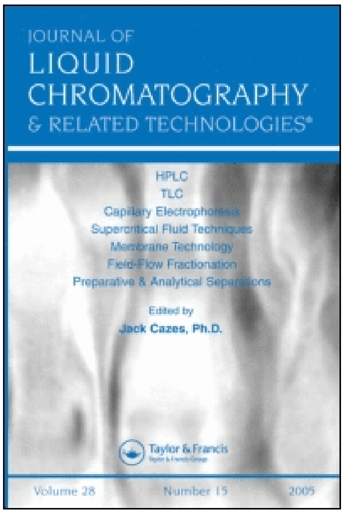

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THE EFFECT OF CITRATE AND PHOSPHATE IONS ON THE MOBILITIES OF METALS

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ABSTRACT

The behaviour of Al, Cu, Fe, Mn, and Pb was examined in a model system simulating natural conditions. The system consists of the ascending chromatography of metals on paper in the tap water as mobile phase. The influences of citric acid and phosphate ions on the mobilities were examined at four pH values 3.7, 5.0, 7.0, and 8.5.

INTRODUCTION

The low molecular weight root exudates (organic acids, amino acids, and sugars) are considered to be directly involved in many processes in the rhizosphere, including mineral weathering and nutrient acquisition. Organic acids, such as malic, citric, and oxalic, released from the plant roots are complexing agents for many essential (iron, zinc, copper, and manganese) or toxic (mercury, cadmium, aluminum, and lead) metals, and complexation

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reactions influence the metals, mobilities through the soil and through the xylem and phloem sap in plants (1–3). Other different factors, such as ambient metal concentrations, pH of soil and water, competition between metals for binding sites of organic ligands, etc., also affect the bioavailability and uptake of metals by plants. As the result of various interactions, different types of complexes are formed whose characteristics determine the behaviour of the metals (4).

The present work is a continuation of previously published papers about the chromatographic mobilities of metals in relation to complexation with humic like compounds and lignin, as a model system simulating natural conditions (5–8). The model comprises the ascending chromatography of metals on paper with tap water as a developer. Paper here may represent the cellulose, the main component of plant cell walls. The chromatographic behaviour of different metals in the presence of citric acid and phosphate ions at various pH simulating natural conditions in the rhizosphere and in the plant were examined and here presented. As the pH of soils varies over a wide range, from 3.5 to 10, the experiments were performed at four pH values: 3.7, 5.0, 7.0, and 8.5. Citric acid, a tricarboxylic acid, is considered to be a most common biologically relevant ligand for a number of metals in plants and soil. The influence of phosphate ions on the complexation and transportation of metals is also important, as they are present in soil and added in artificial fertilizers (4).

EXPERIMENTAL

Chemicals

The chemicals used were of analytical reagent grade purchased from Merck (Germany) and Kemika (Croatia). The aqueous solutions of $Al(NO_3)_3$ $0.05\,mol\,L^{-1}$, $CuSO_4$ $0.025\,mol\,L^{-1}$, $Fe(NO_3)_3$ $0.05\,mol\,L^{-1}$, $MnCl_2$ $0.02\,mol\,L^{-1}$, and $Pb(NO_3)_2$ $0.1\,mol\,L^{-1}$ were used.

Solvent Systems

a) tap water pH 3.72, 5.05, 7.04, 8.47
b) citric acid $0.01\,mol\,L^{-1}$ in tap water pH 3.78, 5.02, 7.01, 8.53
c) KH_2PO_4 $0.01\,mol\,L^{-1}$ in tap water pH 3.70, 5.05, 6.61
d) citric acid $0.01\,mol\,L^{-1}$ and KH_2PO_4 $0.01\,mol\,L^{-1}$ in tap water pH 3.71, 5.10, 7.04, and 8.63

KH_2PO_4 $0.01\,mol\,L^{-1}$ in tap water at $pH > 6.7$ could not be used because of the appearance of a precipitate. Whatman No 4 paper strips (2.5 cm × 9 cm) were used as the stationary phase. The chromatograms were developed by ascending technique with the solvent front reaching approximately 7 cm. R_f values were determined using the arithmetic means of 4–8 runs.

