*A Novel Resin Spot Test for Copper(II) Using a Chelating Resin**,[1]

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(Received August 10, 1961)

"Resin spot test[2]" has proved its widespread utilities by many interesting works of the present author and other chemists[3]. This sensitive test is based mainly on the intense coloration of a few grains of light-colored ion exchangers by the up-take of trace amounts of colored substances from outer solution phase, and are easily attained much higher sensitivities as compared with those of ordinary spot test[4].

In this communication the author suggests a new possibility to lend high selectivities to the resin spot tests through applications of a sort of special resins having chelate-forming groups as functional groups. The resin used here is "Dowex A-1 Chelating Resin", a resin of styrene-divinylbenzene basis with imino-diacetate group, whicih adsorbs preferentially palladium(II) and copper(II) at about pH 5[5].

The commercial resin supplied as sodium form, 50—100 mesh, was packed in a column, converted into ammonium form via free-acid form, washed with de-ionized water, and dried at room temperature. A buffer solution of pH

TABLE I

Ion	Coloration[a]	Limiting proportion[b], Cu(II) (μg): Foreign ion (μg)	
Ti(V)	cl(W↓)	1.4 : 42	(1 : 63)[c]
V(IV)	lmYe(Ol)	1 : 20−	(0.4 : 64)
Cr(III)	blPu(dlGry)	1 : 2†	(1.8 : 2.2)
Cr(VI)	yeGry(Ol)	0.4 : 32†	(1.4 : 13)
Mn(II)	cl(cl)	1 : 900	(0.5 : 1300)
Fe(III)	dlOr(cl)	0.7 : 27−	(1 : 540)
Co(II)	puRe(cl)	0.4 : 180†	(0.4 : 180†)
Ni(II)	plGrn(cl)	1.4 : 8	(0.2 : 21)
Cu(II)	**ltgrnBl(ltgrnBl)**	**0.2**	**(0.2)**
Zr(IV)	cl(W↓)	0.4 : 580+	(0.4 : 580+)
Mo(VI)	cl(cl)	0.2 : 720+	(0.2 : 720+)
Pd(II)	YeOc(YeOc)	1.6 : 48†	(1.8 : 24−)
Ag(I)	cl(ltYe)	1 : 400+†	(0.7 : 520)
W(VI)	cl(cl)	0.7 : 275+	(0.7 : 275+)
Pt(IV)	ltYe↓(ltYe↓)	0.7 : 200+	(0.7 : 200+)
Au(III)	dlreOr↓(ltReYe↓)	1.6 : 67	(1.6 : 67)
Th(IV)	cl(cl↓)	0.7 : 270	(1.2 : 160+)
U(VI)	lmYe(plYe)	0.2 : 360	(0.4 : 320)
Zn(II)	cl(cl)	0.4 : 800	(0.5 : 600)
Cd(II)	cl(cl)	0.4 : 800+	(0.4 : 800+)
Hg(II)	cl(cl)	1 : 390	(1 : 390−)
Al(III)	cl(cl)	0.5 : 1400+	(1 : 1000−)
Ga(III)	cl(cl)	0.7 : 530	(0.7 : 530)
In(III)	cl(cl)	0.3 : 330	(0.5 : 290)
Tl(I)	cl(cl)	0.3 : 680	(0.3 : 680)
Ge(IV)	cl(cl)	0.4 : 90+	(0.4 : 90+)
Sn(II)	cl(cl)	1 : 800+[d]	(——)
Pb(II)	cl(W↓)	0.4 : 2000+	(1 : 1250)
Sb(III)	W↓(W↓)	1.3 : 70+††	(1.6 : 40)
Bi(III)	W↓(W↓)	1.3 : 760+††	(1.6 : 460+)
Te(IV)	cl(cl)	1.4 : 27	(1.2 : 32)
Mg(II)	cl(cl)	0.2 : 1800	(0.4 : 1600)
Ca(II)	cl(cl)	0.25 : 1420+	(0.4 : 1300+)
Sr(II)	cl(cl)	0.3 : 3000	(0.4 : 2800)
Ba(II)	cl(cl)	0.4 : 1140+	(1 : 720+)

