

Fluorescence reactions of inorganic cations heated on a porous glass sheet for thin-layer chromatography

Masanori Yoshioka and Hiroko Araki

Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka 573-01 (Japan)

Madoka Seki and Tadashi Miyazaki

Japan Spectroscopic Co. Ltd. (JASCO), 2967-5, Ishikawa-cho, Hachioji, Tokyo 192 (Japan)

Takeshi Utsuki, Takao Yaginuma and Masaaki Nakano

Ise Chemical Industries Co., Ltd., 2-7-12, Yaesu, Chuo-ku, Tokyo 104 (Japan)

(First received December 17th, 1991; revised manuscript received February 21st, 1992)

ABSTRACT

A porous glass sheet was used as a stationary phase for the thin-layer chromatography (TLC) of inorganic cations. Some cations gave rise to fluorescent compounds when spots on the sheet were heated for detection. The fluorescent cations were screened from commercially available reagents by heating at various temperatures from 100 to 700°C for 15 min. The fluorescent cations found were Mg, Al, Ca, V, Cu, Zn, Ge, Y, Zr, Mo, Ag, Cd, In, La, Ce, Eu, Tb, Tl, Pb and Bi. Detection limits of lead, vanadium and tin were 300 pmol and that of copper was 3 pmol. Their fluorescence spectra were measured *in situ* on the sheet and showed hitherto unknown fluorescent reactions. After the separation, the fluorescent spots were overlapped with the triplicate spots detected with 8-hydroxyquinoline or dithizone, which meant that the fluorescent compounds were not due to impurities.

INTRODUCTION

Thin-layer chromatographic (TLC) plates consist of inorganic or organic powders coated on supporting matrices. The inorganic powders are popularly made of silica gel or alumina. Porous glass powders have also been applied to make thin layers, giving good separations, but the separation power is no higher and the preparation of the glass layer is no more convenient than those for silica gel and alumina described by MacDonell and Williams [1] and Kramer *et al.* [2]. Papers made of glass-fibre impregnated with silica or salts were used in TLC by

Swartwout and Gross [3] and Alberti and Grassini [4]. The separations with such papers were not good enough for practical analyses.

Since the above earlier work, the technology of glass has advanced so that porous glass sheets can be made without the supporting matrices. In a previous study [5], we made a 5 cm × 5 cm × 0.5 mm square sheet of porous glass of pore diameter 700 nm. The sheet acts as both the separation layer and the supporting matrix. The surface of the sheet is mechanically and chemically stable. Further, the sheet is so rigid that it is easy to handle. Using this sheet, we obtained good separation and detection conditions for various organic and inorganic compounds. The sheet was found to be very useful even for conventional TLC. In addition, various advanced detection methods could be directly con-

Correspondence to: Dr. M. Yoshioka, Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka 573-01, Japan.

nected with these TLC sheets. It was possible to measure a Fourier transform IR spectrum and a fluorescence spectrum of a spot on the sheet, because the surface was very smooth compared with those of silica gel and alumina. Because of the large surface of the porous glass, numerous novel dry chemistry reactions were found [5].

Some metal ions became fluorescent after heating without the need for any fluorescent spray reagent. These fluorescent compounds seem to be different from hitherto known fluorescent metal ions. There are well known fluorescent organic metal ion complexes, reviewed by Udenfriend [6], crystalline fluorescent mixtures of inorganic compounds for fluorescent lamps, described by Nakamura and Tamura [7], and atomic fluorescence of metals at extremely high temperature, described by Browner [8].

In this work, we examined these novel fluorescent reactions by using many metal ions and determined the optimum heating temperature for each ion, their fluorescent spectra and their TLC characteristics.

EXPERIMENTAL

Materials

According to our previous method [5], we prepared a porous glass sheet of pore diameter 700 nm. The mean pore volume and specific surface area were 0.46 cm³/g and 6.6 m²/g, respectively, measured by a mercury intrusion method with a mercury penetration porosimeter. The glass consisted of 45–70% SiO₂, 8–30% B₂O₃, 8–25% CaO, 5–15% Al₂O₃, 3–8% Na₂O, 1–5% K₂O and 0–8% MgO. The mixture was heated at 600–800°C for 20 h to effect a phase separation. The glass block was cut into a square sheet of 5 cm × 5 cm × 0.5 mm. The sheet was leached with 1 M HCl at 80–90°C for 4–10 h to etch the B₂O₃ phase to make it porous, washed with water and dried.

