Photoacoustic Determination of Cobalt after Solid-Phase Concentration on an Empore Silica-gel Thin-Layer Plate

Katsumi UCHIYAMA, Keiko OHSAWA, Yoshihiro YOSHIMURA, Junichi MINOWA, Takahiro WATANABE and Kazuo IMAEDA

Department of Analytical Chemistry, Faculty of Pharmaceutical Science, Hoshi University, Ebara, Shinagawa, Tokyo 142, Japan

A method used to determine trace amounts of samples in aqueous solutions is proposed. Cobalt ion was extracted as a 1-(2-pyridylazo)-2-naphthol (PAN) complex into chloroform. The extract was filtered through an Empore silica-gel TLC plate (2.5 cm square) having no backing material. Excessive PAN and other metal-PAN complexes were washed out through the TLC plate by filtering twice 5 ml of chloroform. Using these procedures only the cobalt-PAN complex was concentrated on the surface of the TLC plate. The photoacoustic signal of the TLC plate was detected by using a He-Ne laser as a light source. A linear relationship was obtained between the concentration of cobalt and the photoacoustic intensities in the 0.1 - 20 ppb range. A five-hundred-times concentration of Ni, Cu and Fe did not significantly interfere with the photoacoustic signal. The determination limit of cobalt when the sample volume was 100 ml was about 0.15 ppb.

Keywords Cobalt ion, cobalt-PAN complexes, thin-layer chromatography, photoacoustic spectrometry

Thin-layer chromatography (TLC) is a widely used separation technique which has many advantages, compared with other chromatography techniques. For example, the analysis and pretreatment of a sample is inexpensive and easier since all of the constituents are on the TLC plate and can thus be visualized simultaneously. However, for the detection and determination of samples, it is not superior to other methods.

We have reported on the photoacoustic spectrometry which is used to determine samples which are adsorbed on silica-gel or alumina layers.1-3 When TLC was used to separate complex samples into their constituents, after the TLC plate was scanned by a laser beam a photoacoustic chromatogram was easily obtained. This method is potentially more sensitive than conventional light reflection or transmission-type photometry.

On the other hand, we also tried to determine metal chelate by a combination of photoacoustic spectrometry and TLC.4 The chelating agent used was PAN; cobalt, nickel and iron were used as samples. In our previous report4 cobalt-PAN complexes in aqueous solutions were directly adsorbed by dipping a TLC plate into a stirred solution for over 8 h. A green cobalt-PAN complex was found to be adsorbed to the TLC plate. Other metal-PAN complexes were removed by developing chloroform to the top. The amount of cobalt was photoacoustically determined. Although this concentration method was easy to use, the determination accuracy was not very good for two reasons. First, at the stage of cobalt chelation on the silica-gel surface, it was difficult to form cobalt ion chelates uniformly on the TLC plate. Second, the complete removal of PAN and other metal-PAN complexes could not be achieved by developing chloroform. For a more sensitive and accurate determination, after metal-PAN complexes were extracted into the chloroform, the extract was filtered through the TLC plate. We describe in this paper a concentration method which uses TLC plates without any backing material as a filtration material as well as the photoacoustic determination of cobalt ions.

Experimental

Materials

The TLC plates used as filtration medium were Empore plates (3M Co., Ltd, No. 413501-1, silica-gel 90%, polytetrafluoroethylene 10%) with no backing materials. Standard solutions of nickel, cobalt, copper and iron used were purchased from Wako Pure Chemical (1000 ppm). Sample solutions were made by dilution of the 1000 ppm standard solutions. PAN (Tokyo Kasei) was used without further purification. Milli-Q ultra pure water was used throughout the experiment. The other reagents used were all of reagent grade.

Apparatus

The photoacoustic spectrometer used has been described elsewhere.4 A He-Ne laser (Hughes Aircraft, Model 3230-H-PC, 15 mW) was used as a light source.
The laser beam was chopped by a mechanical chopper and then led to the photoacoustic cell. After the photoacoustic signal was amplified by a self-made pre-amplifier at 40 dB, it was then fed into a lock-in amplifier (NF circuit block, Model 5600). A suction filtration apparatus (Advantec Co., KG-13A) was used to adsorb each sample onto the TLC plate. Figure 1 shows a schematic diagram of the apparatus. The chloroform solution containing metal-PAN complexes was dropped through the Empore TLC plate (cut into 2.5 cm squares) under reduced pressure. The cobalt-PAN complex was concentrated over a small area on a silica-gel surface. The pressure in the system was adjusted using a needle valve and a pressure gauge filled with water.

