

STRIPPING-LIKE PHENOMENON OF METAL DITHIZONATES  
IN GEL CHROMATOGRAPHY

Toshio DEGUCHI, Isao SANEMASA, and Hideo NAGAI  
Department of Chemistry, Faculty of Science, Kumamoto University,  
Kurokami, Kumamoto 860

Dithizonates of some metals, Zn(II), Cd(II), Pb(II), Hg(II), Bi(III), Co(II) and Cu(II) were chromatographed on Sephadex LH-20 gel column using carbon tetrachloride as an eluent. Among them, the metal ions of Zn, Cd, Pb, Hg and Bi were adsorbed at the top of the column, and the liberated dithizone was easily eluted out of the column, while dithizonates of Co and Cu were eluted out unchanged. These phenomena are very curious but somewhat analogous to the stripping procedure in the solvent extraction process. The mechanism of this "stripping-like phenomenon" seems to be difficult to elucidate but it can be conveniently applied to the purification of dithizone reagent as well as to separate some metal dithizonates.

Metal complexes that are insoluble in aqueous media are very frequently used for the separation and determination of some metal ions. Nevertheless, gel chromatographic studies of such complexes, except acetylacetonates,<sup>1)2)</sup> have rarely been made. In this study, gel chromatographic behaviors of some metal dithizonates were investigated.

Carbon tetrachloride was purified by using JIS method.<sup>3)</sup> Dithizone-carbon tetrachloride solution was also prepared by the JIS method. Sample solutions of metal dithizonates were prepared as follows. Zinc(II), cadmium(II), lead(II), mercury(II), bismuth(III), cobalt(II) and copper(II), as their nitrates, were dissolved in distilled water. Each of these solutions was adjusted to its proper pH<sup>4)</sup> with a buffer solution and then extracted with successive fractions of the dithizone-carbon tetrachloride solution (ca. 0.001 % W/V), until the color of the dithizone solution showed no change. These fractions were mixed together and used as the sample solution. Sephadex LH-20 (Pharmacia Fine Chemicals, Inc.) swollen with carbon tetrachloride was packed in a column (1.0 X 5.0 cm). At the top of the column, about 1 ml of the sample solution (metal dithizonate of  $2 \sim 4 \times 10^{-5} M$  in carbon tetrachloride) was fed and then eluted with carbon tetrachloride at  $20 \pm 1^\circ C$ . When a sample solution of Zn, Cd, Pb, Hg or Bi complex was used, the color of the solution immediately turned greenish at the top of the column bed. This green band was easily eluted out by successive elution with carbon tetrachloride and the visible absorption spectrum of the eluate was shown to be identical with a dithizone solution of carbon tetrachloride. On the other hand, the dithizone

complex of Co or Cu was not affected in the same treatment : the absorption spectrum of the eluate showed the complete coincidence with that of the metal dithizonate in carbon tetrachloride. According to the selective adsorption on the gel column, metal ions can be easily separated into two groups : one is retained tightly in the column as a result of the dissociation of the dithizonates (Zn, Cd, Pb, Hg and Bi) and the other is eluted out as their dithizonates (Co and Cu). The metal ions retained in the column were eluted out almost completely with prewashing (ca. 20 ml acetone) and ca. 5 ml of 0.01 M EDTA aqueous solution. Experimental results of the percentage recoveries of the metal ions adsorbed are given in Table I. Quantitative determinations of Hg and Bi were not performed.

Table I Recovery of each cation			
	Taken( $\mu$ g)*	Found( $\mu$ g)**	Recovery(%)
Zn	7.50	7.38	98.4
Cd	8.31	8.46	101.8
Pb	8.49	8.24	97.1

\* Determined by atomic absorption method, after sample solutions were back extracted with dil. hydrochloric acid.

\*\* Determined by atomic absorption method.

Applying this procedure, Zn, Cd and Pb present as impurities in commercial dithizone of analytical-reagent grade were eliminated and were analyzed by atomic absorption method. As the results, Zn(0.016%), Cd(not detectable) and Pb(0.004%) were found. The method described in this paper is applicable to simple and rapid purification of the dithizone reagent in respect of the removal of contaminants such as Zn, Cd, Pb, Hg and Bi.

It is interesting that this "stripping-like phenomenon" has been observed on elution with carbon tetrachloride despite fairly high stabilities of these metal dithizonates. On elution with chloroform (sample solution : metal-dithizonate extract in chloroform), the phenomenon was not so clearly observed as with carbon tetrachloride, that is, the liberated dithizone band (green) was followed by the proper-colored dithizonate band. When acetone was used as the eluent, all the dithizone complexes employed showed no change during the elution process. It is somewhat difficult to elucidate the "stripping-like phenomenon" because gel chromatographic behaviour with non-aqueous eluent is complicated. However, it would be possible to assume that the factors, i.e. the apparent stabilities of metal dithizonates in non-aqueous solvents, the nature of Sephadex LH-20 in various organic solvents and the polarities of the eluents, should play important roles in this characteristic phenomenon.

#### References

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