The salts of the metal ions used were obtained commercially and dissolved in water, 0.1 M HCl (*), 0.1 M HCl containing ethanol (**) or 0.35% hydrogen peroxide (***) to make 0.1 M solutions, which were further diluted with 0.1 M HCl. The following salts were obtained from Wako (Osaka, Japan) and dissolved in one of the above media: LiCl, NaCl, MgCl₂ · 6H₂O (*), AlCl₃ · 6H₂O, KCl, CaCl₂ · 2H₂O (*), VCl₃, CrCl₃ · 6H₂O, MnCl₂ ·

4H₂O, FeCl₂ · nH₂O, FeCl₃ · 6H₂O, CoCl₂ · 6H₂O, NiCl₂ · 6H₂O, CuCl₂ · 2H₂O, ZnSO₄, GeCl₄, SeCl₄, RbCl, SrCl₂ · 6H₂O, YCl₃ · 6H₂O, ZrOCl₂ · 8H₂O, MoCl₅, RuCl₃, PdCl₂, AgNO₃, CdCl₂ · 2½H₂O, InCl₃ · 4H₂O, SnCl₂ · 2H₂O, SbCl₃, TeCl₄ (**), CsCl, BaCl₂, La₂O₃ (***), CeCl₃ · 7H₂O, CeO₂ (***), Pr₆O₁₁ (***), Nd₂O₃ (***), Sm₂O₃ (***), Eu₂O₃ (***), Gd₂O₃ (***), TbCl₃ · xH₂O, YbCl₃ · 6H₂O, WCl₆, IrCl₄, H₂PtCl₆ · 6H₂O, HAuCl₄ · 4H₂O, HgCl₂ (*), TiCl, Pb(NO₃)₂ and BiCl₃ (**).

Fluorescent reaction by heating

A 3-μl volume of each solution was spotted on the sheet and dried. The sheet was heated in an electric muffle furnace (Advantec OPM-16S, Toyoseisakusho, Tokyo, Japan) at various temperatures from 100 to 700°C for 15 min. The spot of Sn on heating was not fluorescent, but became fluorescent by flaming the sheet in the oxidizing flame of a gas burner for 30 s. In the dark, the sheet was irradiated with an ultraviolet lamp at 254 or 366 nm to reveal the fluorescence of the spots. The fluorescence spectrum of the spots were measured with an FP-770 spectrofluorimeter (JASCO, Tokyo, Japan).

TLC of cations

The cations showing fluorescence on heating were analysed by TLC according to our previous method [5]. For spotting the sample solutions, a 1-μl glass capillary (32 mm × 0.1 mm I.D.) (Microcaps) was cut to one tenth of the original length, *i.e.*, 3.2 mm long. The small tip of the capillary was connected with a silicon tube of 0.5 mm I.D. The tip was dipped into the sample solution and 0.1 μl was sucked into it. The tip was applied to the sheet by pushing the silicon tube, dried and developed with *n*-butanol–benzene–1 M HNO₃–1 M HCl (75:69:4:2, v/v) or of acetone–3 M HCl (99:1, v/v). The triplicate spots were detected by the above heating, by spraying a solution of 0.05% dithizone in chloroform or a solution of 1% 8-hydroxyquinoline in methanol, following by exposure to ammonia gas from 28% ammonia solution.

RESULTS

As shown in Table I, fluorescent cations were

TABLE I

COLOURS OF FLUORESCENCES AND UV ABSORBANCES OF METAL IONS HEATED ON THE SHEETS AT VARIOUS TEMPERATURES

The plate was irradiated by a UV lamp at 254 or 366 nm. Colours are abbreviated as follows: B = blue or blueish; D = dark; G = green; L = light; O = orange; P = pink or pinkish; V = violet; W = white; Y = yellow or yellowish. Intensities of the UV absorptions were decided by eye in the increasing order \pm , + and 2+. Asterisks indicate the contour of the spot.

