

# Quantitative Inorganic Chromatography. II

## Determination and Detection of Copper in Zinc\*

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(Received October 1, 1951)

### Synopsis

Chromatographic determination and detection of copper in zinc were studied with filter paper which was impregnated with aluminum hydroxide.

Copper was capable of being separated from zinc by developing with water. 1.9  $\gamma$  of copper was determined in the presence of 50 times as much zinc. And as little as 0.06  $\gamma$  of the former was successfully detected in the presence of 100,000 times as much the latter.

### I. Introduction

If the strips of filter paper which contain a definite amount of aluminum hydroxide in unit area of the paper and possess certain alkalinity are used, the widths or the areas of the developed adsorption zones are directly proportional to the amount of solutes which are adsorbed.<sup>(1)</sup>

The width of the undeveloped adsorption zone varies with concentration of the solution absorbed. The more concentrated the solutions are, the narrower the widths or areas of the zones are. If they are developed thoroughly with ample water, zones with a definite width can be obtained, irrespective of concentration. Thus micrograms of solutes are capable of being determined directly from the widths of adsorption zones.

Certain salts of the same cations, however, give different zone widths. Thus, for example, among the adsorption zones of sulfate, chloride and nitrate of copper, that of copper sulfate is smallest, those of chloride and nitrate being nearly equal. A similar relation is also observed in sulfuric, hydrochloric and nitric acids. Acids and salts with smaller activity coefficients give narrower adsorption zones than those which are obtained with acids and salts with greater activity coefficients.

For the determination of some salts, therefore, zones should be compared with those of the same anion.

### II. Determination of copper in zinc

0.100~0.200 ml of solution was put on a glass plate which had been covered with thin paraffin. The solution was absorbed from the lower end of a strip which hung nearly up right, and then developed thoroughly with water. The strips were about 250 mm long and precisely 1 mm wide.

\* The 31st report of the Research Institute of Mineral Dressing and Metallurgy.

(1) Y. Oka and A. Murata, *Sci. Rep. RITU*, A 3 (1951), 82.

If the solute were adsorbed on the portion of a strip where it is immersed in a drop of sample solution taken and of water for development, it would be impossible to estimate the solute, owing to the loss of proportionality. Sample solution, therefore, was slightly acidified or small amount of an acid was added on the glass plate.

When some acid was added to the solution of copper, zinc, cadmium, nickel, cobalt, or manganese salt, and then adsorbed and developed, the adsorption zone of acid was found below the zones of salts. The width of the acid was not affected by the presence of these salts. Equal zone width was always obtained if the same amount of acid was added. Metallic ion was not observed in the acid zones. It was concluded, therefore, that acids and salts were completely separated from each other.

The results are shown in Table 1.

Table 1. Separation of acids and salts

Acid (M)		Salt (M)		Width of adsorption zone (mm)	
				acid	salt
H <sub>2</sub> SO <sub>4</sub>	5.0 × 10 <sup>-7</sup>	CuSO <sub>4</sub>	5.0 × 10 <sup>-7</sup>	11.0	20.8
"	"	ZnSO <sub>4</sub>	2.0 "	"	18.7
"	"	CdSO <sub>4</sub>	1.5 "	"	22.5
"	"	NiSO <sub>4</sub>	2.0 "	"	37.0
"	"	CoSO <sub>4</sub>	" "	"	33.6
"	"	MnSO <sub>4</sub>	" "	"	41.3
HNO <sub>3</sub>	1.5 × 10 <sup>-7</sup>	Pd(NO <sub>3</sub> ) <sub>2</sub>	" "	13.0	25.3
"	"	Cu(NO <sub>3</sub> ) <sub>2</sub>	1.8 "	"	27.1
"	"	Zn(NO <sub>3</sub> ) <sub>2</sub>	1.0 "	"	25.5
"	"	Cd(NO <sub>3</sub> ) <sub>2</sub>	" "	"	27.0
"	"	Ni(NO <sub>3</sub> ) <sub>2</sub>	" "	"	27.5
"	"	Co(NO <sub>3</sub> ) <sub>2</sub>	" "	"	28.8

Although acids were easily separated from salts, their presence should be controlled so as to give a zone width of about 10 mm. If so much acids were present as to give zone widths of 40~50 mm, that of salts became somewhat smaller, owing to, it seems, the minute quantity of metallic ions remaining in

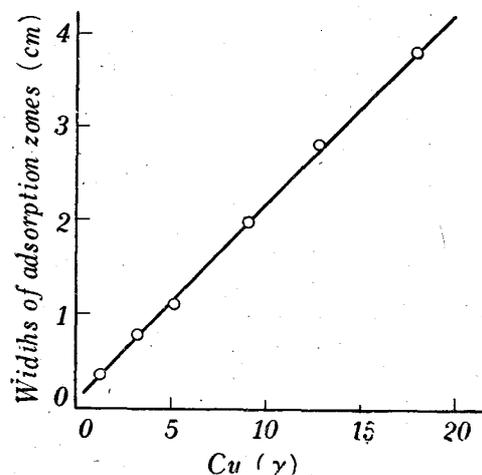


Fig. 1. Adsorption zone width of copper present as copper nitrate.

the region of acids. Their presence, however, could not be recognized by hydrogen sulfide.

