Fluorometric Determination of Cadmium in Polyvinyl Chloride Stabilizers and Polyvinyl Chloride in Nonaqueous Media

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A method for the fluorometric determination of cadmium(II) is proposed. The metal reacts with Calcein in *N,N*-dimethylformamide and the cadmium(II)-Calcein complex formed presents an emission maximum at 534 nm and several excitation maximum, the determination being carried out at an excitation wavelength of either 519 or 496 nm. Over the range 1–70 ng ml⁻¹, the fluorescence intensity is linear with the cadmium(II) concentration; the obtained precision (relative standard deviation) is about 4%. The proposed method permits the determination of cadmium(II) at the trace level. The method was applied to the determination of cadmium in cadmium organic salts, polyvinyl chloride (PVC) thermal stabilizers and PVC polymers.

Keywords Fluorometry, nonaqueous media, cadmium determination, Calcein, polyvinyl chloride

In the industrial field, cadmium is one of the elements that has more versatility. Its applications, whether in pure elements or in the form of organic or inorganic salts, include such areas as semiconductor technology, solder, batteries, corrosion or plastic industries. In this last field, two main uses stand out: as a colorant (cadmium sulfide) and as a polyvinyl chloride (PVC) stabilizer (cadmium organic salts).

The use of cadmium as a PVC polymer stabilizer has been widely extended during the last decades. The discovery of its harmful characteristics has lead to a search for substances that can replace it. Unfortunately cadmium is still being widely and increasingly used.¹ Cadmium stabilizers for PVC are commercially available in two different forms. In the solid state, they are mixed organic salts of barium and cadmium, whose organic form anions are acid radicals with a large number of carbon atoms (stearate, laurate, palmitate); in the liquid state form, they are usually organic salts mixtures of barium-cadmium-zinc (2-ethylhexanoate, naphthenate, phenolate, benzoate, neodecanoate). The percentage of cadmium in PVC stabilizers is between 2 and 7%, while PVC stabilized with cadmium salts containing less than 1%.

In spite of the importance of a cadmium determination, few studies have been published about it in this kind of sample. Thus, atomic absorption spectroscopy²⁻⁴ stands out, though polarography^{5,6} X-ray spectroscopy⁷ and molecular absorption spectrometry⁸ have also been used.

Calcein, synthesized in 1956 by Diehl and Ellingboe⁹, was primarily used as a metallofluorescent indicator in calcium titrimetric determination.^{10,11} Its use was extended rapidly to molecular fluorescent metal deter-

mination;¹² in this sense, papers by Koerbl¹³ for the fluorometric determination of Ca, and Wallach¹⁴ for the fluorometric determination of Al, Zn, Co, Cu and other elements, using Calcein as reagent, should be mentioned. Its acid-base properties^{15,16} and its structure¹⁷, have also been studied. Calcein is currently being used in fluorometric determinations as an immobilized reagent.¹⁸

In this work, a spectrofluorometric method for cadmium determination is proposed. The sample is dissolved in *N,N*-dimethylformamide (DMF), without acid attack, and an aliquot of the sample solution is allowed to react with Calcein in DMF. The method has been applied to cadmium determination in cadmium organic salts, PVC stabilizers and a PVC sample.

Experimental

Apparatus

All measurements were performed with a Shimadzu model RF 510 spectrofluorophotometer. Excitation and emission slits were set at 3 and 5 nm, respectively. One-centimeter quartz cells were used.

Reagents

All chemicals used were of analytical-reagent grade, and obtained from Merck.

Cadmium(II) stock solution, 300 µg ml⁻¹, prepared from cadmium acetate dihydrate by dissolution in DMF.

Cadmium(II) standard solution, 3 µg ml⁻¹, prepared by diluting the stock solution with DMF, immediately before use.

Calcein solution, 0.03% (m/v) in DMF. Prepared daily.

Organic solvent: ethanol, tetrahydrofuran (THF), acetic acid, dimethylformamide (DMF), pyridine and *t*-butylamine (TBA), were examined.

Organic samples

"STREM" Sterate and 2-ethylexanoate cadmium salts.

Cadmium-barium and cadmium-barium-zinc PVC stabilizers, and PVC sample obtained gently from "AISCONDEL" were examined.

Procedure

Place, in a 100 ml flask, an appropriate amount of sample (0.03–0.04 g cadmium salts, 0.3–0.4 g PVC cadmium stabilizer or 2–4 g PVC) and add 20 ml DMF. Heat in a water bath for 30 min. Allow the solution to cool and dilute it to 100 ml with DMF.

Pipet a portion of the sample, or the cadmium(II) standard solution, containing up to 0.7 µg of cadmium (II) into a 10 ml volumetric flask. Add 1 ml of Calcein solution and dilute with DMF. Allow the solution to react for five min. Measure the emission at 534 nm, while keeping the excitation monochromator at 519 or 497 nm. Prepare a blank solution in the same way, but free from cadmium.

Results and Discussion

Effect of bases and acids on fluorescence intensity

The influence of some organic bases on complex emis-

Table 1 Effect of TBA addition on the emission and excitation complex and reagent wavelengths

% TBA (v/v)	λ_{ex}/nm	λ_{em}/nm
—	519	534
0.001	519	534
0.010	520	535
0.10	521	535
1.0	523	539

No changes were observed at 496 nm. [Cd], 20 ng ml⁻¹; [Calcein], 1.11 µg ml⁻¹.

