SOME FACTORS INFLUENCING THE CONSTANCY OF R_F VALUES IN PAPER CHROMATOGRAPHY UNDER AUSTRALIAN FIELD CONDITIONS

A. S. RITCHIE

Newcastle University College, Newcastle, N.S.W. (Australia)

INTRODUCTION

The application of paper chromatographic techniques to geological problems required that, on some occasions, analyses had to be carried out in the field or under base-camp conditions. The methods of WARD AND MARRANZINO[1], NEVILL AND LEVER[2] and RITCHIE[3] certainly were designed for use under these conditions. Published data on R_F values generally relate to laboratory studies made under controlled conditions of temperature and humidity. The realization that the extremes of temperature and humidity which were likely under Australian field conditions, would influence seriously the R_F values prompted the investigations, the results of which are now reported.

As far as possible the data presented have been compiled from field tests. The technique used was by ascending development, using rectangles of Whatman No. 1 paper (25 cm × 30 cm) standing in the solvents in screw-top 6-l polythene jars. Sometimes the "runs" were done in a small tent but more often in a box trailer fitted with a canvas hood. In some cases the field conditions were simulated in laboratory tests with good correlation.

RESULTS

The main results are shown in Table I.

Apart from the variations in the R_F values, the significance of which will be discussed below, extreme humidity presents some special problems. One important difficulty is the maintenance of the paper in a workable condition over periods of weeks in the field. This is a difficulty encountered in Africa by BURSILL[4] as well as in Australia. The ascent of the solvents by capillarity was almost stopped when the paper became moist. The vapour phase seemed to react with the water in the paper and on occasions the metal ions moved downwards under the influence of gravity.

Even on the one chromatogram, inconsistent results were obtained when the vessels were exposed to wind or direct sunlight. The problem was overcome by placing boxes or cardboard cartons over the vessels. Apart from this effect, very consistent results were obtained on any one chromatogram.

The variations which are revealed in Table I may be generalized as follows:

1. Hot-dry conditions are conducive to higher R_F values. Notable exceptions are Co^{2+} and Mn^{2+} in solvent 1.

TABLE

R_F VALUES OF METAL IONS UNDER

Metal ion	Solvent 1				Solvent 2			
	Published	40° Humid 10% Hot-dry	35° Humid 80% Hot-wet	12° Humid 80% Cold-wet	Published	40° Humid 10% Hot-dry	35° Humid 80% Hot-wet	12° Humid 80% Cold-wet
Ag^{+}	0.77 + C	0.90 + C	0.88 + C	0.80 + C	1.0 + C	0.90 + C	0.88 + C	0.92
Pb^{2+}	0.44 + C	0.62 + C	0.57 + C	0.48 + C	0.64 + C		0.64 + C	0.62 + C
Cd^{2+}	0.92	1.0	1.0 + C	0.97 + C	1.0			0.94
Bi^{3+}	0.75	0.97	0.93	0.74	0.85			0.97 + C
Hg^{2+}	1.0	1.0	0.93	1.0	1.0			0.93
Sb^{3+}	0.88	0.95	0.96	0.89	1.0	0.95	0.93	0.83 + C
As^{3+}	0.92	0.92	0.88	0.80	0.92	0.91	0.90	0.59
Fe^{3+}	Up to 0.93	0.89	0.80	0.50	Up to 0.75	0.49	0.40	0.35
Cu^{2+}	0.53	0.34–0.92	0.34–0.67	0.45	0.54C–1.0	C–0.92	C–0.58	0.32
Co^{2+}	0.43	0.28	0.40–0.80	0.42	0.30–0.38	0.28	0.20	0.24
MnO_4^{2-}	0.73	0.78	0.72	0.80	0.53 + C			0.55
Ni^{2+}	0.52	0.27	0.61	0.40	0.32	0.27	0.24	0.28
Mn^{2+}	0.48	0.28	0.33	0.32	0.32	0.28	0.33	0.30
Zn^{2+}	0.94	0.97	0.90	0.90	1.0			0.87
Al^{3+}	0.46	0.52	0.46	0.44	0.36			0.28
Be^{2+}	0.60	0.66	0.62	0.64	0.60			0.46
Mg^{2+}	0.47	0.50	0.47	0.46	0.37			0.28
Au^{3+}	1.0	0.77	0.83	0.93	0.8–1.0			0.94
Pt^{4+}	1.0 + C	0.92 + C	0.88 + C	1.0 + C	1.0 + C			0.85 + C
Cr^{3+}	0.38	0.46	0.40	0.44	0.23			0.28
Ti^{4+}	0.64			0.67	0.43			0.36
UO_2^{2+}	0.46			0.48	0.37–0.43			0.41
V^{5+}	0.47			0.75 + C	0.43			0.33
WO_4^{2-}	0.70	0.70 + C		0.80 + C	0			0

Solvent 1 = Butanol–conc. HCl–conc. HF–water (100:50:2:48).
Solvent 2 = Butanol fraction of butanol–conc. HBr–water (100:10:90) + conc. HBr (40).