The area of the adsorption zone was measured with a glass plate which was graduated in square millimetre.

When the adsorption papers were prepared strictly under definite conditions, widths of zones agreed within the discrepancy of 1 mm.

If discrepancy of 1 mm were allowed to be the maximum error and if the zone width of 5 mm were assumed to be the

smallest one for determination, 1.9  $\gamma$  of copper which was present as copper nitrate could be estimated from chromatogram as is seen from Fig. 1.

Copper salts were generally separated well from other salts. Table 2 shows the zone width of nitric acid, copper nitrate and zinc nitrate.

Equal zone widths were obtained within the permissible

error whether they were present alone or three were coexistent. Copper also could not be detected in the zone of zinc. Thus they may be considered to be separated quantitatively, when they are present in nearly equivalent amounts.

Adding more zinc to copper, limiting amount of the former that could be tolerated was then sought. The results are shown in Table 3.

Table 2. Separation of copper and zinc

Solute (M)	Width of adsorption zone(mm)	
	Present alone	3 coexistent
HNO <sub>3</sub> 1.5 × 10 <sup>-7</sup>	13.0	13.3
Cu(NO <sub>3</sub> ) <sub>2</sub> 1.8 "	27.1	27.5
Zn(NO <sub>3</sub> ) <sub>2</sub> 1.5 "	35.0	36.2

Table 3. Determination of copper in the presence of zinc

Cu taken ( $\gamma$ )	Zn added ( $\gamma$ )	Zn/Cu (by weight)	Adsorption zone width of Cu (mm)
1.9	—	—	5.0 4.9
"	38	20	5.1
"	95	50	6.0
"	190	100	8.8
"	950	500	12.4 12.2
"	9,500	5,000	Cu zone could not be recognized

If discrepancy of 1mm were allowed to be the permissible error and 5mm were assumed to be the limiting width for estimation, 1.9  $\gamma$  of copper could be determined in the presence of 50 times as much zinc. When zinc was increased so much as 500 times copper, the zone width became more than two times larger. In the presence of 5,000 times as much zinc, the adsorption zone of copper could no longer be recognized with hydrogen sulfide. With increment of zinc, the boundary of copper and zinc zones became indistinct. The zone of the former became larger because of, it was considered, the incomplete separation and subsequent remaining of zinc in copper zone, and finally they could not be separated at all.

### III. Detecton of copper in zinc

Decreasing amount of copper nitrate was adsorbed and its limit for detection on chromatogram was sought. The results are shown in Table 4.

When copper was present alone, its adsorption zone was clearly perceived with 0.1  $\gamma$ .

With less than 0.1  $\gamma$ ,

Table 4. Detection of copper which was present alone

Cu taken ( $\gamma$ )	Adsorption zone width of Cu (mm)	Remark
0.9	2.5	distinct
0.5	1.7	"
0.3	1.0	"
0.1	0.7	"
0.06	—	Cu zone could not be recognized

it could not be recognized with hydrogen sulfide.

In the presence of 1,000 times as much zinc, even 0.1  $\gamma$  of it could not be detected by the method hitherto adopted.

When too much zinc was present, the separation became difficult and copper was distributed over a wide range. Therefore, after the solutes had been developed thoroughly with water, a little amount of acid, say, 0.005 N HNO<sub>3</sub> 0.08 ml, was absorbed from the lower end of the strip and then again developed with water. Thus the dispersed copper was collected at the top of the acid zone.

Table 5. Detection of minute amount of copper in the presence of zinc

Cu taken ( $\gamma$ )	Zn/Cu (by weight)	Development	Coloring reagent	Remark
0.1	1,000	once	H <sub>2</sub> S	not detectable
"	"	twice	"	distinct
"	10,000	"	"	"
"	20,000	"	"	barely detectable
"	100,000	"	"	not detectable
0.06	10,000	"	"	detectable
"	20,000	"	"	barely detectable
"	100,000	"	"	not detectable
"	20,000	"	hydrorubianic acid	distinct
"	100,000	"	"	detectable

With hydrogen sulfide, 0.06  $\gamma$  of copper could be detected in the presence of 20,000 times as much zinc, when it was developed twice. And when hydrorubianic acid was used as a coloring reagent, 0.06  $\gamma$  of copper could be perceived in the presence of 100,000 times as much zinc. Anions had no effect on the limit of detection of copper.

The authors wish to express their thanks to Dr. Kenji Ono, Director of the Research Institute of Mineral Dressing and Metallurgy, for his encouragement.