Detection of metals on paper chromatograms with Rhodamine B

It is well known that some metals react with Rhodamine B (R) in hydrochloric acid solution to give red or violet compounds of the type $(RH)Me^{III}X_4$ and (RH)-$Me^{V}X_6$, which can be extracted by suitable solvents and the metals can then be determined qualitatively or quantitatively[1–4]. An aqueous solution of 0.01 % R has been used for the detection of Sb(V) on paper and in visible light[5].

The possible use of this reaction for detecting small quantities of metals on strips of paper was studied. Under U.V. light, R (in hydrochloric acid solution) was found to give intensive blue or violet spots with Au(III), Bi(III), Cd(II), Fe(III), Hg(II), Mo(VI), Sb(V), Tl(I, III), V (V) and W(VI) in the presence of Br^- or I^- ions. The background becomes rose, pink or orange fluorescent according to the hydrochloric acid concentration.

Experimental

20 μg amounts of each metal were applied on Whatman No. 1 paper strips in the usual way. The spots were sprayed with solution of varying concentrations of hydrochloric or sulphuric acid, oversprayed with either 10 % KBr or 10 % KI solution, and then observed in visible and U.V. light (Analytic Quartzlamp, Hanau, λ =

TABLE I

SPOT TESTS OF METALS UNDER U.V. LIGHT WITH HCl, KBr AND KI

Cd, Hg and Tl give no coloured spots under U.V. light.
Colours of spots: b = blue, br = brown, c = carmine, g = gray, r = red, v = violet, y = yellow, d = deep, l = light. Parentheses indicate that the colours may be neglected.

Metal (20 μg)	*Acid*	*Acid KBr*	*Acid KI*		*Kind and concentration of acid*
	U.V.	*U.V.*	*V*	*U.V.*	
Au(III)	gb	—	br	v ⟶ dc	1 *N* HCl
	(gb)	v	br	v ⟶ dc	3 *N* HCl
	gb	br	br	rv ⟶ dc	2 *N* H_2SO_4
Bi(III)	—	lv	y	v ⟶ dc	1 *N* HCl
	—	lv	y	v ⟶ dc	3 *N* HCl
	—	v	y	rv ⟶ dc	2 *N* H_2SO_4
Fe(III)	gb	gb	br	v ⟶ dc	1 *N* HCl
	v	v	br	v ⟶ dc	3 *N* HCl
	gb	(lg)	br	rv ⟶ dc	2 *N* H_2SO_4
Mo(VI)	(gb)	—	—	—	1 *N* HCl
	(gb)	—	—	—	3 *N* HCl
	g	—	—	—	2 *N* H_2SO_4
Sb(V)	—	—	br	rv ⟶ dc	1 *N* HCl
	(lg)	—	br	v ⟶ dc	3 *N* HCl
	(lg)	—	br	br.r	2 *N* H_2SO_4
V(V)	(gb)	gb	br	rv ⟶ dc	1 *N* HCl
	(gb)	(lv)	br	v ⟶ dc	3 *N* HCl
	(lg)	—	br	rv ⟶ dc	2 *N* H_2SO_4
W(VI)	gb	g	—	(g)	1 *N* HCl
	(lv)	v	—	(lv)	3 *N* HCl
	g	gb	—	(g)	2 *N* H_2SO_4

360 nm). Except for Bi, Fe, Sb, V and Au, after spraying with 10 % KI (Table I) the other metals gave no coloured spots or were only very slightly coloured. The sensitivity of this procedure is very low with the exceptions mentioned above.

Another set of metal spots were sprayed consecutively with an 0.025 % R solution in 1 *N* HCl and 10 % KBr, or 10 % KI. After each operation the wet spots were observed in visible and U.V. light. The same experiment was then performed with 3 *N* HCl instead of 1 *N* HCl. The results are given in Table II. The intensity of all spots was compared visually and expressed as values ranging from + to 5 +.

The following practical procedure is recommended: spray the metal spots with a 1:1 mixture of 0.05 % R, in 2 *N* or 6 *N* HCl, and 20 % KBr (the mixture is stable for a week). Examine the spot in visible and U.V. light and then overspray it with 10 % KI and repeat the observation. The last step is necessary if very small amounts of metal are present. The ions which oxidized KI are relatively more sensitive. The results are presented in Table III.

The spots retain their detectability for a longer period (except Bi, Cd, Hg and Mo) if the paper is dried, but they are more distinct when it is wet. After spraying with KI solution the paper becomes brown in time due to iodine formation. The most

TABLE II

SPOT TESTS WITH RHODAMINE B UNDER DIFFERENT CONDITIONS OF SPRAYING

Colours as in Table I. — = negative reaction; ± = slightly positive reaction; + = positive reaction; the intensity of the colour was compared visually from + to 5 +.

