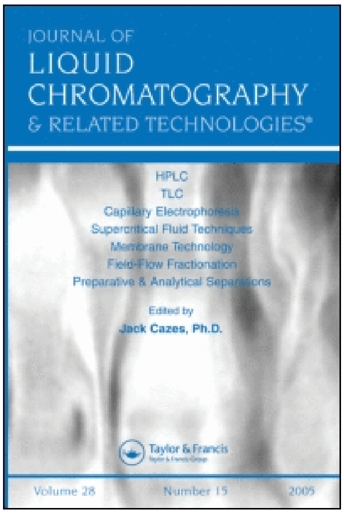


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

CHROMATOGRAPHIC MOBILITY OF METALS ON PAPER IMPREGNATED WITH SOME COMPONENTS OF PLANT CELL WALLS

Nataša Brajenović[a]; Olga Hadžjja[a]; Maja Tonkovic[a]
[a] Ruder Boskovic Institute, Zagreb, Croatia

Online publication date: 24 July 2002

To cite this Article Brajenović, Nataša , Hadžjja, Olga and Tonkovic, Maja(2002) 'CHROMATOGRAPHIC MOBILITY OF METALS ON PAPER IMPREGNATED WITH SOME COMPONENTS OF PLANT CELL WALLS', Journal of Liquid Chromatography & Related Technologies, 25: 12, 1855 — 1862
To link to this Article: DOI: 10.1081/JLC-120005878
URL: http://dx.doi.org/10.1081/JLC-120005878

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

JOURNAL OF LIQUID CHROMATOGRAPHY & RELATED TECHNOLOGIES
Vol. 25, No. 12, pp. 1855–1862, 2002

CHROMATOGRAPHIC MOBILITY OF METALS ON PAPER IMPREGNATED WITH SOME COMPONENTS OF PLANT CELL WALLS

Nataša Brajenović, Olga Hadžjja, and Maja Tonković*

Ruder Boskovic Institute, P. O. Box 180, 10002 Zagreb, Croatia

ABSTRACT

The interactions of various components of the plant cell walls and several essential (Cu, Fe) and toxic (Al, Cd, Hg, Pb) metals were investigated using a model system simulating natural conditions. The system consists of ascending paper chromatography of the metals on paper impregnated with different components of plant cell walls like pectin, galacturonic acid, and model compounds of lignin. The tap water was used as developer. The chromatographic results, compared with those on the free paper, show acceleration or retardation of metals and demonstrate the influence of considered ligands on their mobilities.

INTRODUCTION

The plant cell walls (primary and secondary) are made of cellulose microfibrils, hemicelluloses, pectins, proteins, and lignin.[1–4] Cellulose is a

*Corresponding author. E-mail: tonkovic@rudjer.irb.hr

DOI: 10.1081/JLC-120005878
1082-6076 (Print); 1520-572X (Online)

www.dekker.com

straight-chain polymeric glucan with β-(1 $\rightarrow$ 4) O-glucosidic linkages. Hydrogen bonds hold these glucan chains together to form a cellulose microfibril. Hemicellulose and pectin are also polymeric saccharides. The most abundant component of the pectin polysaccharides are polyuronic acids like α-D-galacturonic acid. Lignin is an amorphous cementing material that binds cellulose fibres, and its chemical structure is not quite clear yet. It is a high-molecular-weight polymer. The type of lignin is characterised by different ratios of the basic units such as cinnamic, p-coumaric, syringic, sinapic, ferulic, p-hydroxybenzoic, etc., acids. The functional groups of these basic units (COOH, OH) are important factors in the process of complexation, which has influence on the metals mobilities through the plant. In the previous chromatographic investigations, the interaction of Fe- oxy/hydroxide (included in the sorbent) with carboxy and hydroxy groups of humic acids and their precursors and degradation products of lignin were investigated.[5–8] The effect of pure cellulose, lignin, some model compounds related to lignin structure, and slices of different woods species on the mobilities of metals was also tested.[9,10] In the present work, a similar system was applied for the investigation of metals reactions with carboxy and hydroxy groups in the surface of the plant cell walls. The chromatographic behaviour of copper, iron, aluminium, cadmium, lead, and mercury on the paper representing cellulose and on the paper impregnated with calcium pectinate, galacturonic acid, and some other compounds related to the lignin structure, was investigated in tap water as the developer.

