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Thin-Layer Chromatography of Cu(II), Co(II) and Ni(II)

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Abstract: The chromatographic behavior of some heavy metals on thin layer of silica gel was studied. The effect of polarity of mixed developing agent systems on the R_f values of metal complexes was investigated. The linear dependence between the R_f values and the polarity of developing agents was deduced and a series of good separations of Cu(II),Co(II) and Ni(II) were obtained successfully. This method was applied to separate Cu(II) and Ni(II) in a real sample.

Keywords: Thin-layer chromatography, dithizonates

INTRODUCTION

With the aggravation of environmental pollution, people pay more attention to the analysis of the poisonous heavy metals ions in environment. Many analytical methods have been applied to this field, such as the atom absorption spectrometry (1), polarography (2), stripping voltammetry (3), ICP-AES (4), and X-ray fluorescence spectrometry(5). However, the concentration of the metal ions in environment are usually very low and some kin metals are usually concomitant, such as Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, and Cu^{2+} etc., so preconcentration and preseparation are usually needed in actual work, for example, precipitation separation (6), solvent extraction (7), vaporization and distillation (8), membrane separation (9) and polymeric syntheticresin for separation (10) etc. But the preparation with the above methods usually

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has medium influence or elements interference, so the selectivity of the determination is restricted.

Thin-layer chromatography (TLC) was used by N.A. Izmailov and M.S. Schraiber in 1938 first and developed on the basis of classical column chromatography and paper chromatography by J.G. Kirchner etc. in the 1950s. It made more quickly progress after Stahl had improved instrument equipments, adsorbent specification and operating mode in 1956 (11). The attractive features of TLC include simple preparation; without requirement of special equipment; parallel sample processing for high sample throughput; accessibility of the sample for post-chromatographic evaluation free of time constraints. Now, the separation objects are primarily in the aspects of medicine and biology (12–14). TLC for separation of metal ions mainly includes: ion exchange thin-layer chromatography (15); partition thin-layer chromatography (16); adsorption thin-layer chromatography (17). The main influence factors for thin-layer chromatography are:

1. property of the separated material, such as solubility, acidity, polarity etc.,
2. adsorbent,
3. developing agents.

The adsorbents used commonly are only a few, but the kinds of developing agents are numerous and their admixtures are countless. The key for TLC is to select the right developing agent that matches the separated material and adsorbent. But systemic studies on mixed developing agents are few. In this paper, 10 developing agents and their mixture were chosen to investigate the effect of solvent polarity on the R_f values of metal complexes. Finally, a proper solvent system was selected for separation of Cu^{2+}, Co^{2+}, and Ni^{2+}. The graphite furnace atomic absorption spectrometry (GFAAS) was coupled to determine trace $Cu^{2+}$and Ni^{2+} in real samples.

EXPERIMENTAL

Reagents and Apparatus

Silica gel GF_{254}(ocean chemical plant, Qingdao); Saturated dithizone in CCl_4; Standard solutions (1.0 mg/mL) of Zn(II), Fe(II), Co(II), Ni(II), Cu(II), Pb(II), Cd(II), Bi(III), Cr(VI), Ag(I); Developing agent: benzene, toluene, CCl_4, $CHCl_3$, CH_2Cl_2, ethyl acetate, dioxane, THF, n-C_4H_9OH, n-$C_5H_{11}OH$; Buffer solution: 0.05M HAc/NaAc (pH = 4.4), 0.075M borax (pH = 8.0), 0.025M $NaHCO_3/Na_2CO_3$ (pH = 9.8). All the chemicals were of analytical grade. National reference materials (Beijing, China)

Graphite furnace atomic absorption spectrometer (WFX-210,Ruili analysis instrument company, Beijing),pH meter(pHS-25 mode, Shanghai).

Procedure

Preparation of Thin Layer Plate

Silica gel GF_{254} and NaAc(mass ratio is 40 : 1) in 0.2% carboxymethyl cellulose sodium solution was equably coated on glass plates, air dried, stored in desiccator.