Metal 20 µg	*Colour of spot with 0.025 % Rhodamine B in 1 N HCl**						*Colour of spot with 0.025 % Rhodamine B in 3 N HCl***					
			+KBr		*+KI*				*+KBr*		*+KI*	
	V	*U.V.*	*V*	*U.V.*	*V*	*U.V.*	*V*	*U.V.*	*V*	*U.V.*	*V*	*U.V.*
Au(III)	rv	db 4 +	rv →y	db 4 +	br	db 5 +	rv	b 4 +	rv	db 4 +	br	db 5 +
Bi(III)	—	—	rv	db 3 +	y	db 5 +	—	—	—	g +	y	db 5 +
Cd(II)	—	—	rv	b 2 +	—	b 3 +	—	—	—	—	—	—
Fe(III)	—	dg 3 +	—	—	ybr	db 5 +	—	dg 3 +	—	g +	br	db 5 +
Hg(II)	rv	—	rv	b 2 +	rv	db 5 +	—	—	rv	—	rv	b 4 +
Mo(VI)	rv	db 4 +	rv	b 3 +	rv	rv 3 +	r	b 2 +	rv	rv +	rv	rv 3 +
Sb(V)	rv	db 4 +	rv	db 4 +	br	db 5 +	rv	db 4 +	rv	b 4 +	br	db 5 +
Tl(I)	—	b 2 +	rv	db 4 +	rv	db 4 +	—	—	rv	b +	rv	b 3 +
Tl(III)	—	b 2 +	rv	db 4 +	rv	db 4 +	—	—	rv	b 2 +	rv	b 3 +
V(V)	r	—	—	g ±	br	db 5 +	—	g ±	—	g ±	br	db 5 +
W(VI)	rv	db 4 +	rv	db 4 +	rv	db 3 +	r	b 2 +	rv	rv +	rv	rv 2 +

* The background is pink coloured and gives rose fluorescence under U.V. light.

** The background is light orange coloured and gives yellow-orange fluorescence under U.V. light.

TABLE III

SPOT TESTS WITH THE RECOMMENDED REAGENT RHODAMINE B

— = negative reaction; ± = slightly positive reaction; + = positive reaction; the intensity of the colour was compared visually from + to 5 +.

Metal 20 µg	*Colour of spot with 0.025% Rhodamine B 10% KBr in 1 N HCl**				*Colour of spot with 0.025% Rhodamine B 10% KBr in 3 N HCl***				*Suitable concentration of acid (N)*
			+ *KI*				+ *KI*		
	V	*U.V.*	*V*	*U.V.*	*V*	*U.V.*	*V*	*U.V.*	
Au(III)	drv	db 5 +	br	db 5 +	drv	b 5 +	br	db 5 +	1
Bi(III)	rv	dv 3 +	y	db 5 +	—	gb +	y	db 5 +	1
Cd(II)	rv	b ±	rv	b 4 +	—	—	rv	b 3 +	1
Fe(III)	—	g ±	dbr	db 5 +	—	g 2 +	dbr	db 5 +	3
Hg(II)	rv	v 2 +	rv	b 4 +	—	—	rv	b 2 +	1
Mo(VI)	rv	v 3 +	—	b 4 +	r	b ±	r	b ±	1
Sb(V)	rv	v 3 +	br	db 5 +	drv	b 5 +	dbr	db 5 +	3
Tl(I)	rv	dv 5 +	rv	db 5 +	rv	b 3 +	rv	b 3 +	1
Tl(III)	rv	dv 5 +	rv	db 5 +	rv	b 3 +	rv	db 4 +	1
V(V)	—	g	ybr	db 5 +	—	g	br	db 5 +	3
W(VI)	rv	v 3 +	rv	bv 2 +	—	g 2 +	—	gb 2 +	1

suitable concentration of HCl for detecting Fe, Sb and V is 3 *N*, while for Au, Bi, Cd, Hg, Mo and Tl it is 1 *N*. However, the most sensitive procedure for Au, Bi, Cd and Hg on paper is spraying with 0.025 R–10 % KBr in water and in the case of very small amounts of these metals is overspraying with 10 % KI. We observed red-violet coloured spots in visible light, deep violet ones under U.V. light or deep blue when KI was applied. Tungsten is best detected when the reagent is used in 2 *N* H_2SO_4. The colour developed by thallium lasts about 1–3 min. The method is suitable for chromatography of metals on paper.

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Received March 14th, 1966