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Source / Izvornik: **Croatica Chemica Acta, 1979, 52, 391 - 396**

Journal article, Published version
Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

Permanent link / Trajna poveznica: https://urn.nsk.hr/urn:nbn:hr:163:785970

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Download date / Datum preuzimanja: **2024-04-28**

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CROATICA CHEMICA ACTA CCACAA 52 (4) 391—396 (1979)

YU ISSN 0011-1643
CCA-1176 544.62
Original Scientific Paper

Sorption Capacity Determination of Cellulose Matrices by Infrared Absorption Spectrometry

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Received October 23, 1978

A method for sorption capacity determination of cellulose matrices as trace metal sorbents has been studied. An analytical method is based on infrared absorption band at 1725 cm^{-1} featuring C=O streching in a polymer molecule. Suitable samples are prepared to construct a calibration curve. Samples are standardized by the potentiometric method in terms of ion-exchange capacity. Some features of the analytical procedure are discussed, particularly with regard to the lower and upper limit of COOH-content determination, the influence of sample structure and the precision of the proposed method.

INTRODUCTION

The knowledge of sorption capacity of cellulose matrices is of great interest in various analytical aspects such as chromatography of inorganic systems[1,2], spot test[3,4], ring oven method[5-7] and collection of trace metals from solutions[8-10]. Cellulose matrices for sorption of trace metals can be characterized in terms of their capability for ion-exchange processes. Ion-exchange capacity of a cellulose polymer depends on a number of carboxylic and enolized carbonyl groups, as well as on lactone and ester groups which can be easily opened[11]. These groups can be determined by chromatographic methods[2,11-14], titrimetric methods[15,16], ring oven method[17] and colorimetric methods[18]. These methods are mostly based on a cation exchange process:

$$m\,(\text{Cell. R})_y\,\text{Y}_n + yn\,(\text{Me}^{m+})_\text{w} \rightleftharpoons y\,\{(\text{Cell. R})_m\,\text{Me}_n\} + mn\,(\text{Y}^{y+})_\text{w} \qquad (1)$$

where the solvated ions are characterized by subscript w. Further meanings of the symbols in eq. (1) are: Cell. R^- = cellulose matrix with affixed groups of single negative charge, other symbols are self-explanatory.

The methods for determination of ion-exchange capacity mentioned above, cannot be applied to any kind of cellulose matrices in a reliable manner, besides, they are taking too much time and chemicals for analysis. To test cellulose matrices which are suitable for sorption of trace metals, it is necessary to characterize them by infrared spectra. We have used spectral data from the 1700—1790 cm^{-1} infrared region and made attempt to show how these data can be used for the quantitative determination of sorption (ion-exchange) capacity of cellulose matrices.

EXPERIMENTAL

Preparation of the Cellulose Samples

Microcrystalline cellulose (E. Merck, A. G. Darmstadt, Germany) and medical cotton (Ph. Jug. III) are utilized as starting materials. Three different procedures are applied.

(i) *Sodium Hypochlorite Oxycelluloses*[19]

The oxidant is prepared by dissolving 29.780 g of sodium hypochlorite, 11.803 g of sodium hydroxide and 60.005 g of sodium dihydrogen phosphate in distilled water and adjusting to 1 litre. By treating 20 g of medical cotton with 1 litre of this diluted solution for 20 and 40 hours at 20 °C, the samples C-Cell 1 and C-Cell 2, respectively, are formed. This diluted solution is 0.04 mol dm^{-3} with respect to hypochlorite, 0.0295 mol dm^{-3} to sodium hydroxide and 0.05 mol dm^{-3} to phosphate. After oxidation the product is washed thoroughly with distilled water, left standing for 1 to 2 hours in 0.1 mol dm^{-3} hydrochloric acid and again washed very thoroughly with distilled water.

