvious that two vicinal hydroxyl groups are necessary for this reaction to occur and only one of the end products is the reactive imidocarbonate, with the other being the unreactive carbamate. The relative amount of the two products is strongly dependent upon the reaction conditions, pH and temperature. A part of the imidocarbonate is undoubtedly cross-linked, so that cross-linking prior to activation may be obviated.[78] Reactions that lead to cleavage are hydrolysis at pH values above 5 and aminolysis at pH values between 8 and 10.[90] The vast amount of experience with this reaction will probably add extra usefulness when applied to the modification of cellulose.

While all of the reactions have "activated" the molecule without degradation, it is also possible to accomplish the activation by ring cleavage. The derivative prepared in this instance has frequently been chlorodeoxycellulose.[91,92] Chlorodeoxycellulose can be prepared by several synthetic routes,[93] but the shortest route is to react the cellulose in dimethylformamide with $POCl_3$ or $SOCl_2$. The problems experienced with chelating celluloses obtained via chlorodeoxycellulose seem to be caused by a combination of low capacity, low selectivity, and/or small formation constants. For neither material has the analytical potential been adequately demonstrated.

B. Immobilization of Chelating Functional Groups

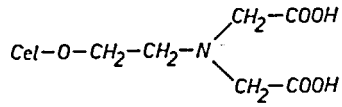
Up to now a fair number of chelating functional groups have been attached to cellulose using one of the above introduced activation procedures together with a more gentle second reaction step. Starting from carboxymethylcellulose with 0.72 meq/g capacity, Baumann et al.[84] have prepared diazonium cellulose and coupled potassium dithizonate (2 to 5% w/v) at pH 11 to 12 by stirring the fresh diazonium cellulose overnight at 10 to 12° C. The maroon product was washed free of base and treated with 2 *N* HCl to yield the green active dithizone in acid form. The product was washed to neutrality with double distilled water and stored dry away from light and air, both of which slowly deactivated it. The capacity of the fresh product was determined to be 0.58 meq/g. The following structure is given for the dithizone cellulose:



In column experiments, this material gave complete recovery of Cu^{2+}, Zn^{2+}, and Ag^{+} at pH 5 and the ions were eluted quantitatively by 2 *N* HNO_3. The columns were reusable. For trace element collection from sea water, 20 g of dithizone cellulose was filled into a column (4.2 cm I.D., 6-cm filling height), and 20 ℓ of sea water were gravity fed at a flow rate of 120 to 150 mℓ/min (~10 to 12 mℓ/min cm^2). Only semiquantitative data were given so that a full assessment of this material is impossible.[84] The generality of the diazo coupling used in the study led to a good many different products with chelating groups like oxine, cupferron, quinalizarin, 2-thenoyltrifluoroacetone, phenylarsonic acid, and *p*-dimethylamino-benzilidene rhodanine.[84]

In continuation of their work in the field of substituted celluloses, Horvath and Nagydiosi[94] prepared in imino-diacetic-acid-ethyl-cellulose (IDE-cellulose) starting from aminoethyl-cellulose (AE-cellulose). The commercially available AE-cellulose (Whatman® AE 11) had a capacity of 0.84 meq/g based on the nitrogen content and was reacted at 70 to 80° C on a steam bath with chloroacetic acid for 5 to 6 hr. The IDE-cellulose was filtered off, washed with water, and dried at 50 to 55° C. The carboxyl content, i.e., the exchange capacity calculated on the basis of points of inflection on the

dynamic titration curve appeared to be 1.68 meq/g. This corresponds to a N/COOH ratio of 1:2 referring to the formation of the imino-diacetic acid group. The two pK_a values of the IDE-cellulose are 2.65 ± 0.08 and 9.1 ± 0.2. The proposed structure is