Table 2 Effect of sulfuric and acetic acids on the emission and excitation wavelengths for the complex and reagent

H ₂ SO ₄ , %(v/v)	λ_{ex}/nm	λ_{em}/nm	CH ₃ COOH, %(v/v)	λ_{ex}/nm	λ_{em}/nm
—	519	534	—	519	534
10 ⁻⁵	516	534	10 ⁻⁴	519	534
10 ⁻⁴	469	523	10 ⁻³	517	533
10 ⁻³	469	517	10 ⁻²	516	533
10 ⁻²	469	516	10 ⁻¹	511	525
10 ⁻¹	469	516	1	506	525
1	468	516	10	470	523

[Cd], 20 ng ml⁻¹; [Calcein], 1.11 µg ml⁻¹.

sion was studied. The addition of small amounts of pyridine (about 5%) slightly enhances the fluorescence intensity ($\% \Delta I = 100(I_{complex} - I_{blank})/I_{blank}$), but further addition of pyridine causes a sharp decrease; the slight enhancement observed does not justify the use of pyridine in the procedure. Addition of TBA also produces an increase in the emission intensity and a decrease in sensitivity; in this case, the spectral maxima of emission and excitation show shifts to longer wavelength (Table 1).

More than 0.001% (v/v) acetic acid and the presence of sulfuric acid in low concentrations (10⁻⁵%(v/v)), produces a sharp drop in the sensitivity, and sudden changes in the emission and excitation spectra. Table 2 shows the shift of the maximum emission and excitation wavelengths obtained upon the addition of sulfuric and acetic acids. This drop becomes sharper when using sulfuric acid (Fig. 1). These effects could be explained on the basis of the change of the hydronium ion concentration, which affects the complexation and fluorescent properties of Calcein.

Effect of organic solvents on fluorescence intensity

Ethanol produces an emission maximum of both complex and reagent as well as a minimum sensitivity (Fig. 2); likewise, the emission and excitation maxima shift less than with acetic or sulfuric acids. The presence of THF or water produces a similar effect as ethanol, though the addition of larger proportions of THF produces a maximum sensitivity; the spectral changes obtained with THF are less sharp (Table 3).

Fig. 1 Fluorescence intensity [$\% \Delta I = ((I_{complex} - I_{blank})/I_{blank}) \times 100$] variations of cadmium-Calcein on addition of organic acids: □, acetic acid; ♦, sulfuric acid. Parameters used are those specified in Table 2.

Fig. 2 Fluorescence intensity variations of cadmium-Calcein in ethanol, THF or water: $\blacklozenge$, ethanol; $\blacksquare$, THF; $\square$, water. Parameters used are those as specified in Table 3.

Fig. 3 Cadmium-Calcein complex and calcein alone, emission and excitation spectra in DMF (20 ng ml⁻¹ cadmium and 1.11 μ g ml⁻¹ calcein).

Table 3 Effect of THF, water and ethanol on the emission and excitation of the complex and reagent wavelength

THF, %(v/v)	λ_{ex}/nm	λ_{em}/nm	Water, %(v/v)	λ_{ex}/nm	λ_{em}/nm
—	519	534	—	519	534
10	519	534	0.5	519	534
20	515	532	1	519	534
30	512	530	2.5	518	534
50	512	530	5	514	532
80	512	530	10	509	530
100	511	530			

Ethanol, % (v/v)	λ_{ex}/nm	λ_{em}/nm
—	519	534
1	519	534
5	519	534
10	514	532
25	508	527
50	497	521
60	497	520
70	496	520
80	496	520

[Cd], 20 ng ml⁻¹; [Calcein], 1.11 μ g ml⁻¹.

Effect of reagent concentration and reaction time

At the wavelength of the maximum emission of a cadmium(II)-Calcein complex in DMF (534 nm), a blank solution also emits (Fig. 3), probably due to the presence of fluorescein as an impurity.¹⁹ For that reason the Calcein concentration must be kept to a minimum.

In this work, 1.11 μ g ml⁻¹ of the reagent was considered as being the optimum. On that condition, the complex was formed in five min; its fluorescence intensity remained constant for at least 90 min.

Calibration graph and precision

Over the range 1–70 ng ml⁻¹ of cadmium(II) in the final solution, the fluorescence intensity at 534 nm (519 or 496 nm excitation wavelength) was linear with the cadmium(II) concentration. The relative standard deviation for ten replicate determinations of 20 ng ml⁻¹ of cadmium was 4%.

Interference study

The effect of barium and zinc, the only elements associated with cadmium in that kind of samples, was studied. Less than 1 μ g of barium and 0.6 μ g of zinc do not interfere in the determination of 0.2 μ g of cadmium. Larger zinc concentrations do not interfere when 519 nm is used as the excitation wavelength. These results permit a cadmium determination in PVC cadmium stabilizer samples, since the weight ratio Ba/Cd or Zn/Cd is less than 1.5.²⁰

Applications

The method was applied to a cadmium determination in cadmium organic salts (cadmium stearate and cadmium 2-ethylhexanoate) with a certified cadmium content (16.55% and 28.19% respectively), in PVC barium-cadmium solid stabilizer and barium-cadmium-zinc liquid stabilizer and in a sample of PVC prepared

Table 4 Cadmium determination in cadmium organic salts, PVC cadmium stabilizers and PVC sample

Sample	Cadmium, %			RSD, % ^a	RSD, % ^b
	Certified	Found ^a	Found ^b		
Stearate	16.55	16.27	16.28	4	3
2-Ethyl hexanoate	28.19	28.93	28.60	4	3
Stabilizer (Ba-Cd)	—	5.78	5.42	4	4
Stabilizer (Ba-Cd-Zn)	—	2.60	2.40	3	3
PVC	0.28	0.31	0.30	3	4

a. 519 nm excitation wavelength. b. 496 nm excitation wavelength. RSD, relative standard deviation ($n=10$).

with the barium-cadmium-zinc stabilizer mentioned above. The obtained results using the standard addition method are presented in Table 4.

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(Received October 6, 1989)

(Accepted January 20, 1990)