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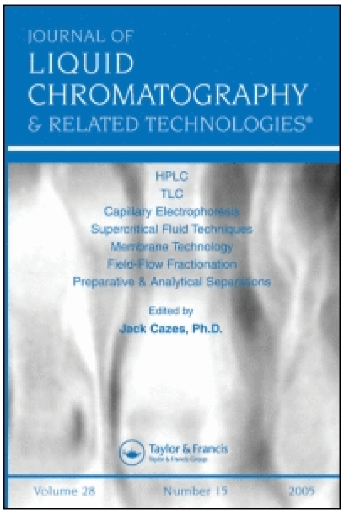

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The Influence of Malic Acid, Phosphate Ion, and Urea on the Mobility of Metal Ions

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ABSTRACT

The interactions of malic acid, phosphate ion, and urea with metal ions (aluminum, copper, iron, lead, manganese, and mercury) at different pH values (3.7, 5.0, 7.0, and 8.5) were investigated using a model system simulating natural conditions. The system consists of the ascending paper chromatography of metals in the tap water or in the solution of malic acid and mixture of malic acid, urea, or phosphate ion as developer. The chromatographic results show that malic acid increases the mobilities of all examined metals except mercury.

Key Words: Paper chromatography; Mobility of metals ions; Malic acid; Phosphate ion; Urea.

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INTRODUCTION

Many factors have influence on the metal mobilities through the soil and the plants. The complexation of the metals with organic acids like citric, malic, succinic, etc. is one of them.[1–5] The degree of metal complexation depends on the type of organic acid (number and proximity of carboxyl group) and metal, their concentrations, and on pH of the solution. Organic acids with only one carboxyl group (e.g., lactic acid) have a very small metal complexing ability, while citric, malic, and oxalic acids have a good affinity for metals, especially for trivalent ones such as aluminum or iron.[2] Generally, citric and malic acids are present in the greatest concentrations in the xylem exudates.[4] These acids are effective in maintaining Al^{3+} and Fe^{3+} soluble, which is very important for biological fluids, in the processes of detoxification of metals by plants and in dissolution of soil minerals.[2,6,7] The different complexes of metals with malic acid were identified and characterised.[6–9] The structure of these complexes varied depending on the pH of solution and the concentrations of reactants.

In our previous experiments, we had already tested the influence of citric acid on the mobilities of metal ions.[10,11] In order to continue the study of influence which the organic acids have on the mobilities of metal ions, we investigated the activity of malic acid in the chromatographic behavior of the metal ions. In distinction from citric acid, malic acid has two carboxylate groups and one hydroxyl group. The model system simulating natural conditions consists of the paper chromatography of the metal ions in the tap water, in the solution of malic acid, mixture of malic acid and urea, or phosphate as mobile phases. The influence of urea and phosphate ion on the complexation of metals with malic acid is interesting, as they are components of artificial fertilisers.[12–14] The experiments were performed at four pH values: 3.7, 5.0, 7.0, and 8.5 because the pH of soils vary in a wide range from 3.5 to 10.

EXPERIMENTAL

All chemicals used were of analytical reagent grade purchased from Merck (Germany), Sigma (USA), and Kemika (Croatia).

The aqueous solutions of $Al(NO_3)_3$ 0.05 mol L^{-1}, $Fe(NO_3)_3$ 0.1 mol L^{-1}, $CuSO_4$ 0.008 mol L^{-1}, $MnCl_2$ 0.1 mol L^{-1}, 0.1 $Pb(NO_3)_2$ 0.1 mol L^{-1}, and $HgCl_2$ 0.1 mol L^{-1} were used.

Solvent Systems

(a) Tap water pH 3.71, 5.01, 7.01, 8.51; (b) Malic acid 0.01 mol L^{-1} in tap water pH 3.70, 5.01, 7.05, 8.51; (c) Malic acid 0.01 mol L^{-1} and KH_2PO_4

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0.01 mol L^{-1} in tap water pH 3.70, 5.00, 7.06; (d) Malic acid 0.01 mol L^{-1} and urea 0.01 mol L^{-1} in tap water pH 3.70, 5.04, 7.03, 8.51.

KH_2PO_4 0.01 mol L^{-1} in tap water at pH >7 could not be used because of appearance of a precipitate.

Whatman No. 1 paper strips (3.2 cm × 24 cm) were used as stationary phase. The chromatograms were developed by ascending techniques with the solvent front reaching approximately 21 cm. R_f values were determined using the arithmetic means of 4–8 runs.

Detection

The metals were detected by dipping the strips in saturated ethanolic solution of alizarin for Al^{3+} and Fe^{3+} and in 0.25% solution of 1-(2-pyridilazo)-2-napthol (PAN) in ethanol for Cu^{2+}, Mn^{2+}, Pb^{2+}, and Hg^{2+}, and placing chromatograms into a chamber with ammonia vapor.