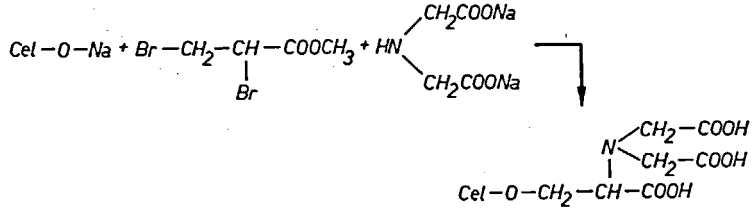


One of the major advantages of this material is its long-term stability: for years it can be stored at 4° C without loss of capacity, either in the H^+ or in the NH_4^+ form.[95] Analytically this material has so far been used primarily in connection with atomic absorption spectrometry. A 10- to 20-fold enrichment of Cd, Co, Cu, Fe, Hg, Mn, Ni, Pb, and Zn has been employed for water analysis. The preconcentration was carried out with acetate buffer at pH 5 to 6. A relative SD of less than 10% was claimed in the flame AA determination following the preconcentration procedure.[96]

IDE-cellulose could also retain trace elements from soil extracts.[97] Air-dried soil was extracted with 200 mℓ of 1 *N* neutral ammonium acetate solution, ascorbic acid (20 mg) was added, and the extract was poured through 200 mg of the NH_4^+ form of IDE-cellulose which was placed on a small piece of purified cotton wool packed in the stem of a polyethylene funnel. The flow rate was 1 ~ 7.8 mℓ/min. The IDE-cellulose was washed with 100 mℓ of high-purity water to remove the interstitial solution. Ca^{2+}, however, remains on the column and elutes together with the heavy metals. A 1000-fold weight excess of Ca does not interfere with the concentration. The heavy metals were eluted with 1 *N* HCl. The addition of ascorbic acid improved the elution of Fe, since Fe^{3+} forms complexes too stable to be eluted by 1 *N* HCl. The stability order of the ions investigated is Cu > Ni > Zn > Co >> Ca ≃ Mg.

Recently, IDE-cellulose preconcentration has also been modified for electrothermal atomization.[98] The modified procedure calls for washing the column after concentration with ammonium citrate/citric acid buffer to remove effectively the remaining Ca^{2+} and Mg^{2+}, as these interfere with the trace metal determination by flameless atomic absorption spectrometry. In this case the elution is accomplished with 1 *N* HNO_3.

Another reaction path leading to immobilized iminodiacetic acid on cellulose was proposed by Kojdl.[99]



Mercerized cellulose powder is thoroughly mixed with the solid disodium salt of iminodiacetic acid and suspended in acetone. The suspension is refluxed for 3 hr at 70° C while an acetonic solution of 1,2-dibromopropionicmethyl ester is slowly added to the mixture. After washing with ethanolic acetic acid solution and distilled water, the product is air dried as an acetonic suspension. The capacity is 0.29 to 0.30 meq/g. As column filling, this material removes trace species such as CrO_4^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, and Cd^{2+} from aqueous solutions containing up to 10% NaCl, $MgSO_4$, or $CaCl_2$.[100]

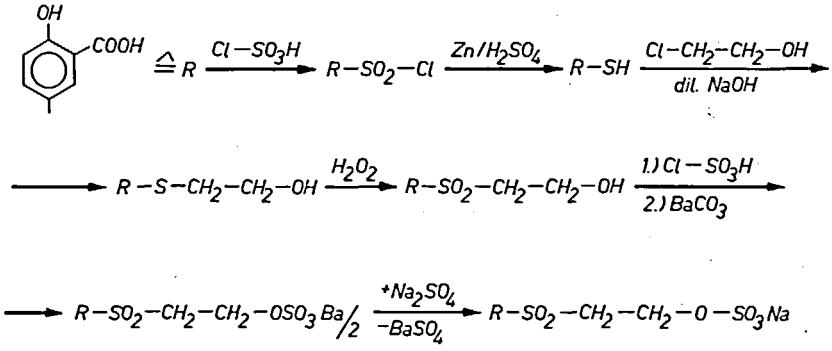
A great number of chelating celluloses was prepared by Lieser and co-workers. They have adopted the synthetic principle for the production of "Remazol"-dyes by Hoechst.[101] The reactions can be written as:[85]

