

CCA-1179

YU ISSN 0011-1643

544.65:546.48

Original Scientific Paper

Estimation of Cadmium Ion on Thin Layer Chromatograms by Fluorescence Scanning

N. Turina and S. Turina

Economic Faculty, University of Zagreb, 41000 Zagreb, Trg J. F. Kennedy 6, Yugoslavia; Institute of Materials Research, University of Zagreb, 41000 Zagreb, Salaja 2, Yugoslavia

Received July 2, 1979

A procedure for the quantitative estimation of Cd ions in aqueous solution, in the presence of other heavy-metal ions is proposed. Separation of Cd is made by TLC, with a solvent system containing acetic acid. The latter is necessary in order to obtain Cd spots suitable for fluorescence scanning after the formation of a fluorescent complex. Al ions cannot be separated from Cd ions by this procedure. Therefore, the fluorescent cadmium complex is generated with Titan Yellow, a reagent that does not react with aluminum ions. The practical value of the procedure is, however, limited by the narrowness of the useful Cd-concentration range.

Two major problems had to be solved before reliable results could be expected from the title method. Firstly, a chromatographic procedure had to be devised by which the cadmium spot will remain completely separated from and free of any species that might affect the formation of the fluorescent cadmium product, to be developed in situ, or to interfering with its light emission. Secondly, we had to decide on a convenient reaction to generate the fluorescent complex.

In attempts at solving the first problem we have examined the chromatographic properties of mixtures containing cadmium and potentially interfering ions¹. As far as the cadmium ion was concerned, we tried to base a chromatogram development procedure upon this ion's aptitude to form a stable complex, $[\text{CdCl}_4]_2\text{H}_2$, in a hydrochloric acid medium, and this complex easily forms hydrogen bonds to oxygen-containing organic liquids (butanol, acetone, etc.). However, with a solvent system containing *n*-butanol and hydrochloric acid, we initially observed that the cadmium ions move with the solvent front. The hydrochloric acid content was, therefore, reduced to hold cadmium ions behind the solvent front, but the spots on dried chromatograms were then rather diffuse. This appearance of the spots was attributed to an excessively too high energy barrier for Cd-ion phase transfer. By replacing a part of the chloride in the tetrachloro complex with acetate ligands we obtained a complex having a faster phase transfer, which gave satisfactory, well-defined cadmium spots. Other ions of interest also migrated in a satisfactory manner when treated by the procedure thus developed.

The second problem was far more difficult to solve. Preliminary experiments reduced our choice of reagents generating fluorescent products with cadmium to 8-hydroxyquinoline or Titan Yellow (Direct Yellow: 2,2'-[(diazonium)di-*p*-phenylene]bis[6-methyl-7-benzothiazolesulfonic acid] disodium salt). The first reagent seems to offer better advantages, especially, the range of linearity of the fluorescence intensity vs. concentration relationship is fairly wide with this reagent. Nevertheless, we finally decided to use Titan Yellow as a fluorogenic reagent. The reason for this decision was that 8-hydroxyquinoline also gave a fluorescent product with aluminum, a metal that we never succeeded in separating completely from cadmium, whereas Titan Yellow does not form a fluorescent aluminum complex. However, with samples from which aluminum is absent, the use of 8-hydroxyquinoline instead of Titan Yellow is recommended.

The cadmium complexes fluoresce most intensely in the presence of ammonia. However, as ammonia volatilizes rapidly from chromatograms, the fluorescence intensity declines too soon thus preventing quantitative evaluation. This shortcoming was overcome by using cyclohexylamine instead of ammonia. The small loss in fluorescence intensity with cyclohexylamine as opposed to the intensity with ammonia was largely offset by the gain in fluorescence stability.

EXPERIMENTAL

Samples used to test the procedure were aqueous solutions containing CdCl_2 in different concentrations, to which 0.1 mg/cm^3 of a foreign ion was added; three series were prepared, one with AlCl_3 , another with ZnCl_2 , the third with FeCl_3 .