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RESULTS AND DISCUSSION

The experiments performed in the present paper show the influence of malic acid, phosphate ion, and urea on the chromatographic mobilities of metal ions at different pH values. The results of these experiments are presented in Fig. 1 and Table 1. The factors of mobilization F (Table 1) were calculated from the following equations:

$$F_1 = \frac{R_{\text{fma}} - R_{\text{fw}}}{R_{\text{fma}}}$$

$$F_2 = \frac{R_{\text{fma+ph}} - R_{\text{fw}}}{R_{\text{fma+ph}}}$$

$$F_3 = \frac{R_{\text{fma+ur}} - R_{\text{fw}}}{R_{\text{fma+ur}}}$$

R_{fw}, R_{fma}, $R_{\text{fma+ph}}$, and $R_{\text{fma+ur}}$ are R_f values obtained in tap water, malic acid, and in the mixture of malic acid and phosphate or urea. Schroeder et al. expressed, in a similar manner, the differences in the R_f values on the impregnated and plain plates as parameter B%.[15] In the tap water at all examined pH values, manganese and iron had two spots, which can be a result of the process of partial polymerization. In the presence of malic acid only one spot appeared and both metals moved nearly to the front. From Table 1 it is evident that the effect of malic acid on the mobilities of iron, aluminum, and lead is greater in acid media (Fe > Al > Pb) than in neutral or alkaline media.

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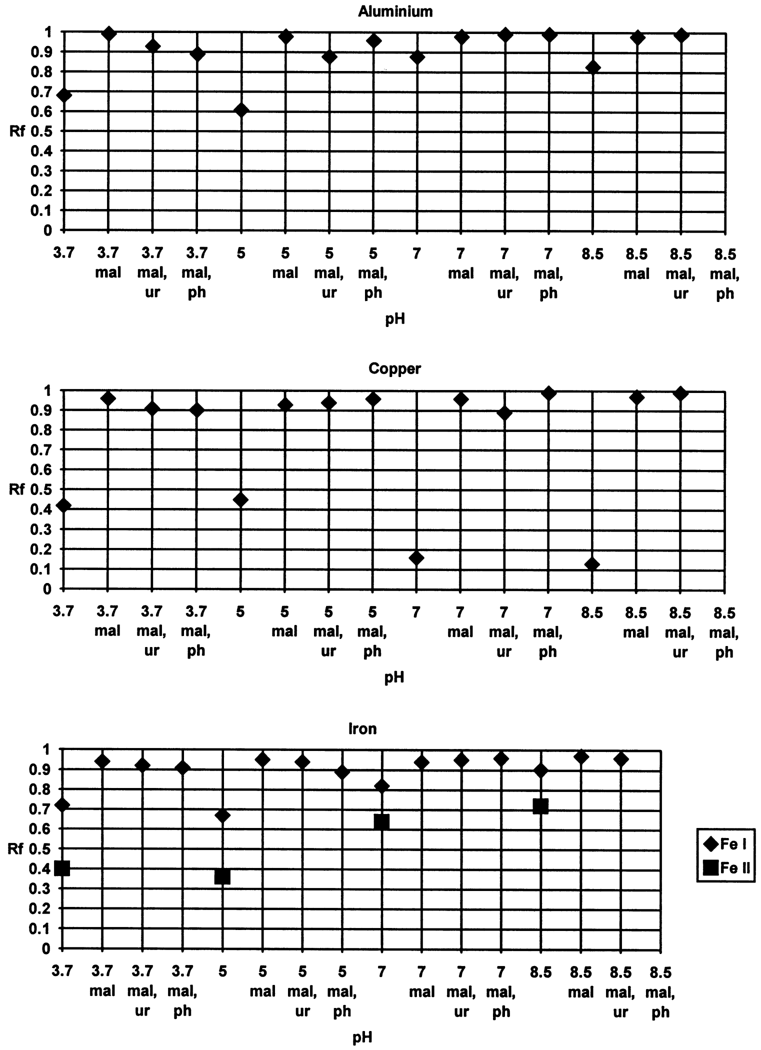

Figure 1. Plots of R_f vs. pH and the composition of mobile phases.