2. Hot-wet conditions produce values slightly lower than the hot-dry.

3. Cold-wet conditions produce lower R_F values than the hot conditions but not always lower than the published results which were obtained near 20°.

Some disadvantage is revealed in that, within the range of conditions experienced, identification of ions cannot be made by reference to the published R_F values obtained under controlled laboratory conditions. The disadvantage may be overcome by running parallel chromatograms in such a way that known and unknown ions may be compared[3].

Advantageous features appear to be a better separation at temperatures from 35° to 40° with less variation of R_F over small temperature ranges. Further results obtained at more critical temperatures might reveal that, for the solvents used, 20° ± 1° is an unfavourable temperature for R_F determinations.

CONCLUSIONS

R_F values of common metal ions vary considerably under the influence of:

1. temperature,

I

AUSTRALIAN FIELD CONDITIONS

Solvent 3				Solvent 4			
Published	*40° Humid 10% Hot-dry*	*35° Humid 80% Hot-wet*	*12° Humid 80% Cold-wet*	*Published*	*40° Humid 10% Hot-dry*	*35° Humid 80% Hot-wet*	*12° Humid 80% Cold-wet*
0.13 + C		0.12 + C	0.13 + C	0.59 + C	0.76 + C	0.70 + C	0.55
0.45 + C	0.81 + C	0.72 + C	0.45 + C	0.48 + C	0.81 + C	0.76 + C	0.54 + C
0.96	0.93	0.90	0.77	0.77–0.83	0.94		0.58
0.88	0.89	0.88	0.76	0.85	0.88	0.82 + C	0.86 + C
1.0	1.0	0.95	0.90	1.0	0.95	0.92 + C	0.94 + C
0.80 + C	0.95 + C	0.88 + C	0.67	0.82	0.90	0.85	0.90 + C
0.92	0.88	0.86	0.71 + C	0.65	0.94	0.92	0.80 + C
0.73	0.86	0.85	0.62	0.86	0.97	0.92	0.74
0.65	0.77	0.72	0.73 + C	0.56	0.87	0.80	0.45
0.70	0.74	0.72	0.66	0.45–0.55	0.58	0.42	0.26
0.60	0.55	0.50		0.83–0.92	0.90 + C	0.90 + C	1.0 + C
Up to 0.67	0.77	0.65	0.58	0.03	0.02	0.02 + C	0.25 + C
0.70	0.72	0.70	0.72	0.25	0.27	0.15	0.15
0.94		0.95		0.90	0.65	0.75	
0.75	0.84	0.80		0.02	0	0	0
0.86	0.88	0.86		0.22	0.28	0.26	0.28
1.0	0.78	0.82	0.78	0.03	0.46	0.26	0.24
0.91	0.95	0.92		0.97	0.95	0.90	1.0
0.90 + C	0.86 + C	0.86 + C	0.87	0.93 + C	0.90 + C	0.91 + C	0.97 + C
0.73		0.73	0.73	0.06	0.10	0.10	0.08
0.76	0.82	0.78	0.69	0.64	0.84	0.76	
0.76		0.78		0.58–0.64	0.52	0.48	0.62
0.74	0.80	0.75	0.61	0.64	0.65	0.62	0.92
1.0	1.0	1.0	1.0	1.0 + C	1.0 + C	1.0 + C	0.97 + C

Solvent 3 = Ethanol–methanol–2 *N* HCl (60:60:80).
Solvent 4 = Acetone–conc. HCl–conc. HF–water (180:10:2:8).

2. humidity (which affects the moisture content of the paper),
3. temperature variations from one side of the vessel to the other.

The difficulties thus created can be overcome to some extent by using a comparative method in which known metal ions are chromatographed alongside the unknown ions. An air-tight container kept dry by silica gel should overcome the moisture problem.

SUMMARY

R_F values of metal ions obtained under Australian field conditions are reported. The effects of temperature and humidity are shown. Precautions leading to effective use of the technique in the field are mentioned.

REFERENCES

1 F. N. WARD AND A. P. MARRANZINO, *U.S. Geol. Surv., Bull.*, No. 1036-J, 1957.
2 H. F. C. NEVILL AND R. R. LEVER, *Australasian Inst. Mining & Met. Proc.*, No. 191 (1959) 141.
3 A. S. RITCHIE, *Econ. Geol.*, 57 (1962) 238.
4 C. BURSILL, personal communication, 1961.