Chromatographic Separation

A 50 μL standard solution of metal ion, 2.0 mL buffer solution, and proper dithizone solution were transferred into separating funnel, oscillated, demixed, then the organic phase was spotted on the plate, finally spotted plates were placed in a chromatographic chamber until the developing agent front traveled about 10 cm.

Sample Handling

A 1000 mL water sample was filtrated and then concentrated to 100 mL.

Quantitative Analysis

After layer developed spots were scrapped to graduation centrifuge tube, dissolved by addition of 1.0 mL 5% HCl, oscillated, and centrifugal separated, the upper clear solution was analyzed by graphite furnace atomic absorption spectrometry under the conditions of Table 1.

RESULTS AND DISCUSSION

Selection of pH

The metal ions were reacted with dithizone solution respectively in three buffer solutions: HAc/NaAc (pH = 4.4), borax (pH = 8.0),

Table 1. Operating conditions for GFAAS

Element	Cu	Ni
Wavelength/mm	324.7	232.2
Slit/nm	0.4	0.2
HCL.Current/mA	3	3
Graphite Furnace		
Dry temp/°C	100	100 (ramp 10 s, hold 20 s)
Ashing temp/°C	400	600 (ramp 20 s, hold 10 s)
Atomization temp/°C	2400	2600 (ramp 0 s, hold 5 s)
Cleaning temp/°C	2600	2700 (ramp 0 s, hold 2 s)

$NaHCO_3/Na_2CO_3$ (pH = 9.8). Results showed that at pH = 4.4 complexes were stable including Ag^+ and Cr(VI), at pH = 8.0 complexes were stable including Ni^{2+}, Co^{2+}, Cd^{2+} and Fe^{3+},at pH = 9.8 complexes were stable including Ni^{2+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} and Bi^{3+}. So each ion was reacted with dithizone at the proper pH respectively.

The Amount of Dithizone

When dithizone is superfluous it will cover up the color of complexes, because the color of dithizone is dark, and spots will form tailing. So volume of dithizone solution chosen was 0.5 mL.

Single Developing Agent Systems

In considering the property of metallic dithizonates, 10 developing agents whose polarity parameter was less than 5.0 were chosen. They were benzene, toluene, CCl_4, $CHCl_3$, CH_2Cl_2, ethyl acetate, dioxane, THF, n-C_4H_9OH, n-$C_5H_{11}OH$. The results are given in Table 2, which showed: (1) The R_f values of 10 metal complexes were all 0 when developed with CCl_4 (2). The R_f values of Co^{2+}, Ni^{2+} and Cu^{2+} were 0.44, 0.61, 0.68 respectively when developed with benzene toluene, and the R_f values were 0.66, 0.79, 0.82 respectively when developed with benzene. The R_f values of Ni^{2+} and Cu^{2+} were close, their separation was not entire. The other 7 metal complexes were decomposed in the process of developing (3). The R_f values of 10 metal complexes all were 1 when developed with the other seven developing agents. The effect of the polarity of developing agents on the R_f values of metal complexes is obvious. It could be seen from the above data that Ni^{2+} and Cu^{2+} could not be separated in a single developing agent, so it is necessary to select a properly mixed developing agent system.

Mixed Developing Agent Systems

An ideal separation requires the spots to be clear, concentrative and the R_f values in the range of 0.2–0.8. In order to obtain the proper solvent system

Table 2. R_f values of ions in various developing agent

Ions	CCl_4	Benzene	Toluene	CH_2Cl_2, $CHCl_3$	Ethyl acetate, dioxane, THF n-C_4H_9OH,n-$C_5H_{11}OH$
Co^{2+}	0	0.66	0.44	≈1	≈1
Ni^{2+}	0	0.79	0.61	≈1	≈1
Cu^{2+}	0	0.82	0.68	≈1	≈1
M^a	0	Decompose	Decompose	Decompose	≈1

[a] M = Ag^+, Cr (VI),Cd^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, Bi^{3+}.

that can separate Co^{2+}, Ni^{2+} and Cu^{2+}, the nonpolar developing agent and the other polar developing agents were selected as mixed developing agent systems. The concentration of polar developing agents altered to obtain the relation of the polarity of developing agents with the R_f values and to find the concentration range of developing agent that the complexes could be separated efficiently.