Detection

Detection of the metals was performed by dipping the strips in saturated ethanolic solution of alizarin for Al^{3+} and Fe^{3+} and 0.25% solution of 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol for Cu^{2+}, Mn^{2+}, and Pb^{2+}, and placing the chromatograms into a chamber with ammonia vapor.

RESULTS AND DISCUSSION

The results of chromatographic investigations are presented in Figure 1, as plots of R_f values vs. the pH and composition of the mobile phase. The results generally demonstrate an influence of pH, added organic ligand and phosphate ions on the mobilities of metals.

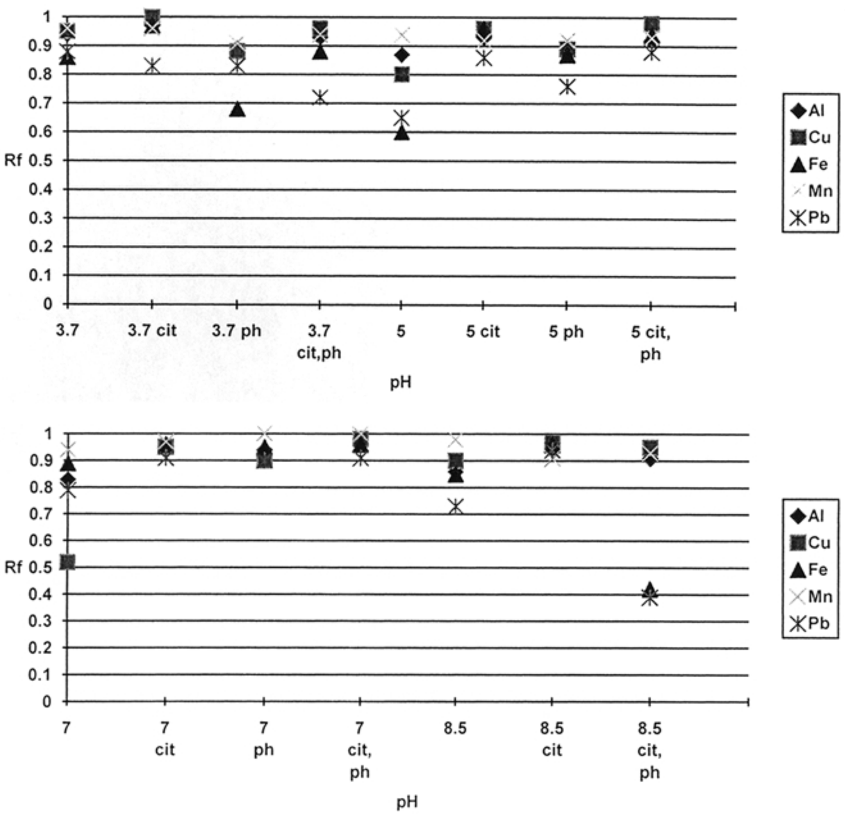

Figure 1. Plots of R_f vs. pH and the composition of mobile phase.

In tap water at pH 3.7, the metals do not show significant differences in mobilities. The greatest separation of metals is observed at pH 5 (Fe^{3+} has the smallest and Mn^{2+} the greatest mobility). At pH 7 Cu^{2+} has a distinctive low R_f value in relation to other metals. In the examined pH range, Mn^{2+} has high and very similar R_f values. In the presence of citric acid, the mobilities of Fe^{3+}, Al^{3+}, Cu^{2+}, and Mn^{2+} are generally the same or greater than in tap water, and do not change in the examined pH range. The influence of phosphate ions was investigated at pH 3.7, 5.0, and 6.6. At pH 3.7 all metals move slower, especially Fe^{3+}. At pH 5, aluminum and manganese move equally as in tap water, while iron, copper, and lead move faster. At pH 6.6, Cu^{2+} moves remarkably faster than in tap water at pH 7. The addition of citric acid beside the phosphate ions, increase the mobilities of metals (except Pb^{2+}) at pH 3.7 and pH 5. At pH 7 mobilities are very similar in the presence of citric acid, or without it. At pH 8.5, Fe^{3+} and Pb^{2+} move very slowly; Al^{3+}, Cu^{2+}, and Mn^{2+} move equally as in tap water with citric acid, i.e., phosphate ions have no influence on their mobilities at high pH.