$$R-SO_2-CH_2-CH_2-OSO_3Na \xrightarrow[-Na_2SO_4,\ -H_2O]{+NaOH} R-SO_2-CH=CH_2 \qquad a$$

$$R-SO_2-CH=CH_2 \xrightarrow[Alkali]{Cel-OH} R-SO_2-CH_2-CH_2-O-Cel \qquad b$$

$$R-SO_2-CH=CH_2 \xrightarrow{H_2O} R-SO_2-CH_2-CH_2-OH \qquad c$$

To avoid the side reaction c the synthesis is carried out in dimethylsulfoxide. Since the starting material itself has to be synthesized in a fairly cumbersome sequence of reactions, only the salicylic acid derivatives have been prepared in this way:



The frequent purification and crystallization steps necessary make the validity of O'Carra's argument in favor of a modular solid-phase approach obvious.[73] In fact, Lieser himself has taken this second route in most of the cases using a diazo coupling as last step in the synthesis.

Starting with microcrystalline, formaldehyde cross-linked cellulose, a salicylic acid derivative was obtained with a capacity of ~0.7 meq/g and with a fairly good stability towards 3 *M* HCl or HNO_3 and 1 *M* NaOH. The material has a particularly good selectivity for Th^{4+} and Fe^{3+}.[102] The kinetic properties of this material were studied by nonisotopic exchange and isotopic exchange reactions.[103] Fast kinetics coincided with a low capacity where only easily accessible hydroxyls were derivatized. The optimum reaction time was 15 min for the last step, but significant differences in exchange rates and capacity have been observed for cross-linked "amorphous" cellulose and microcrystalline cellulose, the latter giving faster exchange rates and higher capacities. Yet, only 0.19 meq/g capacity is obtained under the recommended reaction conditions.

Tiron (1,2-dihydroxybenzene-3,5-disulfonic acid) was diazo coupled to cellulose yielding a product with 0.2 meq/g exchange capacity:[104]

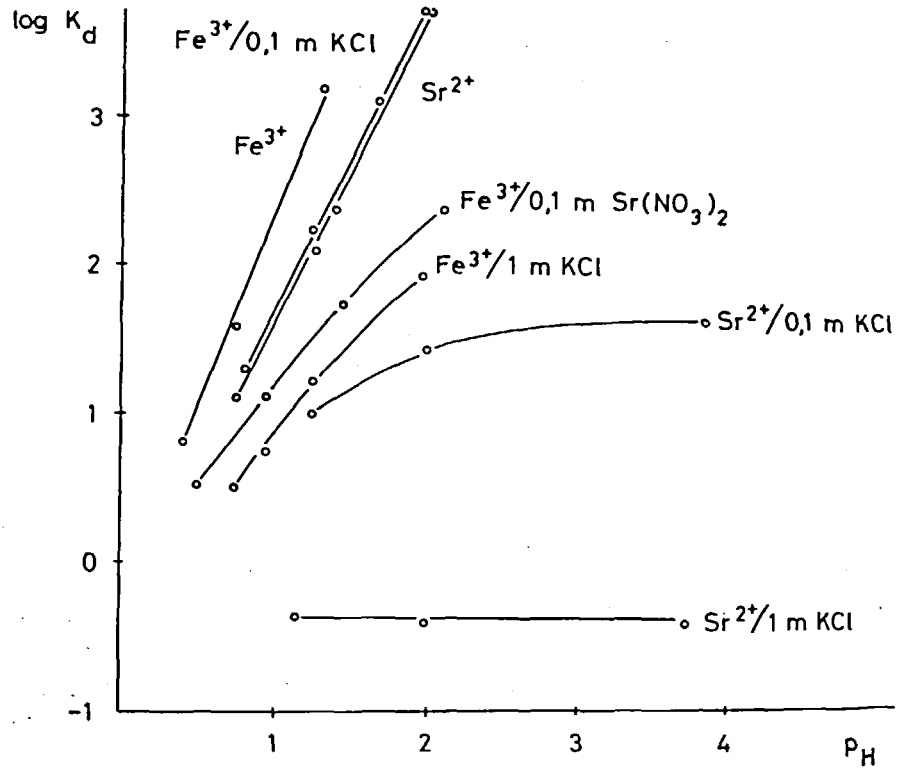
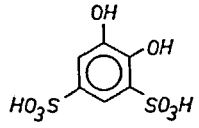