EXPERIMENTAL

The compounds used for the impregnation were from: pectin (Demexico, BA, Mexico), α-D-galacturonic acid (Serva, Germany); model compounds of lignin (BDH, England; Fluka, Switzerland; Kemika, Croatia). All other chemicals were of analytical reagent grade. Whatman No 1 paper non-impregnated or impregnated was used as the stationary phase. The impregnation was performed by dipping the paper into 0.6% water solution of pectin and, after drying, into a water solution of $Ca(NO_3)_2$ 0.5 mol dm^{-3} forming Ca-pectinate, into 6% water solution of α-D-galacturonic acid and into ethanolic solutions of vanillin (5%), 4-hydroxybenzoic (2.5%), p-coumaric (1%), salicylic (5%), 4-hydroxyphenylacetic (1%), and cinnamic (5%) acids. The metals were detected by dipping the developed chromatograms into a solution of 0.05% dithizone in carbon tetrachloride for Pb, Hg, and Cd, into 0.25% solution of 1-(2-pyridyazo-2-napthol) (PAN) in ethanol for Cu, and into a saturated ethanolic solution of alizarine for Al and Fe, and placing the chromatograms into a chamber with ammonia vapour. The chromatograms were developed by an acsending technique with tap water as the mobile phase. The ascent of the water was about 8 cm. R_f values were determined using the arithmetic means of four to eight runs.

RESULTS AND DISCUSSION

Metals mobilities in the plant, from the roots to upper parts, depend on their interactions with active functional groups of structural units of cell walls. In the performed experiments, the influence of these functional groups (carboxy and hydroxy) was investigated using paper chromatography of metals ions in tap water as a developer. The compounds used as impregnants are presented in Table 1 and 2. Compound I is the free paper modelling the cellulose, the main component of plant cell walls. In Table 3, the R_f values of examined metals are shown. To make the differences in mobilities more evident, "factor of mobilization" was calculated for each support according to the equation:

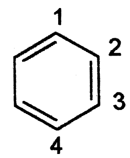
$$F = \frac{R_{\text{funimp}} - R_{\text{fimp}}}{R_{\text{funimp}}}$$

and, results are presented in Table 4. This factor is expressed in a similar manner as parameter B% by G. Schroeder et al.[11] From Table 3, it can be seen that on the cellulose (unimpregnated paper) cadmium exhibits the greatest mobility, while copper the smallest one. On paper impregnated with Ca-pectinate and with galacturonic acid the mobilities of all examined metals decrease. We can suppose that the differences in the mobilities of metals exist with respect to the kind of the functional groups. Cellulose has practically nonreactive hydroxy groups, while pectin and galacturonic acid have carboxyl groups, which can bind metals. It is

Table 1. Compounds Used in Stationary Phases

	Compound	Abbreviation	Functional Groups
I	Cellulose		OH (alcoholic)
II	Ca-pectinate		COOH, OH (alcoholic)
III	α-D-Galacturonic acid	Gal Ac	COOH, OH (alcoholic)
IV	Vanillin	Val	CHO, OH (phenolic)
V	4-hydroxybenzoic acid	4-OHBAc	COOH, OH (phenolic)
VI	p-Coumaric acid	p-CAc	CH=CH−COOH, OH (phenolic)
VII	Salicylic acid	SAc	COOH, OH (phenolic)
VIII	4-Hydroxyphenyl acetic acid	4-OHphacAc	CH_2−COOH,OH (phenolic)
IX	Cinnamic acid	CinAc	CH=CH−COOH

Table 2. Model Compounds of Lignin



		1	2	3	4
IV	Vanillin	CHO	–	OCH_3	OH
V	4-Hydroxybenzoic acid (4-OHBAc)	COOH	–	–	OH
VI	p-Coumaric acid (p-CAc)	CH=CH−COOH	–	–	OH
VII	Salicylic acid (SAc)	COOH	OH	–	–
VIII	4-Hydroxyphenyl acetic acid (4-OHphacAc)	CH_2COOH	–	–	OH
IX	Cinamic acid (CinAc)	CH=CH−COOH	–	–	–

also known that pectin, although soluble in water, may form insoluble salts with some metals, which can influence the metal mobilities. There is no significant difference between metals mobilities on cellulose impregnated with Ca-pectinate and with galacturonic acid, which was expected, considering pectin is a polymer consisting of units of uronic acids like galacturonic. The complexes of copper, iron, and aluminum, with polygalacturonic and galacturonic acid, pectin, and pectic acid were isolated and characterized.[12–15].