Chromatoplates, $20 \times 20 \text{ cm}$, coated with a 0.1-mm layer of microcrystalline cellulose (no indicator), were purchased from KEMIKA, Zagreb.

Spotting: 10-mm^3 portions of a sample were traced over a 2-cm length of the starting line; six samples were run on the same plate.

Solvent system: *n*-butanol—water—acetic acid—hydrochloric acid, 70 : 10 : 18 : 2. [These ratios were found by Deming's optimization procedure²]. Chromatograms were developed in a solvent vapor-saturated atmosphere until the solvent front had advanced 15 cm above the starting line.

Fluorescent complex formation: air-dried chromatograms were sprayed with one of the reagents, then kept for five minutes at 95°C , and finally subjected to fluorescence scanning.

Reagent A (to be used with samples containing aluminum) had the following composition:

Titan Yellow	100 mg
Cyclohexylamine	1 cm^3
Ethanol	10 cm^3
Water	90 cm^3
Potassium carbonate	1 g

Reagent B (to be used with samples free of aluminum):

8-Hydroxyquinoline	100 mg
Cyclohexylamine	1 cm^3
Ethanol	100 cm^3

Fluorescence scanning: a CAMAG-Turner fluorometric scanner was used. Light emission was excited with filtered 254-nm radiation from a UV lamp provided additionally with a cut-off filter (400 nm). The emitted radiation was detected with a photomultiplier, and the photomultiplier output was recorded automatically. The area under the recorded curve was estimated by the Monte Carlo method³.

RESULTS

Figure 1 shows how well Cd- ions were separated from other ions. In figure 2 the results of quantitative analysis are shown. The obtained points lie on the proposed function (short dashed curve). Corresponding linear approximation, calculated as regression line, is given by the straight line (full line).

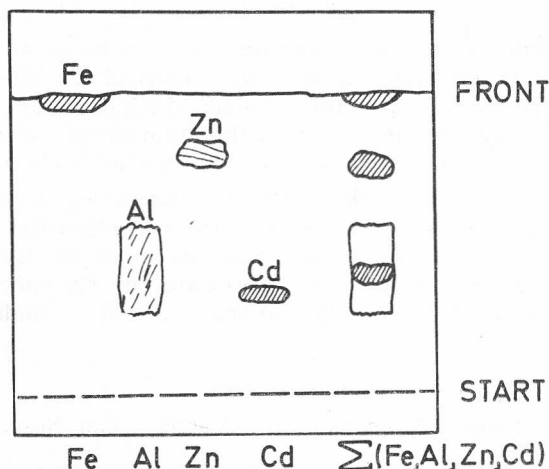


Figure 1. A thin layer chromatogram of Fe^{3+} , Al^{3+} , Zn^{2+} , Cd^{2+} and the mixture of the same. The chromatogram is obtained on the microcrystalline cellulose developed by a solvent: n-butanol, water, acetic acid and hydrochloric acid in volume proportion 70 : 10 : 18 : 2. Visualisation of spots was carried out under UV light after spraying with reagent: 8-Hydroxyquinoline (100 mg), Cyclohexylamine (1 cm³) and Ethanol (100 cm³).

