

CHROM. 22 037

Note

Thin-layer chromatography of some metals on silica gel layers impregnated with salicylic, syringic and *o*-phthalic acid

I. ŠKVORC and N. ZAMBELI

Faculty of Pharmacy and Biochemistry, 41001 Zagreb, Croatia (Yugoslavia)

and

S. ISKRIC* and O. HADŽIJA

Ruder Bošković Institute, P.O. Box 1016, 41001 Zagreb, Croatia (Yugoslavia)

(First received July 11th, 1989; revised manuscript received September 28th, 1989)

The thin-layer chromatography of metals on supports impregnated with humic acids¹, soils² and modified soils² has been reported, some information being given about the movement of various metals, partially simulating natural conditions.

The movement of metals through soils is mainly governed by complexation with active functional groups of humic substances, *i.e.*, hydroxy and carboxy groups^{3,4}. Degradation methods such as acid hydrolysis and oxidation^{5,6}, when applied to humic material yield, in addition to other compounds, salicylic and syringic acids. These acids and phthalic acid contain functional groups (vicinal carboxy and hydroxy, vicinal carboxy and carboxy, and hydroxy, carboxy and methoxy groups, respectively) which can be found in the presumed structure of humic acid⁷. This prompted us to investigate the chromatographic behaviour of some metals on thin layers of silica gel impregnated with the above-mentioned acids, using distilled and tap waters as developers, simulating natural river and rain water. This represents an extension of our previous work on the interaction of such functional groups with iron as the impregnant^{8,9}.

EXPERIMENTAL

Phenolic acids and phthalic acid were purchased from Fluka (Buchs, Switzerland) and Merck (Darmstadt, F.R.G.). All other chemicals were of analytical-reagent grade. Precoated plates of silica gel 60F₂₅₉ (Merck), plain and impregnated with phenolic and phthalic acids (by spraying with a 5% ethanolic solution), were used. Distilled water (I) and tap water (II) were used as developers. Detection was performed by spraying with bromocresol green indicator reagent, by inspection under UV light or by exposure to ammonia followed by hydrogen sulphide vapour¹⁰. The chromatograms were developed by the ascending technique with a solvent ascent of 8-11 cm. R_F values were determined using the arithmetic means of 2-5 runs.

RESULTS AND DISCUSSION

In Table I, the R_F values of metals on plain and impregnated plates with developers I and II are presented. All metals behave very similarly in both waters. It can be seen that on the plain plates no separation can be obtained for any of the metals as they all have very small R_F values in spite of being soluble in water. This could be a consequence of their binding to the silanol groups of silica gel.

Phenolic and phthalic acids were used as impregnants because of their low solubility in water and hardly any movement with water as developer. On plates impregnated with salicylic acid, Co and Hg can be separated from all other metals. The separation of Cu from all metals except Co can be achieved on plates impregnated with phthalic acid. Fe and Pb exhibit poor separation.

On plates impregnated with salicylic acid and phthalic acid, Co and Cu show considerable movement, whereas on syringic acid-impregnated plates the effect is weaker. Regarding the molecular structure of the impregnants, the mobility of the metals generally increases on impregnated plates in the order phthalic > salicylic > syringic acid. This phenomenon may indicate the complexation affinity of the metals for the functional groups of the impregnants. Thus, two vicinal carboxy groups and also carboxy and hydroxy groups are more efficient than carboxy and hydroxy groups in 1,4-positions in binding the metals and consequently causing a better solubility in water.

Extending the results obtained to natural conditions, it can be concluded that the hydroxy and carboxy groups of humic material influence the mobility of metals through soils, depending on the characteristics of the complexes formed, which confirmed our previous findings.

TABLE I

$R_F \times 100$ VALUES OF METALS ON PLAIN SILICA GEL PLATES AND PLATES IMPREGNATED WITH PHENOLIC AND PHTHALIC ACIDS

Developers: (I) distilled water; (II) tap water.

Metal ^a	Developer	Impregnated plates			
		Phthalic acid	Salicylic acid	Syringic acid	Plain plates
Co	I	78	76	37	23
	II	79	70	29	13
Cu	I	74	35	18	11
	II	74	32	20	16
Fe	I	12	25	10	11
	II	10	24	9	11
Hg	I	11	0	8	7
	II	12	9	12	10
Pb	I	9	21	20	10
	II	7	26	23	11

^a As water-soluble nitrates.

ACKNOWLEDGEMENTS

Thanks are due to the Research Council of SR Croatia for financial support.

REFERENCES

- 1 T. Tamakatsu, R. Kusakabe and T. Yoshida, *Soil Sci.*, 136 (1983) 371.
- 2 R. P. Singh, S. K. Saxena and K. Kumari, *J. Liq. Chromatogr.*, 8 (1985) 1319.
- 3 M. Schnitzer and S. I. M. Skinner, *Soil Sci.*, 99 (1965) 278.
- 4 M. Schnitzer and P. A. Poabst, *Nature (London)*, 213 (1967) 598.
- 5 E. T. Degens, J. N. Reuter and K. N. F. Shaw, *Geochim. Cosmochim. Acta*, 28 (1964) 45.
- 6 I. Kögel and R. Bochter, *Soil Biol. Biochem.*, 17 (1985) 637.
- 7 G. Eglinton and M. T. J. Murphy, *Organic Chemistry*, Springer, Berlin, 1969, p. 554.
- 8 O. Hadžija, S. Iskrić and M. Tonković, *J. Chromatogr.*, 402 (1987) 358.
- 9 O. Hadžija, S. Iskrić and M. Tonković, *J. Chromatogr.*, 464 (1988) 220.
- 10 E. Stahl, *Thin-Layer Chromatography*, Springer, Berlin, 1969, p. 854.