FIGURE 4. Distribution coefficients (K_d) between water and Tiron cellulose for Fe^{3+} and Sr^{2+} in presence of different concomitant ions.



This material shows complete equilibration with Fe^{3+} ions within 2 min and affinity towards alkaline earth ions as well as transition metal ions. While transition metal ions coordinate preferably with the two phenolic OH groups, alkaline earth ions react with the sulfonic acid moieties in the meta position. Ionic strength effects are much more pronounced for Sr^{2+} than for Fe^{3+} (Figure 4), leading to a sharp decrease in stability of the complexes. Another interesting effect is a change in affinity order for Ca^{2+} and Sr^{2+}. While Ca^{2+} forms stronger Tiron complexes in solution, steric reasons are stressed for the stronger affinity of Sr^{2+} towards the immobilized Tiron.[104]

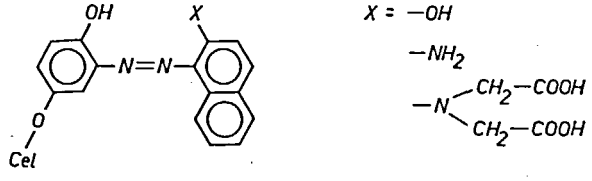
The use of immobilized chromotropic acid[105] as a preconcentration medium brought up a couple of problems that are fairly symptomatic for most of the modified celluloses prepared to date. For a rather nonselective functional group like chromotropic acid, an exchange capacity of 0.15 meq/g is far below the capacity that would be required for an analytically useful material. In most aqueous samples, alkali and alkaline earth metals will occur: 5 ppm of Na or Ca reduced the recovery of chromotropic acid-cellulose significantly, leading to wrong results. Additionally sub-ppb amounts of Fe, Zn, Cu, and Sr have a deleterious effect on the validity of calibration, even if present in concentrations equal to that of the analyte ion. To arrive at samples that can be measured by a technique sensitive to the geometry of the sample, e.g., X-ray fluorescence analysis, special efforts

Table 3
CHARACTERIZATION OF HYPHAN CELLULOSE EXCHANGERS BASED ON DIFFERENT CELLULOSES

Cellulose	Particle size	Origin	Capacity (mmol/g)
Mircrocrystalline	20—100 μm	Avicel®, Merck	0.5—1.0
"Bead"	200—400 mesh	J. Stamberg[106]	0.5
Amorphous	20—150 μm	Schleicher and Schüll, 123/45	0.5—1.0
Short-fiber	400—600 mesh	Schleicher and Schüll 123/3	0.4—0.6
Long-fiber (80% viscose, 20% cotton)	Some centimeter	Dr. Hartmann, medical cotton	0.8
Cotton fabric	5 × 5 cm^2	Textile fabric (25 mg/cm^2 area weight)	0.3

have to be made. Lieser chose to sandwich 50 mg of cellulose exchanger between two sheets of Whatman® filter paper which reduced the sensitivity as compared to a filter consisting of exchange material only and gave relative SDs of 18 to 23%. All of these problems must lead to completely unreliable results for all but the very purest aqueous solutions containing nothing but a few ppb of trace metals; even then, precision remains a problem.