The Mixed Developing Agent Systems of Ethyl Acetate/CCl_4 and Dioxane/CCl_4

Altering the concentration of ethyl acetate and dioxane in mixed developing agent systems of ethyl acetate/CCl_4 and dioxane/CCl_4 the dithizonates of Co^{2+}, Ni^{2+} and Cu^{2+} were investigated. The effect of polar developing agents concentration in mixed solvent on the R_f values was shown in Figs.1 and 2. It could be seen that the increasing of the polarity of solvents concentration resulted in increased R_f values in low concentration, and the R_f values tended to 1 at the concentration of 10%. Co^{2+}, Ni^{2+}, and Cu^{2+} could be separated in the concentrate range of 2.0%–8.0%. The linear equation between the R_f values and the concentration of polar developing agents are present in Tables 3 and 4. The separation effect in mixed developing agents is better than single developing agents.

The Mixed Developing Agent Systems of Benzene/CCl_4 and Toluene/CCl_4

Altering concentration of benzene and toluene in mixed developing agent systems of benzene/CCl_4 and toluene/CCl_4,the developing results of

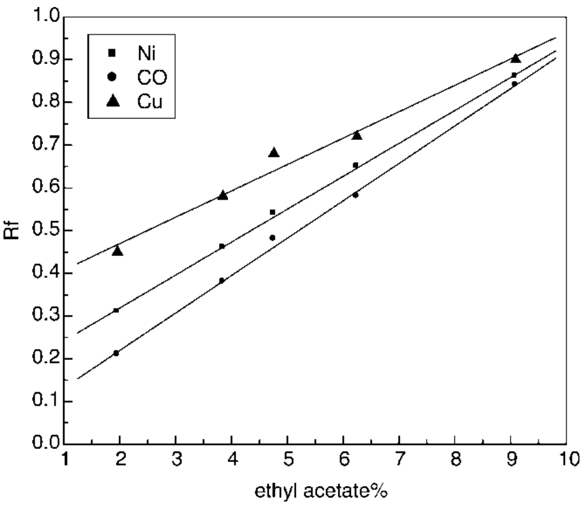

Figure 1. Effect of ethyl acetate concentration in mixed solvent on R_f values.

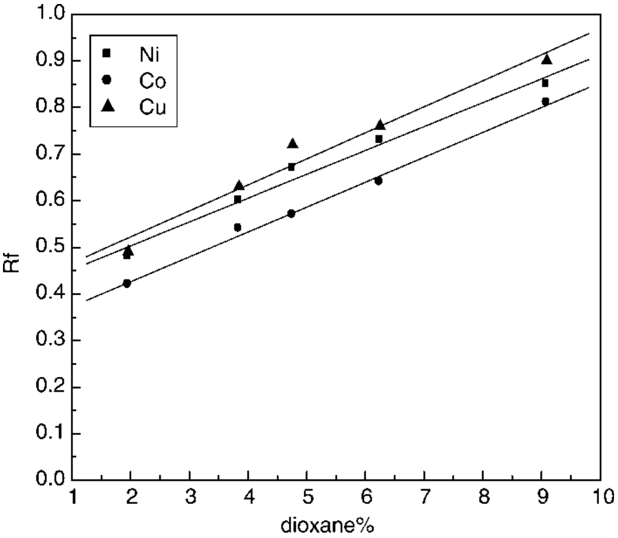

Figure 2. Effect of dioxane concentration in mixed solvent on R_f values.

metallic dithizonates in mixed developing agent systems were shown in Figs. 3 and 4. The results showed that Co^{2+}, Ni^{2+}, and Cu^{2+} had a better resolution than in single developing agents and in mixed developing agent systems of ethyl acetate/CCl_4 and dioxane/CCl_4, especially Ni^{2+} and Cu^{2+}. The R_f values of the complexes increased with the polarity of solvents increasing and it was linearly increscent when the concentration lower low than 80%. The separation range was wider than in ethyl acetate/CCl_4 and dioxane/CCl_4 mixed system, and the R_f values of complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} are more different. The linear equation between the R_f values and the concentration of polar developing agents are present in Tables 5 and 6. This proved that the stronger polarity of developing agents results in stronger eluting power and the bigger R_f value in normal-phase chromatography. 66.7% toluene in CCl_4 was selected as the developing agent to separate Cu^{2+} and Ni^{2+}.