Comparing R_f and F values of metals on 4-hydroxybenzoic acid (V) and salicylic acid (VII) support, it might be concluded that vicinal carboxy and hydroxy groups are somewhat more efficient than carboxy and hydroxy groups in 1,4 positions in complexing the metals and, consequently, cause a better mobility in water. 4-hydroxyphenyl acetic acid (VIII) is the most ineffective ligand; it reacts only with copper and iron. Only lead is retained by cinnamic acid in the start position. Copper reacts with all ligands; Ca-pectinate and galacturonic acid make its movement slower on cellulose, while other ligands accelerate it. The complexes of copper with cinnamic acid and its derivatives were synthesised and characterised.[16] Besides Ca-pectinate and galacturonic acid, p-coumaric acid also reacts with all metals and decreases their mobilities (except copper). Salicylic acid influence the mobilities of aluminium and cadmium very poorly, but other metals move better in its presence. Not one of the examined ligands does increase cadmium mobility. Otherwise, the experiments in vivo showed that cadmium was

Table 3. R_f Values of Metals on Non-Impregnated Paper, and on Paper Impregnated with Calcium Pectinate, Galacturonic Acid, and with Compounds Related to Lignin Structure

	R_f								
Metal	Cellulose I	Ca-Pectinate II	Gal Ac III	Val IV	4-OH BAc V	p-CAc VI	SAc VII	4-OHph acAc VIII	CinAc IX
Cu	0.54	0.29	0.37	0.80	0.76	0.63	0.85	0.67	0.78
Fe	0.78	0.34	0.32	0.76	0.77	0.49	0.87	0.63	0.52
Al	0.88	0.44	0.38	0.78	0.72	0.47	0.88	0.90	0.71
Pb	0.58	0.27	0.44	0.69	0.54	0.40	0.69	0.58	0.07
Hg	0.62	0.38	0.30	0.67	0.54	0.57	0.81	0.57	0.57
Cd	0.92	0.32	0.44	0.94	0.96	0.78	0.85	0.86	0.91

Table 4. Factor of Mobilization F for Metals and Different Impregnants

	F							
Metal	Ca-Pectinate II	Gal Ac III	Val IV	4-OH BAc V	p-CAc VI	SAc VII	4-OH phacAc VIII	CinAc IX
Cu	0.46	0.31	−0.48	−0.41	−0.17	−0.57	−0.24	−0.44
Fe	0.56	0.59	0.03	0.01	0.37	−0.11	0.19	0.33
Al	0.50	0.57	0.11	0.18	0.47	0.00	−0.02	0.19
Pb	0.53	0.24	−0.19	0.07	0.31	−0.19	0.00	0.88
Hg	0.39	0.52	−0.08	0.13	0.08	−0.31	0.08	0.08
Cd	0.65	0.52	−0.02	−0.04	0.15	0.08	0.07	0.01

easily transported to stems and leaves in plants, and the mobility of cadmium was better than that of lead.[17,18] The chromatographic behaviour of Cd and Pb is in good agreement with these findings; showing all supports moved slower than cadmium.

In all these experiments the tap water was used as a developer, simulating natural river water, but in distilled water, simulating rainwater, the results were very similar.

The performed experiments show that mobilities of metals through plants are dependent on the composition of specific plant cell walls along which the metals are moving; and offer preliminary information about the binding abilities of a particular ligand and its effect on the transport of metals through the plant. The complexes formed during the chromatographic process showed different stabilities and solubilities in water and, accordingly, moved slower or faster on cellulose impregnated with complexing agents.