Recognizing that materials with higher capacity and better selectivity are needed, Lieser and co-workers turned to a different class of chelating groups. Using the same reaction principles,[106] 2-naphthol, 2-naphthylamine, and 2-naphthylamine,-N,N-diacetic acid were immobilized on *o*-aminophenol cellulose, giving materials with 0.95, 0.45, and 0.30 mmol reagent per gram of cellulose, respectively. Since the diazonium material which was used as reactant has also 0.95 mmol/g, 100% yield is found for the coupling of 2-naphthol.[106]



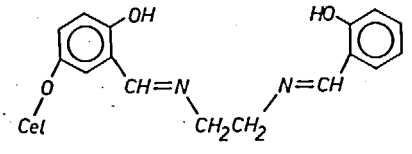
In a subsequent paper[107] the influence of the cellulose substrate was investigated. Microcrystalline cellulose, amorphous cellulose, "bead" cellulose,[108] short-fiber cellulose, long-fiber cellulose, and cotton fabric were compared with respect to loading with 1-(2-hydroxyphenylazo)-2-naphthol (Hyphan). These results are given in Table 3. "Bead" cellulose and cellulose with short fibers are used as column fillings, while cellulose with long fibers is suited for the production of filter paper. Cotton fabric gives the smallest degree of substitution and medical cotton cannot be formed to give filters of sufficient mechanical stability. The generality of the diazo coupling was demonstrated by the immobilization of a variety of chelating functional groups. A summary of the synthesized materials, their capacity and their analytical potential is given in Table 4. The reaction conditions can be found in Reference 107. Extensive analytical studies were made of these chelating celluloses by the original authors.[109-114] The Hyphan cellulose

Table 4
CHELATING CELLULOSE EXCHANGERS AND THEIR ANALYTICAL POTENTIAL

H_2N content of o-aminophenol-cellulose based on Schleicher and Schüll 123/3 (mmol/g)	Chelating functional group	Capacity (mmol/g)	Trace elements
0.65	alizarin	0.30	Al, In, Th, Zr
0.65	2-(thiazolyl-(2)-azo)-4-methoxyphenol (TAM)	0.30	Hg
0.65	arsenazo III	0.15	Hf^{4+}, Th^{4+}, U^{IV}, Lanthanides
0.65	5-(4-dimethylaminobenzyliden)-rhodanin	0.32	Hg, precious metals
0.70	brenzcatechin	0.60	NbO_2^+, TiO^{2+}, Fe^{3+}
0.70	chinalizarin	0.35	Al, Ga, In, Sc, U
0.70	4-(pyridyl-[2]-azo)-resorcinol (PAR)	0.50	Pb, Co, U
0.70	glyoxalbis(2-hydroxyanil)	0.30	UO_2^{2+}
0.75	pyrogallol	0.45	Bi, Nb, Sb, Ta

had high formation constants for transition metal ions. The dependence of the distribution constants from pH was determined for a good many ions (Figure 5). Of this cellulose exchanger, 100 mg were suspended in 100-mℓ sample solutions and the trace ions could be collected by stirring at pH 7.5 for 1 hr.[109,113] After filtration the fibers were analyzed by X-ray fluorescence spectrometry for Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, and UO^{2+}. This simple procedure gives good results between 0.2 and 20 ppm, even in presence of 0.5 mol/ℓ NaCl. X-ray fluorescence interferences were held responsible for variations of about ± 20%; in the light of the results published by Leyden and co-workers,[1] this appears to be an unlikely explanation. For lower concentrations a column procedure has to be employed first; the trace metals are eluted with 1 *M* HCl in a second step and then neutralized and further concentrated by the above-described batch procedure. The recovery was between 90 and 99% and up to 5ℓ of water could be fed through the column (20 g Hyphan cellulose) in less than 6 hr.[109]

For the separation of uranium from high-salinity waters, the flow rate could be increased to 25 to 30 mℓ/min (8 to 10mℓ/min cm^2).[110] This reduced the time needed for the analysis of 5ℓ of water to 3 to 4 hr. Chelating celluloses with Hyphan or Salen (bis-salicylaldehyde-ethylendiamine) as anchor groups gave good uranium recoveries even in solutions containing 0.5 *M* NaCl.