a Coloration of the resin beads after about an hour caused by the large amounts of foreign ion only. Color code: bl, bluish; Bl, blue; cl, colorless; dl, dull; grn, greenish; Grn, green; Gry, gray; lm, lemon; lt, light; Oc, ocre; Ol, olive; Or, orange; pl, pale; pu, purplish; Pu, purple; re, reddish; Re, red; W, white; ye, yellowish; Ye, yellow. ↓ shows the precipitation on the resin beads.

b +: The limiting proportion was improved with the lapse of time. −: The limiting proportion was rather lowered with time. †: The color at the very edge of the resin beads was observed. ††: A drop of supernatant solution after mixing each one drop of the buffer solution and the test solution was subjected to the test.

c In parentheses are shown the articles in the case, when after about 10 min. a drop of 1 F phosphoric acid is added.

d This value of limiting proportion was obtained only after being kept overnight in a moist chamber.

* Microanalysis with the Aid of Ion-exchange Resins. XVII.

1) Part XVI of the Series: M. Fujimoto, This Bulletin, 33, 864 (1960).

2) M. Fujimoto, ibid., 30, 283 (1957).

3) M. Fujimoto, *Chemist-Analyst*, 49, 4 (1960).

4) M. Fujimoto, This Bulletin, 29, 600 (1956).

5) W. I. Childs, "Properties of a Chelating Resin", Preprint of a paper from 135th Meeting, American Chemical Society, Boston, Mass., April, 1959; "Dowex A-1 Chelating Resin", Brochure of The Dow Chemical Company, Code No. 164—80 (1959), p. 2.

TABLE II

Time after mixing		10 min.	20 min.	3 hr.	2 d.
Limit of identification for copper(II) in μg. by	Resin spot test	0.8	0.4	0.16	0.1
	Resin centrifuge method	0.2	—	—	0.2

4.7 was prepared from 1 F acetic acid and 1 F ammonium acetate.

In Table I are shown colorations of the resin beads with diverse metal ions under various conditions. In some cases the coloration in the resin beads for copper(II) was found to be rather improved in a slightly acid medium added with phosphoric acid. The following procedure was thus proposed for the specific detection of minute amount of copper(II) with the chelating resin without any specific reagents added.

In a depression of a white spot plate mix a few grains of Dowex A-1 Chelating Resin in the ammonium form with a drop (0.04 ml.) of the 1 F acetate buffer of pH 4.7. (Minute amount of tiny resin beads can easily be added in the depression only by touching a clean tip of a thin glass rod with the resin beads in a reservoir and by tapping gently the rim of the deppression with the tip portion of the rod). After a few minutes, add a drop of the test solution and allow to stand for about ten minutes. Then observe a more or less intense yellowish green to light greenish blue color developed in the *edge* of the resin beads under magnification. If the beads are covered with some other colors, add a drop of 1 F phosphoric acid and again observe the change in color at the edge of the resin beads. Since the chelate formation in the resin phase seems to be somewhat delayed, it would be desired to wait for an hour or more, preferably overnight, the spot plate being kept in a moist chamber free from any dust. It is also recommended to use the "resin centrifuge method[1]" to attain rapidly the highest sensitivity (see Table II). The time-dependency of the limit of identification for copper(II) in the present test is shown in Table II.

The influences of diverse metal ions on the present test are also summarized in Table I, in which are shown the limits of identification for copper(II) and limiting proportions in the presence of other metal ions. Further details for the proposed method will be reported elsewhere.

The author is indebted to Dr. A. J. Barnard, Jr., The J. T. Baker Chemical Company, and to Dr. J. R. Skidmore, Dow Chemical Company, for their kindness supplying him a sample of Dowex A-1 Chelating Resin and many valuable informations through the data sheet.

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