(ii) *Sodium Hypobromite Oxycelluloses*[19]

The oxidant is prepared by dissolving 13.92 g of sodium bromate and 60 g of sodium bromide in distilled water and adjusting to 1 litre. A quantity of 200 cm^3 of this solution is pipetted into a 1 litre measuring flask and 200 cm^3 of 1 mol dm^{-3} sulphuric acid is added very quickly. After 30 minutes, the solution is chilled to 10—15 °C and 250 cm^3 of 2 mol dm^{-3} sodium hydroxide is added. The temperature of the solution is regulated to 20 °C and the measuring flask filled to the mark with distilled water. The solution is 0.1 mol dm^{-3} with respect to the hypobromite and sodium hydroxide. It is stored protected from light.

The oxidation is effected in a dark flask at 20 °C for about 20 (sample microcrystalline cellulose C-Cell 3, sample medical cotton C-Cell 5) and 40 (sample microcrystalline cellulose C-Cell 4, sample medical cotton C-Cell 6) hours, with 20 g of cellulose and 1 litre of the oxidant. The flask is shaken occasionally. The powder or fibre is washed free from hypobromite in a dark room equipped with red light, shaken with 0.1 mol dm^{-3} hydrochloric acid for 2 hours and finally washed very thoroughly with distilled water and dried in air.

The dry sample C-Cell 6 treated several times alternatively with 0.1 mol dm^{-3} sodium hydroöide and 0.1 mol dm^{-3} hydrochloric acid is marked as a sample C-Cell 7.

(iii) *Chelating Cellulose with α(β)-Alanine-N,N-diacetic Acid Anchor Groups*[20]

Alkaline cellulose is prepared by treating 10 g of microcrystalline cellulose with 44.8% sodium hydroxide and macerating it for 4 hours .The cellulose sample is then pressed to remove the liquid and to lower the weight to 1/4 of the starting weight. After standing for 6 hours in air-free atmosphere the alkaline cellulose is mixed with 8.4 g of the disodium salt of iminodiacetic acid and suspended in 20 cm^3 of acetone. 50 cm^3 of acetone solution containing 4.1 g of 1,2-dibromo methyl propionate is added into the suspension with stirring. The mixture is vigorously stirred and refluxed at 70 °C for 3 hours. After cooling, solid particles are suspended into the 255 cm^3 of ethanol-water-glacial acetic acid (25 : 25 : 1) mixture. Chelating cellulose is washed several times with distilled water, ethanol and acetone and dried in air. Three series of samples prepared by this procedure are marked as IDA-Cell 1, IDA--Cell 2 and IDA-Cell 3.

Commercial sorbents e. g. microcrystalline cellulose, m-Cell; carboxymethyl cellulose, CM-Cell (Macherey-Nagel, Düren, Germany) and oxidized regenerated cellulose, Surgicel 1—3 (Johnson & Johnson, New Jersey, USA) are also used as experimental materials.

Apparatus

(i) Perkin Elmer Model 457 double beam grating infrared spectrophotometer is used for analysis. The recordings are performed using slit setting »3« and speed setting »slow«.

(ii) Orion research digital pH Meter Model 701 with combination pH electrode is used.

Exchange Capacity Measurements

(i) *Calcium Acetate Method*[21]

The capacity of cellulose matrix is obtained from the volume of titrant at the inflection point of the titration curve by the potentiometric method.

About 0.5 g of acid form cellulose sample is equilibrated in air and weighed accurately to four points. The sample is then stirred for 30 minutes in 50.00 cm^3 of calcium acetate aq. solution (1 : 50). The released protons are titrated with 0.01 mol dm^{-3} sodium hydroxide. The used volume of standard sodium hydroxide solution is corrected by the titration of 50.00 cm^3 of calcium acetate aq. solution (1 : 50). It is necessary to use freshly prepared solution of calcium acetate.

(ii) *Infrared Spectrophotometric Procedure*

The method of sorption capacity determination of cellulose matrices is based upon the characteristic streching band at 1725 cm^{-1} (5.8 μm) belonging to the carboxylic and carbonyl group.