Salen cellulose

For use with X-ray fluorescence measurements, Röber[115] has produced a filter paper from Hyphan cellulose with an area weight of about 30 mg/cm^2 (2-cm diameter, 0.1-cm

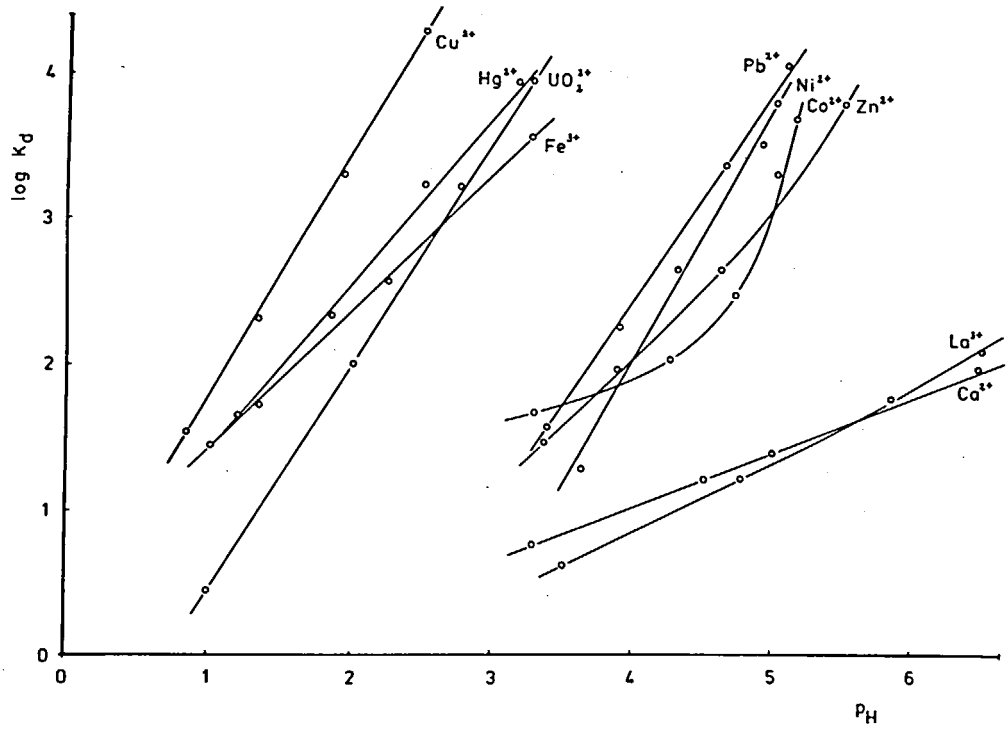
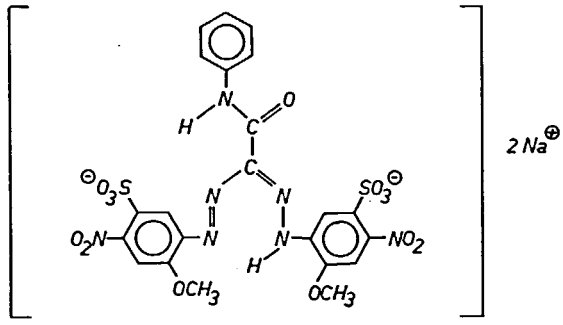


FIGURE 5. Distribution coefficients between water and Hyphan cellulose.