Citric acid is a complexing agent for essential metals, as well as for toxic ones, in a wide range of pH. The complexation reactions make these metals soluble and transportable through the soil and plants. The effects of complexation with citric acid at various pH, are observable in thin layer chromatography of heavy metals and aluminum in the solutions of citric acid as developer. The formation of complexes can be proven by comparison with the R_f values of Fe(III)-citrate hydrate (Fluka) and Pb(II)-citrate trihydrate (Aldrich) determined at different pH. As can be seen from Table 1, the R_f values of Fe-citrate and Pb-citrate chromatographed in tap water and in 0.01 $mol\,l^{-1}$ KH_2PO_4 in tap water are very close to the R_f values of these metals in citric acid and in the mixture of citric acid and KH_2PO_4.

Aluminum(III) species calculations showed that $AlH_{-1}citrate^-$ is the most important species in pH region 3.0–8.0 in the aqueous solutions (9). $Fe\text{-}citrate^0$ is the prevalent species at pH values < 5.5, whereas at higher pH, $Fe(OH)_2{}^+$ is predominant, although the Fe-citrate is also present. If the phosphate ions are present, $FeHPO_4{}^+$ is formed in the pH range 5.5–6.0 to a minor extent (4). In the rhizosphere, the situation is more complex and, therefore, different due to the presence of humic acids, which form complexes, other cations like Ca, Mg, etc., or specific complexing phytosiderophores, such as mugineic acid. Even so, some conclusions can be drawn from our experiments. The mobilities of examined metals are greater in the presence of citric acid except for lead at pH 3.7. The presence of phosphate ions reduces the mobilities of lead(II) and iron(III) significantly in alkaline region.

Generally, lead has the smallest, while manganese has the highest mobilities at the pH 3.7–8.5 in this simple model system. In the presence of citric acid and phosphate ions, the metals move better in slight acidic and neutral solutions than in acidic ones. This is in accordance with results of Vazquez et al.,

Table 1. Comparison of R_f Values of Commercial Fe- and Pb-Citrate with R_f Values of Fe^{3+} and Pb^{2+} in the System Water-Citrate-Phosphate

	R_f														
pH	3.7				5.0				7.0				8.5		
	a	b	c	d	a	b	c	d	a	b	c	d	a	b	d
Fe(III)	0.86	0.97	0.68	0.88	0.60	0.96	0.87	0.94	0.89	0.96	0.95	0.96	0.83	0.96	0.42
Fe-cit	0.95		0.91		0.97		0.91		0.97		0.91		0.97		
Pb(II)	0.88	0.83	0.83	0.72	0.65	0.86	0.76	0.88	0.79	0.91	0.90	0.91	0.73	0.94	0.39
Pb-cit	0.79		0.73		0.84		0.90		0.89		0.87		0.93		

a – tap water, b – citric acid 0.01 $mol\,L^{-1}$ in tap water, c – KH_2PO_4 0.01 $mol\,L^{-1}$ in tap water, d – citric acid 0.01 $mol\,l^{-1}$ and KH_2PO_4 0.01 $mol\,L^{-1}$ in tap water.

about the effect of water acidity on accumulation and within-plant distribution of heavy metals (10). The results showed that heavy metals uptake was lower in acid than in near-neutral waters. The mobilities of metals in oxalic acid–oxalate systems at different pH on Silica-gel plates, were investigated by Qureshi et al (11). The behaviors of Al, Fe, Cu, and Pb are considerably different in the oxalate presence than in citrate presence. Only manganese has a high and constant R_f in the pH range 0.7–7.6 as in the case of citrate. The grounds for such behaviour are better complexing characteristics of citric acid and different solubilities of citrates and oxalates of these metals.

We suppose that this simple model system can be used in the preliminary investigations about the action of artificial fertilizers on the bioavailabilities of metals for plants.

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