Ion	Irradiation (nm)	Temperature (°C)							
		20	100	200	300	400	500	600	700
Mg ²⁺	254					LW	W		
	366		\pm	\pm	\pm	LB	LB	LO	
Al ³⁺	254						LW		
	366		\pm	\pm	\pm	LB	LW	\pm	
Ca ²⁺	254			\pm	\pm		W*	W*	
	366		\pm	+	+	+	W*	WO*	LW*
V ³⁺	254	+	2+	+	+	+	+	LY	LY
	366	+	2+	+	+	+	+	O	O
Cu ²⁺	254	+	+	+	B	B	B	B	BG
	366	+	+	+	+	+	+	\pm	
Zn ²⁺	254			LW			W*	B*	
	366			LW	LW	\pm	W*	LW*	LW*
Ge ⁴⁺	254				\pm	\pm			
	366		+	\pm	LB*	LB	+	\pm	
Y ³⁺	254					BW			
	366		+	\pm		BW	+		
Zr ⁴⁺	254			LW	LW	BW	W		
	366			LW	W	BW	W		
Mo ⁵⁺	254	2+	2+	2+	2+	2+	+	\pm	Y
	366	2+	2+	2+	2+	2+	+	+	LO
Ag ⁺	254	+	2+	2+	+	2+	B	B	B
	366	+	2+	+	+	2+	2+	LO	LO
Cd ²⁺	254					LOW			
	366		\pm	+*	+	OW*	+		
In ³⁺	254			BG	LW	BW*	LW*	LW*	LY
	366		\pm	LWV	W	W	LO	+	LO
La ³⁺	254			LW	LW	LW*	LB*		
	366			LY	LW	W	+	+	+
Ce ³⁺	254	V	V	V	+	+	+	+	+
	366		V	B	+	+	+	+	
Ce ⁴⁺	254	+	LV	+	+	+	+	+	+
	366	+	\pm	+	+	2+	2+	\pm	
Eu ³⁺	254	LP	LP	DP	P	P	P	P	P
	366	LP	DP	+	+	DP	DP	LP	LDP
Tb ³⁺	254	YG	LYG	LYG	LY	YG	YG	YG	YG
	366	LW	\pm	LG	+	+	+	+	+
Tl ⁺	254	\pm		LB	LB	LB	LB		
	366	LW	\pm	BW	LB	LB	LB	LB	
Pb ²⁺	254	+	+	+	+	\pm	B	B	B
	366		\pm	\pm	\pm	O*	\pm		
Bi ³⁺	254	+	2+	2+	+	2+	2+	2+	O2+
	366	+	2+	2+	2+	2+	+	\pm	\pm

screened from the reagents described under *Materials*. The fluorescent colours were dependent on the heating temperature and the wavelength of excitation. Some cations showed fluorescence only at high temperatures, but UV absorption at low temperatures. Vanadium showed strong UV absorption at 100°C, changing to light absorption at 200–500°C and yellow fluorescence at 600°C. Copper(II) showed UV absorption at 100–200°C, changing to blue fluorescence at 300–600°C and green fluorescence at higher temperatures. Germanium showed blue fluorescence at 300–400°C, but not at higher temperatures. Indium showed blueish-green fluorescence at 200–600°C, changing to blue fluorescence at 700°C, but no fluorescence above 700°C. Tin was not fluorescent after heating in the furnace, but gave rise to a pink fluorescence after being heated in the flame of the gas burner. The other fluorescent cations also gave rise to the same fluorescence in the flame as in the furnace. The reproducibilities of the fluorescences in the furnace were better than those in the flame. Cerium(III) showed blueish fluorescence at 100–200°C, but only absorption at the higher temperatures. Terbium was al-

ways fluorescent at any temperature. Thallium showed light blue fluorescence at 200–500°C, but no fluorescence at other temperatures. However, it showed stronger fluorescence in the flame than the furnace. Lead showed absorption at low temperatures, changing to blue fluorescence. Molybdenum showed yellow fluorescence at 700°C. Hence all these cations had characteristic temperatures for their fluorescences.

Limits of detection of these fluorescent reactions are summarized in Table II. Dilute solutions were spotted on the sheet and heated at each optimum temperature in the above manner. The detection limit of germanium was 0.3 μmol , those of vanadium(III), tin and lead were 300 pmol and that of copper(II) was 3 pmol. This high sensitivity is comparable to that of atomic spectrometric techniques.

These fluorescent reactions were applied to detection for TLC. The metal ions shown in Fig. 1 were well separated. The R_F values of the ions are summarized in Table III. The spots detected by heating overlapped the triplicate spots detected by spraying with 8-hydroxyquinoline or dithizone solution. Hence the fluorescent compounds were not due to impurities in the metal reagents.

TABLE II
DETECTION LIMITS PER SPOT OF CATIONS

For conditions and abbreviations, see Table I.