Table 3. R_f values of metal ions in mixed solvent of ethyl acetate

Ions	Ethyl acetate	Ethyl acetate + CCl_4 (ethyl acetate % = 3.8%)	Equation 2.0% < ethyl acetate % < 9.1%
Co^{2+}	0.99	0.38	$R_f = 0.01324 + 9.21242C_{\text{ethyl acetate}}$
Ni^{2+}	0.99	0.46	$R_f = 0.07405 + 9.11732C_{\text{ethyl acetate}}$
Cu^{2+}	0.91	0.58	$R_f = 0.34475 + 6.1779C_{\text{ethyl acetate}}$

Table 4. R_f values of metal ions in mixed solvent of dioxane

Ions	Dioxane	Dioxane + CCl_4 (dioxane% = 4.8%)	Equation 2.0% < ethyl acetate % < 9.1%
Co^{2+}	0.99	0.67	$R_f = 0.31865 + 5.33356C_{dioxane}$
Ni^{2+}	0.99	0.57	$R_f = 0.39968 + 5.12161C_{dioxane}$
Cu^{2+}	0.99	0.72	$R_f = 0.40946 + 5.58721C_{dioxane}$

Working Curve, Limits of Detection and Precision

According to this experimental method, Ni^{2+} and Cu^{2+} were separate at pH = 9.8 and were determined by GFAAS, the results of which are shown in Table 7. The working curve was linear over the range of 0–500 ng · mL^{-1}. The LODs are expressed as three times the standard deviation of the blank. The relative standard deviation (R.S.D.) was determined at the concentration of 200 ng · mL^{-1}(n = 3).

Sample Determination

Determination of Ni^{2+} and Cu^{2+} in Environmental Reference Material

According to this method, Ni^{2+} and Cu^{2+} in environmental reference material were separated and determined. The results are shown in Table 8. The measured values were in good agreement with the certified values.

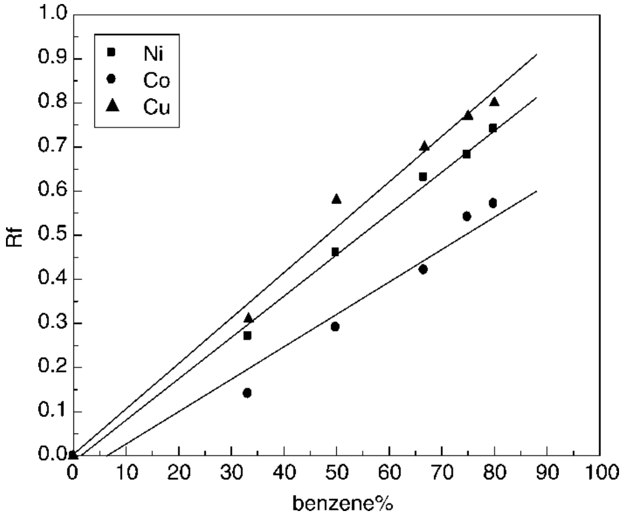

Figure 3. Effect of benzene concentration in mixed solvent on R_f values.