Infrared spectra of cellulose samples are recorded by KBr-disks made from KBr of appropriate purity and reduced amount of water. A blank pellet containing 300 mg of KBr is recorded in the 1900—1500 cm^{-1} infrared region to show degree of purity and amount of present water. All weighings are done on an analytical balance. 2 mg of cellulose sample and 300 mg of KBr are homogenized in agate mortar. The obtained mixture is then subjected to a load of $2.4 \cdot 10^6$ kg m^{-2} for 5 minutes to make the pellet. The measurement of the height (in mm) of the absorption peak at 1725 cm^{-1} is performed in a way shown in Figure 1.

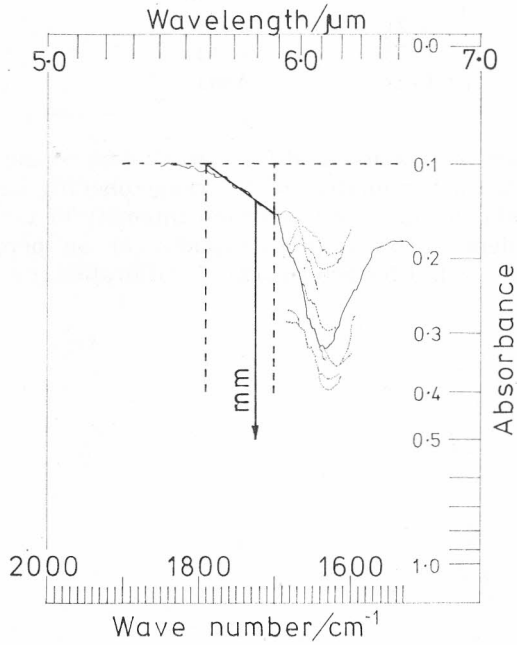

Figure 1. Graphic determination of the effect of C=O streching.

RESULTS AND DISCUSSION

Potentiometric determination of sorption capacity of 15 cellulose matrices for collection of trace metal ions have shown that the cellulose sorbents ranging in capacity from 0.02 to 4.10 mval g^{-1} can be prepared. Table I contains

TABLE I

Results of potentiometric sorption capacity determination of cellulose matrices as an ion-exchange capacity (IEC) and related values of specific analytical signal obtained by infrared spectroscopy

Samples	Potentiometric method		Average value of infrared specific signal (mm) at 1725 cm^{-1}
	% of COOH	IEC/mval g^{-1}	
m-Cell	0.08	0.017	0.0
C-Cell 1	0.15	0.033	1.0
C-Cell 2	0.13	0.028	2.0
C-Cell 3	1.10	0.244	9.5
C-Cell 4	1.19	0.263	14.0
C-Cell 5	0.66	0.147	5.0
C-Cell 6	1.90	0.422	23.0
C-Cell 7	1.47	0.326	19.0
CM-Cell	2.80	0.622	34.0
IDA-Cell 1	1.93	0.429	15.0
IDA-Cell 2	4.59	1.019	34.0
IDA-Cell 3	8.51	1.890	40.5
Surgicel 1	15.21	3.379	43.5
Surgicel 2	16.72	3.713	40.0
Surgicel 3	18.43	4.093	39.5

results. The obtained results are used for construction of the calibration curve, $x = g(C)$, and for the determination of the range obeying Lambert-Beer's law. The results also indicate that the absorption intensity of C=O streching band at 1725 cm^{-1} (x) depends on sorption capacity or on percentage of COOH groups in a sample (C). Characteristics of calibration curve are shown in Figure 2.