thickness). With a filtration rate of 67 mℓ/min (~20 mℓ/min cm^2) the recovery was 55% for Cr^{3+}, 51% for Fe^{3+}, 57% for Co^{2+}, 40% for Ni^{2+}, 76% for Cu^{2+}, 35% for Zn^{2+}, 43% for Hg^{2+}, and 45% for Pb^{2+} at concentrations of 60 to 180 ppb. By adding 1 g of sodium acetate to 1ℓ of water, the recoveries could be improved significantly without serious reduction in flow rate.[113,115] For sea water, thicker filters (~90 mg/cm^2) and lower flow rates of about 17 mℓ/min (~5 mℓ/min cm^2) gave a recovery between 50 and 95% as compared to the 80 to 100% obtained by the column method. As expected, the filter method led almost consistently to lower values than the batch adsorption. Reasonable agreement between X-ray fluorescence, neutron activation, and atomic absorption was found in spite of these problems.[113]

For the analysis of mineral waters, a combination of column and batch preconcentration was employed to improve the recovery of the Hyphan cellulose.[116] Prefiltered mineral water samples of 2ℓ at pH 6 to 8 were passed through a column containing 2 g Hyphan cellulose. The flow rate was about 10 mℓ/min cm^2, and this separation took 1 hr. The retained trace elements were eluted with 50 mℓ of 1 *M* HCl, 0.1 g of Hyphan cellulose was added and the suspension brought to pH 7.5 with NaOH. After shaking for 30 min, the Hyphan cellulose was filtered off to give a thin layer that could be directly analyzed by XRF. The concentration factor of the combined procedure is 2×10^4, with X-ray detection limits in the sub-ppb range.

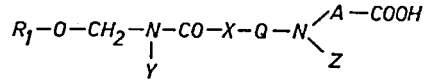
Grote and Kettrup[117] attempted to couple formazans to cellulose. They reduced the nitro groups in 1,5-bis-(2-methoxy-4-nitrophenyl-5-sulfonic acid)-3-phenylcarbamoyl-formazane disodium with secondary sodium sulfide,



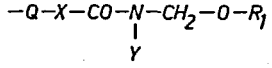
reacted the resulting amino group with 1,3,5-trichloro-s-triazine and coupled it to cross-linked Ecteola cellulose.[118] The very low capacity of 0.04 meq/g was explained by hydrolysis of the triazine-formazane.

While all of the chelating celluloses reviewed up to now had the anchor groups covalently bound, a couple of patents claim immobilization of chelating reagents by sorption and/or ionic interactions with the substrate. A German patent granted to the W.C. Heraeus company describes a polyethyleneimine-impregnated cellulose that absorbs copper.[119] A high excess of other concomitant metal ions does not reduce the recovery of Cu at trace levels.[120] It also removes vanadate (8.8 mg/g cellulose), molybdate (8.5 mg/g), and tungstate. Palladium is absorbed from a 0.1 to 10% HCl solution and can be separated from Cu, Ni, Co, Cd, Pb, Zn, Al, Fe, and Cr. A contact time of 10 min is needed.

For the immobilization of anionic chelating groups, Ziegler[121] used DEAE and TEAE cellulose. The preparation of these ionic adducts is very simple, as it requires only the mixing of the cellulose with a solution of the chelating molecule at an appropriate pH. Material synthesized in this way is washed with water to neutral pH and then dried. Table 5 gives a summary of the reagents that can be bound to cellulose. Some of the metal capacities are compiled in Table 6. The flow rates are between 1 and 6 mℓ/min. For the column described in Reference 121, this amounts to 8 to 48 mℓ/min cm^2. Recently, an adsorption material on cellulose basis was invented that contains at least one chelate-forming amino acid group, preferably an aminocarboxylic acid group.[122] A general representation of the anchor groups is



wherein Y represents hydrogen, lower alkyl or $-CH_2-O-R_2$, X represents the direct bond, $-O-$, $-S-$ or $>N-R_3$, each of R_1, R_2, and R_3 independently represents hydrogen or lower alkyl, Q represents a C_1-C_8 alkylene or phenylene $-C_1-C_4-$ alkylene radical, Z represents lower alkyl, $-B-COOH$ or the group of the formula



and each of A and B independently represents C_1-C_8-alkylene which is unsubstituted or substituted by lower alkyl, lower alkoxy, or phenyl. Compounds of this type are dissolved in water and filter paper is impregnated at elevated temperatures to exhibit a considerable weight gain. It could be demonstrated that these materials pick up trace