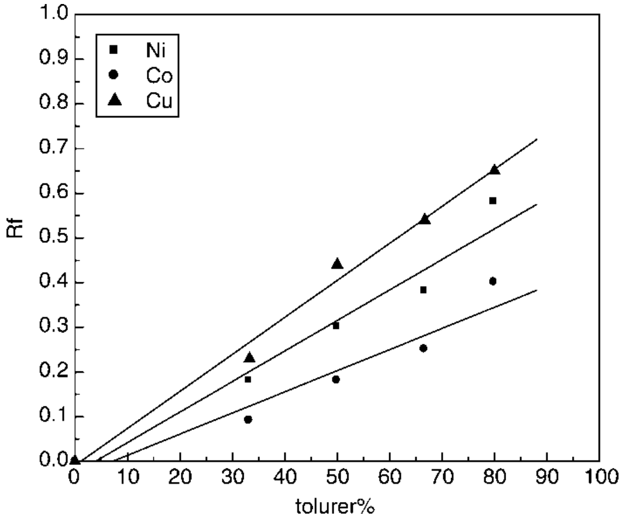

Figure 4. Effect of toluene concentration in mixed solvent on R_f values.

Table 5. R_f values of ions in mixed solvent of C_6H_6

Ions	Benzene	Benzene + CCl_4 (benzene = 50%)	Equation (benzene = 80%)
Co^{2+}	0.66	0.29	$R_f = 0.04685 + 0.00735C_{benzene}$
Ni^{2+}	0.79	0.46	$R_f = 0.01291 + 0.00937C_{benzene}$
Cu^{2+}	0.82	0.58	$R_f = 0.00342 + 0.01029C_{benzene}$

Table 6. R_f values of ions in mixed solvent of C_7H_8

Ions	Toluene	Toluene + CCl_4 (toluene% = 66.7%)	Equation (toluene% = 80%)
Co^{2+}	0.44	0.25	$R_f = -0.0337 + 0.00473C_{toluene}$
Ni^{2+}	0.61	0.38	$R_f = -0.02636 + 0.00683C_{toluene}$
Cu^{2+}	0.68	0.54	$R_f = -0.00899 + 0.00828C_{toluene}$

Table 7. Working curve, detecting limit and precision

Ions	Linear equation	R	LOD ($ng \cdot mL^{-1}$)	R.S.D. $C = 200\,ng \cdot mL^{-1}$, $n = 3$
Cu^{2+}	$A = 0.01825 + 0.0034c$	0.9967	0.37	4.9%
Ni^{2+}	$A = 0.0111 + 0.00281c$	0.9988	0.74	3.1%

Table 8. Determination of Cu^{2+} and Ni^{2+} in standard water

Sample	Ions	Measured (μg/mL)	Certified (μg/mL)
GBW(E)080194[a]	$Cu^{2\pm}$	40.62 ± 1.03	40.65 ± 2.35
	$Ni^{2\pm}$	31.55 ± 1.47	33.15 ± 2.00

[a] National reference materials (China).

Table 9. Determined results and the percent recovery of this method

Sample	Ions	Found $\mu g \cdot mL^{-1}$	Added $\mu g \cdot mL^{-1}$	Determined $\mu g \cdot mL^{-1}$	Recovery %
Distilled water	Cu^{2+}	ND[a]	3.0	2.95	98.3%
			5.0	4.91	98.1%
	Ni^{2+}	ND[a]	3.0	2.98	99.3%
			5.0	4.74	94.7%
Lake water	Cu^{2+}	0.98	4.0	4.83	97.0%
			6.0	7.11	101.9%
	Ni^{2+}	0.93	4.0	4.68	94.9%
			6.0	6.40	92.4%

[a] Not detected.

Determination of Real Sample

The proposed method was applied to the determination of Ni^{2+} and Cu^{2+} in distilled water and Slender West Lake water. The standard addition method was used. The analytical results and the recovery are present in Table 9. The good recovery results had been obtained.

CONCLUSIONS

In this paper, the influence of the polarity of developing agents on the R_f values had been investigated. The R_f values increased with the polarity of solvents increasing in normal phase chromatography, and it was linear increscent in definite range. According to the quantificational relation of the R_f values with the polarity of developing agents, the $R_f$values could be controlled in the ideal separating range and the separation effect would be better. In the benzene/CCl_4 and toluene/CCl_4 mixed developing agent systems, the R_f values of complexes of Co^{2+}, Ni^{2+}, and Cu^{2+} were different than in single developing agents. Trace $Cu^{2+}$and Ni^{2+} in environmental reference material and in water sample were determined successfully and the results were satisfactory.

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