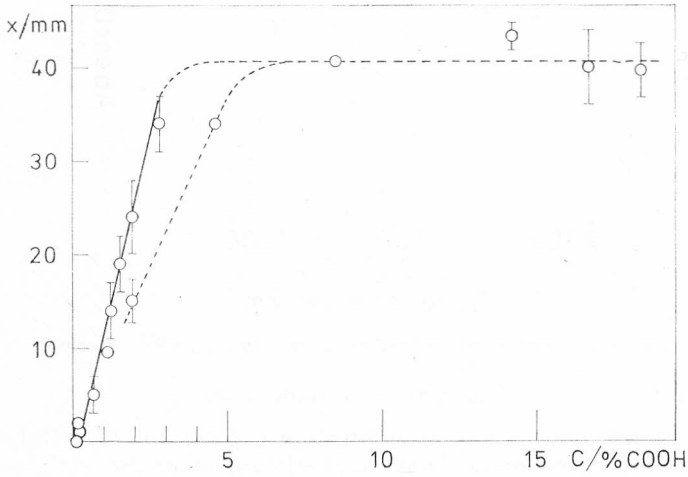

Figure 2. Calibration curve.

It may be concluded that calibration curve, $x = g(C)$, is not the same for all cellulose sorbent types containing C=O group in a polymer molecule, since the different percentage of COOH groups in a polymer can exhibit the same values of specific analytical signal. For example, 2 mg of CM-Cell and IDA--Cell 2 in KBr-pellet produce under given conditions the absorption peak with the same height, $x = 34$ mm. It means that the structure of sorbent will influence the formation of analytical signal. A shown formula of basic unit of cellulose sorbent (Figure 3) can contain, for example, at position R different

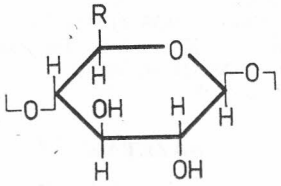

Figure 3. Basic unit of cellulose matrix.

groups such as COOH and CH_2OCH_2COOH (samples C-Cell, Surgicel and CM-Cell) or $CH_2OCH_2CH[N(CH_2COOH)_2]COOCH_3$ (samples IDA-Cell). This is probably the reason why it is not possible to construct a general calibration curve. Therefore, the equation of regression line will not hold for samples IDA-Cell. Figure 2 also shows that linearity of calibration function is observed up to about 3% of COOH in a sample, which includes the majority of cellulose derivatives prepared by oxidation.

The lower limit of carboxyl content determination by the proposed method is about 0.2% of COOH which means 0.044 mval g^{-1}. The equation of regression line of calibration curve which holds for $C \leqq 3\%$, is

$$\text{specific analytical signal } (x) = 14.701\ C - 3.515 \tag{2}$$

On the other hand, the amount of carboxylic groups (e. g. for celluronic acid, pectinic acid and alginic acid) or related lactones can be calculated from the inverted equation of regression line:

$$\%\ \text{of COOH}\ (C) = 0.068\,x + 0.239 \tag{3}$$

$$(\text{mval g}^{-1}) = (\%\ \text{of COOH}) \cdot 0.2221 \tag{4}$$

This simple and fast method for the determination of sorption capacity of cellulose matrices does not appear to be highly precise. For example, standard deviation of CM-Cell samples is 3.17, for $n = 12$ and $\bar{x}_i = 34.0$.

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SAŽETAK

Određivanje kapaciteta sorpcije celuloznih matrica infracrvenom apsorpcijskom spektrometrijom

V. Grdinić i S. Luterotti

Proučavana je metoda određivanja sorpcijskog kapaciteta celuloznih matrica koje se koriste za skupljanje tragova iona iz otopina. Analitička metoda temelji se na infracrvenoj apsorpcijskoj spektrometriji kod 1725 cm^{-1} što je karakteristično za istezanje skupine C=O u molekuli polimera. Za izradu kalibracijske krivulje pripremljeni su pogodni uzorci, standardizirani određivanjem ionsko-izmjenjivačkog kapaciteta potenciometrijskom metodom. Diskutirane su neke osobine analitičkog postupka, posebno s obzirom na donju i gornju granicu određivanja sadržaja COOH, utjecaj strukture uzorka i preciznost predložene metode.

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Prispjelo 23. listopada 1978.