For copper and manganese, this effect is greater in neutral and alkaline media (Cu > Mn). The mobilities of mercury are a little reduced at pH 5; otherwise they are not significantly affected by the malic acid. The mobility of aluminum in acid solution of malic acid is reduced a little by urea and phosphate ions, while the mobility of lead is increased in their presence. The mobilities of

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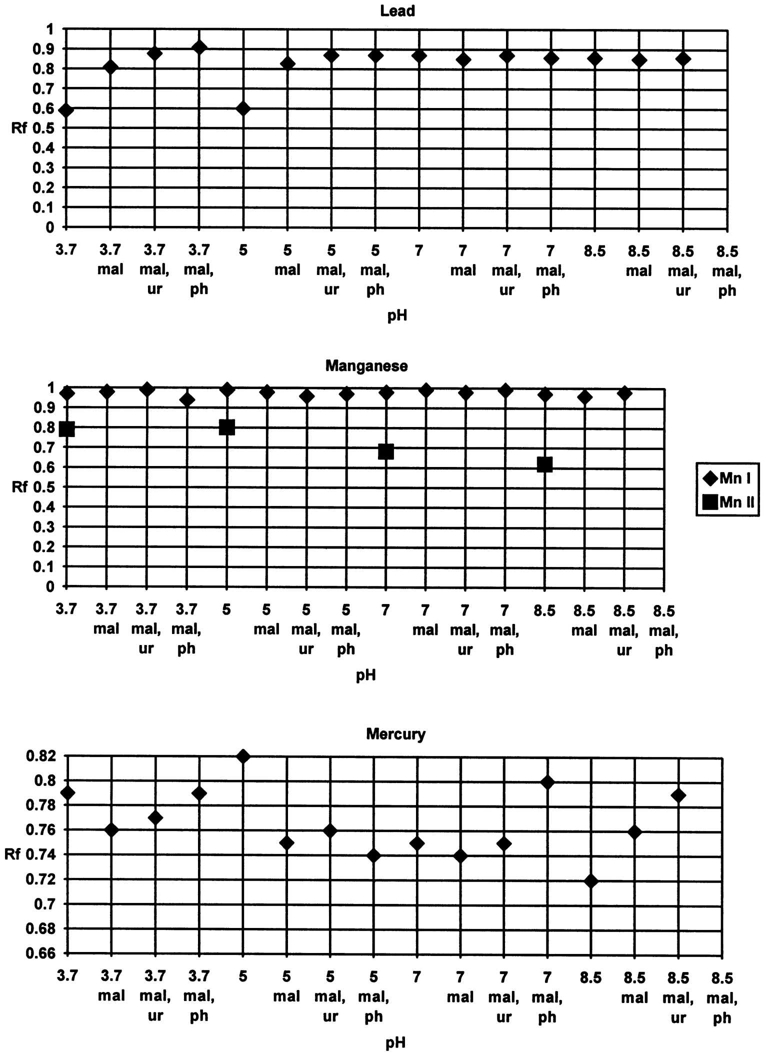

Figure 1. Continued.

other metals are not affected by phosphate ions and urea. All examined metals, except mercury, move near or to the front due to the presence of malic acid in the pH range from 3.7 to 8.5.

Very similar results were obtained in experiments with citric acid, although the effects of citric acid were a bit greater. The mobilities of

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Table 1. *F* values for metals at different pH.

	pH										
	F_1				F_2			F_3			
	3.7	5.0	7.0	8.5	3.7	5.0	7.0	3.7	5.0	7.0	8.5
Fe	0.57	0.62	0.32	0.26	0.56	0.60	0.33	0.57	0.62	0.33	0.25
	0.23	0.29	0.13	0.07	0.21	0.25	0.15	0.22	0.29	0.14	0.06
Mn	0.19	0.18	0.31	0.35	0.16	0.18	0.31	0.20	0.17	0.31	0.37
	0.01	−0.01	0.01	−0.01	−0.03	−0.02	0.01	0.02	−0.03	0.00	0.01
Cu	0.56	0.52	0.83	0.87	0.53	0.53	0.84	0.54	0.52	0.82	0.87
Al	0.31	0.38	0.10	0.15	0.24	0.36	0.11	0.27	0.31	0.11	0.16
Hg	−0.04	−0.09	−0.01	0.06	0.00	−0.11	0.06	−0.03	−0.08	0.00	0.09
Pb	0.27	0.28	−0.02	−0.01	0.35	0.31	−0.01	0.33	0.31	0.00	0.00

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these metals were examined in the oxalic acid–oxalate systems on silica gel—G layers at different pH by Qureshi et al.[16] The chromatographic behavior of some metals were different; lead had very low R_f and is independent of pH, while R_f of Fe^{3+}, Al^{3+}, and Hg^{2+} were dependent of pH. Only manganese had R_f values, which were high and independent of pH. Both citric and malic acid have been identified in the root exudates of a variety of vegetables and trees, as well as in the stem exudates. Their role in the solubilization of microconstituents from the solid phase of soil and in the transport of metals through the plants is the issue of permanent studies in vitro and in vivo. The described method of thin layer chromatography on paper at various pH can predict the influence of some added substances, like artificial fertilizers, on the processes of complexation and mobilization of metals through the plants.

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