REFERENCES

1. Ting, I.P. Carbohydrates and Organic Acids. In *Plant Physiology*; Addison-Wesley Publishing Company: London, 1982; 255–282.
2. Goodwin, T.W.; Mercer, E.I. The Plant Cell Wall. In *Introduction to Plant Biochemistry*; Pergamon Press: Oxford, 1986; 55–91.
3. Shevchenko, S.M. Theoretical Approaches to Lignin Chemistry. Croat. Chem. Acta **1994**, *67* (1), 95–124.
4. Bidlack, J.; Malone, M.; Benson, R. Molecular Structure and Component Integration of Secondary Cell Walls in Plants. Proc. Okla. Acad. Sci. **1992**, *72*, 51–56.
5. Hadžija, O.; Tonković, M.; Iskrić, S. The Behaviour of Some Phenolic Acids and Aldehydes on Thin Layers of Silica Gel Impregnated with Fe(III). J. Liq. Chromatogr. **1986**, *9* (16), 3473–3478.
6. Hadžija, O.; Iskrić, S.; Tonković, M. Mobility of Fe(III)-Phenolic Acid Complexes in Thin-Layer Chromatography. J. Chromatogr. **1987**, *402*, 358–360.
7. Hadžija, O.; Iskrić, S.; Tonković, M. Mobility of Some Carboxy- and Hydroxybenzene Derivatives on Thin Layers of Plain and Iron(III)-Impregnated Silica Gel. J. Chromatogr. **1988**, *464*, 220–222.
8. Iskrić, S.; Hadžija, O.; Kveder, S. Behaviour of Humic Acids on Fe(III)-Impregnated Silica Gel Compared with Model Substances. J. Liq. Chromatogr. **1994**, *17* (7), 1653–1657.
9. Brajenović, N.; Kveder, S.; Iskrić, S.; Hadžija, O. Chromatographic Mobility of Some Metals on Paper Impregnated with Lignin. Chromatographia **1997**, *44* (11/12), 649–650.

10. Brajenović, N.; Hadžija, O.; Iskrić, S.; Kveder, S.; Regula, I. Chromatographic Mobility of Metals on Paper Impregnated with Model Compounds Related to Lignin Structure and on Wood Slices. Anal. Chim. Acta **2000**, *406*, 279–281.
11. Schroeder, G.; Leska, B.; Gierczyk, B.; Eitner, K.; Wojciechowski, G.; Rózalski, B.; Bartl, F.; Brzezinski, B. Studies of Complexation of Metal Cations by tris(3,6-Dioxaheptyl)amine in Solution. J. Mol. Struct. **1999**, *508*, 129–138.
12. Deiana, S.; Erre, L.; Micera, G.; Piu, P.; Gessa, C. Coordination of Transition-Metal Ions by Polygalacturonic Acid: A Spectroscopic Study. Inorg. Chim. Acta **1980**, *46*, 249–253.
13. Micera, G.; Deiana, S.; Gessa, C.; Petrera, M. Spectroscopic Studies on the Binding of Iron(II) and (III) Ions to Polygalacturonic Acid. Inorg. Chim. Acta **1981**, *56*, 109–113.
14. Deiana, S.; Gessa, C.; Solinas, V.; Piu, P.; Seeber, R. Analytical Study of the Interactions of D-Galacturonic Acid with Iron(III) and Iron(II) in Solution and with Iron(III)-Bentonite. Anal. Chim. Acta **1989**, *226*, 315–322.
15. Farago, M.E.; Mahmoud, I.E.D.A.W. Metal Compounds of Pectin. Inorg. Chim. Acta **1983**, *80*, 273–278.
16. Drew, M.G.B.; Mullins, A.P.; Rice, D.A. Synthesis, Characterization and Structural Properties of Some Copper(II) *trans*-Cinnamates and Related Compounds. Polyhedron **1994**, *13*, 1631–1637.
17. Khan, D.H.; Frankland, B. Effects of Cadmium and Lead on Radish Plants with Particular Reference to Movement of Metals Through Soil Profile and Plant. Plant Soil **1983**, *70* (3), 335–345.
18. Moral, R.; Palacios, G.; Gomez, I.; Navarro-Pedreno, J.; Mataix, J. Distribution and Accumulation of Heavy Metals (Cd, Ni and Cr) in Tomato Plant. Fresenius Environ. Bull. **1994**, *3* (7), 395–399.

Received March 18, 2002
Accepted April 24, 2002
Manuscript 5817