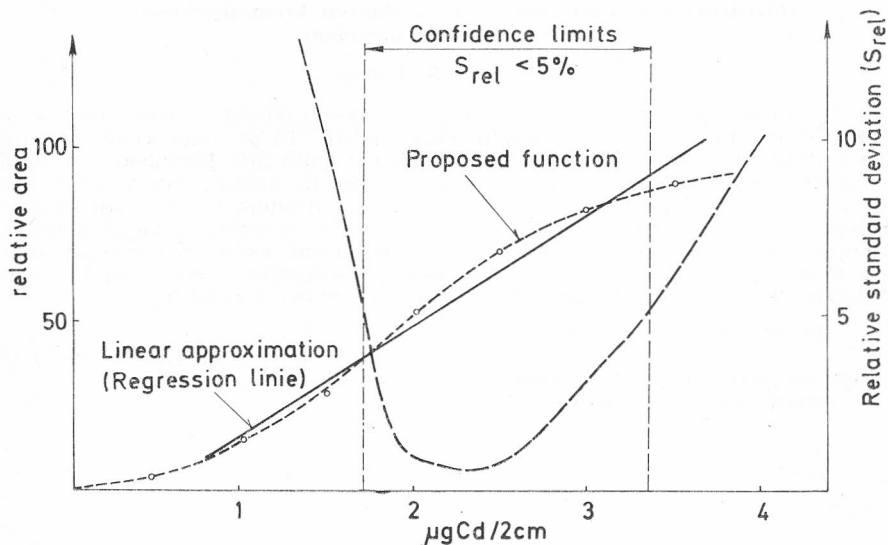


Figure 2. Relationship between the amount of cadmium applied on the start and relative area under the chromatographic curves. The short dashed line shows the proposed function of the relationship. The straight line (full line) is a linear approximation (regression line). The relative standard deviation of the regression line is given by the normal dashed line. The range of the linear relationship between the area under the recorded chromatographic curve and amount of Cadmium is limited by vertical lines.

The change of standard deviation of the regression line is shown by the normal dashed line, calculated from obtained data by means of equations given by Snedecor⁴. The range of the linear relationship between the area under the recorded curve and the amount of cadmium, where the relative standard deviation of estimation is under 5%, is limited by vertical lines.

DISCUSSION

Our results demonstrate that cadmium ions can be neatly separated from Zn and Fe ions, but not from Al ions, by means of TL chromatography on microcrystalline cellulose. Despite the presence of Al, cadmium can be estimated from fluorescence scan recordings when the fluorescent cadmium complex is generated with Titan Yellow which does not react with aluminum ions.

However, the usefulness of this method is limited by the narrowness of the concentration range within which the fluorescence intensity depends linearly on the concentration. Therefore, each analysis must be carried out in two steps. The first step should serve to appreciate the Cd concentration of the sample, and the second step would be the analysis proper, made with a suitably diluted sample.

REFERENCES

1. J. Michal, *Inorganic Chromatographic Analysis*. Van Nostrand-Reinhold Co., London 1973, p. 90.
2. S. Deming and S. Morgan, *Anal. Chem.* **45** (1973) 278A.
3. S. Turina and L. Klasinc, *Chromatographia* **7** (1974) 203.
4. G. W. Snedecor, *Statistical method*, Iowa State College Press, Ames, Iowa 1956, p. 122.

SAŽETAK

Određivanje kadmij-iona na tankoslojnim kromatogramima fluorescencijskom metodom

N. Turina i S. Turina

Opisan je postupak određivanja kadmija iz vodenih otopina pomoću tankoslojne kromatografije i mjerenja fluorescencije skaniranjem. To je omogućeno rješenjem problema dobivanja pogodnih mrlja kadmija, kao i dobivanja kompleksa sa stabilnom fluorescencijom. Poteškoću je izazivala činjenica da kadmij stvara čvrste kloro komplekse i time prelazi u mobilnu fazu i putuje s frontom otapala. Djelomičnom zamjenom klora s acetato ligandom postigla se bolja ravnoteža između mobilne i stacionarne faze, te je kadmij formirao dobro definirane mrlje odvojene od ostalih metala. Postojana fluorescencija mrlja dobivena je prskanjem s otopinom Titan žute uz dodatak cikloheksilamina, koji održava pH vrijednost konstantnom.

EKONOMSKI FAKULTET

i

INSTITUT ZA ISTRAŽIVANJE MATERIJALA
SVEUČILIŠTE U ZAGREBU
41000 ZAGREB

Prispjelo 2. srpnja 1979.