Cation	Heating temperature for 15 min (°C)	Amount (μmol)	Colour	Excitation (nm)
V ³⁺	700	$3 \cdot 10^{-4}$	LO	254
Cu ²⁺	400	$3 \cdot 10^{-6}$	B	254
Ag ⁺	700	$3 \cdot 10^{-1}$	B	254
In ³⁺	400	$3 \cdot 10^{-2}$	BG	254
Sn ²⁺	Flame	$3 \cdot 10^{-4}$	P	254
Ce ³⁺	100	$3 \cdot 10^{-2}$	B	254
Tb ³⁺	700	$3 \cdot 10^{-2}$	YG	254
Tl ⁺	Flame	$3 \cdot 10^{-2}$	LB	254
Mo ⁵⁺	700	$3 \cdot 10^{-2}$	Y*	254
Mg ²⁺	400	$3 \cdot 10^{-1}$	LB*	366
Zn ²⁺	700	3	LO	254 or 366
Al ³⁺	400	$3 \cdot 10^{-2}$	W	254 or 366
Zr ⁴⁺	400	$3 \cdot 10^{-1}$	LB*	366
Bi ³⁺	700	$3 \cdot 10^{-2}$	LO	254
Y ³⁺	400	$3 \cdot 10^{-2}$	W	254 or 366
Cd ²⁺	400	$3 \cdot 10^{-1}$	LO	366
La ³⁺	300	3	LB	254 or 366
Pb ²⁺	700	$3 \cdot 10^{-4}$	B	254
Ge ⁴⁺	Flame	$3 \cdot 10^{-1}$	LB	254

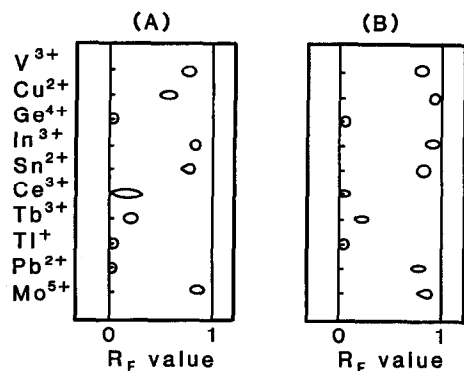


Fig. 1. Chromatograms of metal ions developed with (A) *n*-butanol-benzene-1 *M* HNO₃-1 *M* HCl and (B) acetone-3 *M* HCl. The developed sheet was cut in the development direction into small pieces for each ion, and each piece was heated at the particular optimum temperature described in Table I.

TABLE III

R_F VALUES OF FLUORESCENT CATIONS AS SHOWN IN FIG. 1

Cation	<i>R_F</i> value	
	Fig. 1A	Fig. 1B
V ³⁺	0.78	0.81
Cu ²⁺	0.56	0.93
Ge ⁴⁺	0.04	0.06
In ³⁺	0.81	0.93
Sn ²⁺	0.78	0.85
Ce ³⁺	0.15	0.04
Tb ³⁺	0.22	0.22
Tl ⁺	0.04	0.04
Pb ²⁺	0.04	0.81
Mo ⁵⁺	0.85	0.89

It was possible to measure fluorescence spectra *in situ* on the sheet. As shown in Fig. 2a, copper showed an excitation maximum at 254 nm and an

emission maximum at 450 nm. Lead showed an excitation maximum at 254 nm and an emission maximum at 400 nm (Fig. 2b). However, the quantum

