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A HIGHLY SELECTIVE METHOD FOR THE SPECTROPHOTOMETRIC DETERMINATION OF CADMIUM(II) WITH DITHIZONE AND *o*-PHENANTHROLINE

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A new method for the separation of cadmium(II) from zinc(II) with dithizone in the presence of *o*-phenanthroline was proposed. A green cadmium(II) dithizonate is extracted into chloroform at pH 2 and the green complex changes to red by shaking the extract with ammonia. The complete separation of cadmium(II) from zinc(II) is possible by the present method.

Dithizone is widely known as a sensitive reagent for the spectrophotometric determination of cadmium(II)[1]. However, the separation of cadmium(II) from zinc (II) with dithizone is a difficult problem. Meanwhile, we have shown that the selectivity in the metal chelate extraction can be improved by using a phenomenum, so-called synergistic effect[2]. In addition, we also found that the degree of the synergistic effect in the extraction of cadmium(II) with dithizone was more remarkable than in the case of zinc(II)[3]. By this finding, the complete separation of cadmium (II) from zinc(II) results.

Extraction procedure is as follows: The aqueous phase containing 0.01M *o*-phenanthroline, 0.1M sodium chloride, 1×10^{-6}M metal ions, ^{65}Zn and ^{115m}Cd tracers was vigorously shaken for 10 min. in a separatory funnel with an equal volume of the organic phase containing 0.002% dithizone. After the phases were allowed to separate, γ-ray activity of each phase was measured with a γ-ray spectrometer consisting of a NaI(Tl) well crystal and a Hitachi RAH 403 type 400 channel pulse height analyser, and the percent extraction (E) was obtained as a function of pH.

The resulting extraction curves are shown in Fig. 1. In the absence of *o*-phenanthroline, the separation of cadmium(II) from zinc(II) is difficult as far as single extraction procedure is employed. The extraction curve of cadmium(II) obtained by adding *o*-phenanthroline appears in lower pH region, compared with that of zinc(II). As a result, complete separation of cadmium(II) from zinc(II) can be performed by extracting the former ion at about pH 2. In this case, the extracted species is a green complex having absorption maxima at 443nm and 605nm, which changes to a red complex by shaking the extract with 5M ammonia. The red cadmium(II) dithizonate was confirmed to be stable at least for 3 hrs. A calibration curve for the red dithizonate is linear at 505nm, the sensitivity being 0.0020$\mu g/cm^2$.

The method was applied to the spectrophotometric determination of trace amounts of cadmium(II). In the extraction of cadmium(II) at about pH 2 with a 0.002% dithizone-chloroform solution in the presence of 0.01M *o*-phenanthroline, 100μg each of manganese(II), iron(II), cobalt(II), nickel(II), zinc(II), lead(II) and tin(II) did not interfere. The interference caused by the presence of a large amount of zinc(II) is eliminated by increasing the *o*-phenanthroline concentration. Mercury(II) and copper(II) interfered seriously and iron(III) oxidized dithizone. In order to establish a method for the determination of cadmium in a metallic zinc, the following separation scheme is proposed: Take an aliquot of a sample solution in a separatory funnel, and adjust the pH to ca. 2 by adding hydrochloric acid solution. Add 20ml of 0.002% dithizone in chloroform and shake the mixture for 5 min. Discard the organic phase and then add 10ml of 0.2M *o*-phenanthroline aqueous solution(pH = 2). The volume of the resulting aqueous phase should be about 20ml. Add 0.002% dithizone in chloroform and shake the mixture for 10 min. Allow the phases to separate and transfer the organic phase to another separatory funnel. Wash the organic phase with 20ml of 0.01M *o*-phenanthroline aqueous solution(pH = 2), and then with 10ml of 5M ammonia. Measure the absorbance of the resulting organic phase at 505nm against the reagent blank.

The above procedure was applied to the analysis of cadmium in a metallic zinc, which was found to contain 224 ppm of cadmium. The result agrees with the value obtained by atomic absorption spectrometry (223 ppm).

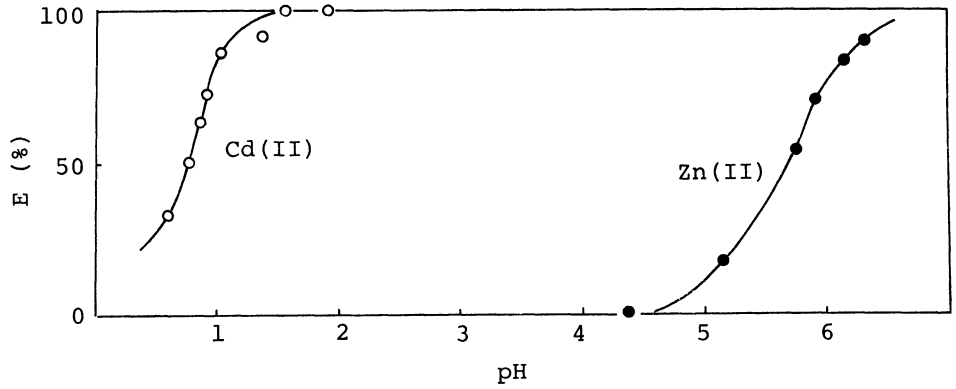

Fig. 1. Extraction curves

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