Table 5
CHELATING REAGENTS IMMOBILIZED ON DEAE- AND TEAE - CELLULOSE BY IONIC INTERACTIONS

Common name	Chemical name	Used for
Alizarinesulfonate	1,2-dihydroxyalizarine-3-sulfonic acid sodium	Al, Ca, Cu, Fe, Zn, Mg, Ti
Beryllon II	8-hydroxy- naphthalene-2,6-disulfonic acid-(1- azo-2')-1',8'-dihydroxynaphthalene-3',6'-disulfonic acid tetra sodium	Be
Carminic acid	—	Pb
Ferron	7-iodo-8-hydroxychinoline-5-sulfonic acid sodium	Fe, Al
Gallus acid	pyrogallol-5-carboxylic acid	Sb
Nitroso-R-salt	1-nitroso-2-naphthol-3,6-disulfonic acid sodium	Co, Fe
Tiron	1,2-dihydroxybenzene -3,5-disulfonic acid disodium	Ti, V, Fe
Titan yellow	methylbenzothiazol-(2,3)-4,4'-diazoamino-phenyl-(2,2')-disulfonic acid sodium	Ti, V, Fe
Violuric acid	5-isonitrosobarbituric acid as oxime	Fe^{2+}, Pd, Cu
Zincon	2-carboxy-2'-hydroxy-5'-sulfoformazyl-benzene sodium	Zn
	5-sulfosalicylic acid	Ti, Fe, Cu
	2-oxo-3-methyl-5-(4-hydroxy-2-sulfo-5-methyl-3-carboxybenzhydryliden)-cyclohexadien-(3,6)-carboxylic acid (I)	Al
	pyrogallol-4-carboxylic acid	Bi
	pyrogallol	Sb

Table 6
METAL BINDING CAPACITIES OF SOME IMMOBILIZED CHELATING REAGENTS

Chelating group	Element	Capacity (mg metal/g cellulose)
Beryllon II	Be	0.016
Carminic acid	Pb	3.8
Tiron	Fe	~15
Titan yellow	Co	1.5
	Mg	4.3

ions, but no analytically useful data were given. It remains to be seen how good the recovery is under analytical conditions.

V. CONCLUSIONS

The wide availability and good flow properties of cellulose have stimulated its use as solid support for functional groups with complexing properties for trace ions. Cellulose can be used in bead or fiber form. The form and other structural properties dictate the obtainable density of functional groups on the surface.

Even though capacities of up to 10 meq/g of cellulose are possible for ion exchange celluloses, the low selectivity prevents the extensive use in preconcentration: most natural

waters contain ionic materials like alkali and alkaline earth metals in far higher concentrations than heavy metals. The active sites of such an ion-exchange cellulose are then occupied by the abundant ions and in many instances preconcentration of trace elements is not possible.

Chelating celluloses avoid this problem, but more gentle procedures have to be employed in preparing them. Frequently, an "activation" step is carried out before the attachment of the ligand is accomplished. Even though a good many ways have been proposed to introduce reactive groups in the molecular structure of cellulose, only one of them gained wider use: the activation of cellulose by 4-(β-sulfatoethylsulfonyl)-2-aminophenol with subsequent diazotization. After attaching suitable ligands, a preconcentration factor of up to 2×10^4 can be obtained.

The experience in routine analysis is still very limited for most materials prepared to date and considerable effort will be necessary to produce chelating celluloses with high capacity, appropriate selectivity, and sufficient long-time stability. In the light of the large number of organic reagents for inorganic analysis the era of the immobilized reagents has just started.

Given the above mentioned requirements concerning capacity, selectivity, and stability, the greatest potential lies in the simplicity of the preconcentration procedure making this approach suitable for situations where a high sample throughput is mandatory: A simple filtration step may yield a sample suitable for the analysis of water at ppb levels.

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