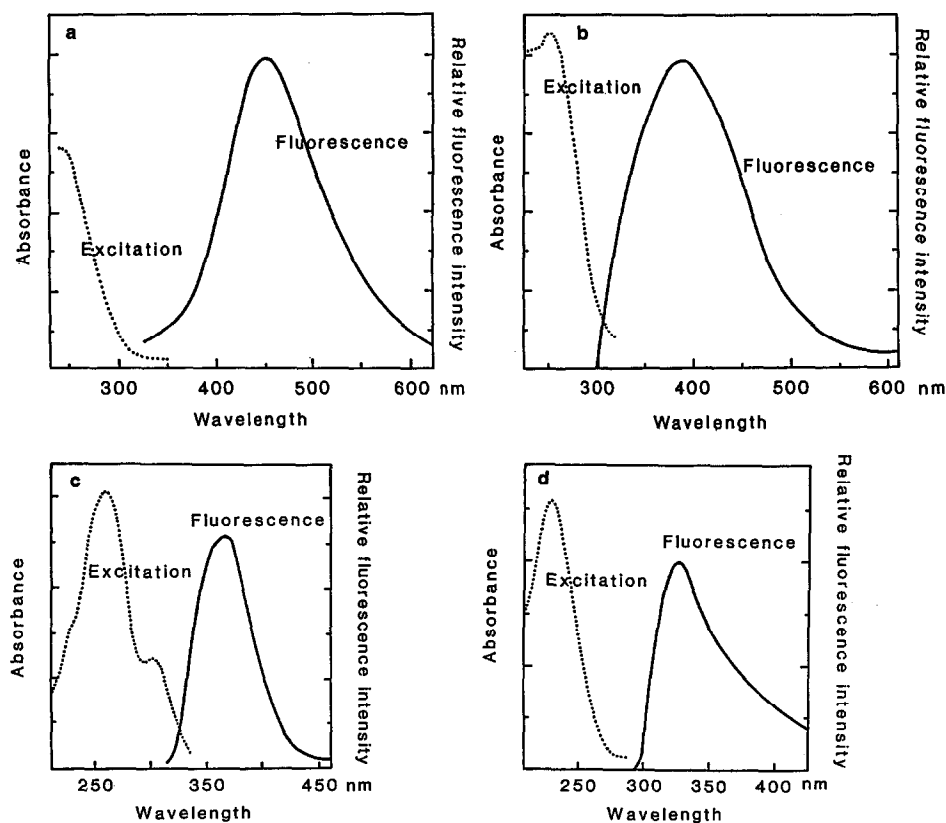


Fig. 2. Fluorescence spectra of metal ions heated on the sheet. a = Copper; b = lead; c = cerium; d = thallium.

yields of the products from both metals were only a few percent. Cerium(III) showed an excitation maximum at 260 nm and an emission maximum at 375 nm for blue fluorescence (Fig. 2c). Thallium showed an excitation maximum at 230 nm and an emission maximum at 325 nm for light blue fluorescence (Fig. 2d).

DISCUSSION

We have found new phenomena in the fluorescence reactions of some metal ions on the new glass sheet. The fluorescent compounds produced on the sheet are stable at room temperature more than 1 month. These fluorescence reactions are not observed on thin layers of silica gel or in a test-tube heated at the temperatures used. Hence specific reactions occur on the porous glass surface. When the spot is heated, the fluorescent compounds are fused in the glass phase. In the fusion, the starting forms of the cations are essential factors for the fluorescence reactions, because endogeneous cations such as Ca, Mg and Al do not show a fluorescent background.

From the broad spectra as shown in Fig. 2, the fluorescences are different from the atomic fluorescences reviewed by Browner [8]. Many kinds of fluorescent compounds have been found. Inorganic chelating agents can be used to prepare fluorescent chelates for inorganic analyses, *e.g.*, 8-hydroxyquinoline, morin [6]. The systematic analysis of inorganic cations has been investigated by TLC using silica gel plates. The detection was based on conventional chromogenic reagents as described by Seiler and Rothweiler [9] and Ajmal *et al.* [10]. Inorganic crystalline fluorescent mixtures have been impregnated in the silica gel layer to detect some metal ions [7]. The present fluorescent reactions are simpler for TLC detection, although they are limited to the particular cations reported here. Some cations, such as copper, lead, vanadium and tin, are very sensitive with results comparable to atomic spectrometry.

Inorganic crystals of mixtures of several atoms are strongly fluorescent with almost 100% quantum yields. These crystals, such as the blueish white (Zn, Cd)S–Cu, Al + ZnS–Ag, the red phosphor Y_2O_3 –Eu and the green phosphor Zn_2SiO_4 –Mn, In, have been used for making fluorescent lamps [7]. These materials are different from the present fluorescent

products in their compositions and amorphous states. If the quantum yield in the glass can be increased, it will provide a new method to prepare fluorescent lamps.

Other photoluminescences are found in high-temperature superconductors, such as are ErBaCuO, NdBaCuO and GdBaCuO. Their photoluminescences excited by an argon ion laser are observed at 77 K and are influenced by the environmental crystalline conditions. The present fluorescent products are also different from the superconductors in principle as reported by Fujiwara and Kobayashi [11]. The new glass sheet may provide a simple way to make new materials in which the solutions of metal ions are easily combined and heated at high temperature.

It is very difficult to identify these new fluorescent compounds, because the chemical yields are not high and they are included in the glass. The glass matrix seems to stabilize the fluorescent compounds at room temperature, as seen in thermally activated delayed fluorescence of organic fluorescent substances in solid supports such as sodium acrylate polymer and filter-paper as described by Onoue *et al.* [12]. Time-resolved fluorescence spectroscopy has been applied to study the fluorescent characteristics of immobilized pyrene on an alkylated silica surface, as described by Wong *et al.* [13]. This kind of study is one of the ways to characterize fluorescent compounds. However, it is worth investigating these novel phenomena further in order to open up a new field of dry chemistry and also a new detection method for TLC.

ACKNOWLEDGEMENTS

We express our gratitude to Mr. T. Nishimura and Mr. T. Takahara of the Electron Tube and Device Division, Horikawacho Works, Toshiba (Kawasaki, Japan) for their advice on the inorganic fluorescent compounds and the measurement of quantum yields of the fluorescence on the sheet.

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