Procedure

Extraction of metal-PAN chelate was carried out according to the method reported by Galik. After a 50 ml portion of the sample solution containing these metals was placed in a Pyrex beaker, the pH was adjusted within the 5.0 to 6.5 range. Potassium bromide was then added to the solution to give a final concentration of 0.1 M. One milliliter of 5×10^-4 M PAN in an ethanolic solution was added to the sample solution; this was then allowed to stand for 2 h to complete chelation. The metal PAN chelates were extracted three times with 5 ml of chloroform into a round-bottomed flask. The chloroform was then evaporated to dryness under reduced pressure at 60°C, and the residual metal-PAN dissolved in chloroform and measured up to 5 ml.

Results and Discussion

In photoacoustic measurements the detection limits are usually determined by the background signal intensities and their reproducibilities. We first tried to examine the pretreatment of the TLC plate. Control plates were prepared by pouring a chloroform extract without cobalt onto Empore TLC plates treated by various methods. Four pretreatment procedures were examined. The first was tested without any treatment using a commercially available plate; the second one was treated with acetylacetone and ethanol; the third one was the same as the second, but with PAN deposited onto it; the fourth plate was successively treated with hydrochloric acid, methanol, acetylacetone and ethanol. Figure 2 shows the effect of the pretreatment on the photoacoustic signal intensities.

When PAN was deposited onto the TLC plate a large background photoacoustic signal was observed, since a large amount of the PAN was not completely removed by the chloroform. Since the TLC plate that was not treated with PAN (only acetylacetone) tended to retain the PAN in the sample solution, the background photoacoustic signal was larger than that for no treatment. The plate treated with hydrochloric acid showed a comparable background signal to that without any treatment. In order to prevent any deviation between lot numbers, TLC plates should be treated with hydrochloric acid.

We now discuss the way in which cobalt-PAN complex was effectively adsorbed on the TLC plate. There are many parameters that affect any reproducible and quantitative adsorption of cobalt-PAN complexes onto a TLC plate. Figure 3 shows the relationship between the applied sample volume (of which the amount of cobalt was constant at 32 ng) and the photoacoustic signal intensities. The photoacoustic signal decreased concomitantly with an increase in the sample volume to more than 4 ml. Although the decrease in the photoacoustic signal is thought to show that the cobalt-PAN complex was developed by a large amount of chloroform, no green cobalt-PAN complex was found on the other side of the plate. The signal intensity showed a maxima at a sample volume of 4 ml. To obtain a large reproducible photoacoustic signal, the sample volume was adjusted to 5 ml followed by a volume reduction of the extract by
rotary evaporation. Excessive amounts of PAN and other metal-PAN complexes were then removed by filtering twice with 5 ml of chloroform.

The method proposed here is similar to liquid chromatography with a short column. Because the retention behavior of the sample was fixed by the flow rate of the eluent, when the flow rate was faster than the dissolution rate of the sample to the eluent, the flow rate for suction of the sample solution would affect the development depth for metal-PAN complexes and excess PAN to the Empore TLC plate. Figure 4 shows the relationship between the flow rate of suction and the photoacoustic signal intensity. Excessive PAN remains on the TLC surface at a flow rate greater than 4.0 ml/min. A flow rate below 2.5 ml/min was recommended so as to reduce the background signal. Moreover, the reproducibility of the photoacoustic signal intensities across the different plates is almost dependent upon the reproducibility of the flow rate.

A linear relationship was obtained between the concentration of cobalt and the photoacoustic intensity in the 0.1–20 ppb range. Though the photoacoustic signal was measured at both 20 and 78 Hz, there seemed to be no difference between the two frequencies regarding signal saturation. To obtain a large photoacoustic signal it is better to measure the signal at 20 Hz. The determination limit was about 15 ng per plate, the amount corresponding to 0.15 ppb cobalt in a 100 ml sample solution. Although a greater sensitivity can easily be obtained if the sample volume is increased, in this case interference of the matrix should be studied.

Figure 5 shows the interference of metal ions which can chelate with PAN. At first, the interference of metal ions which form complexes with PAN was tested. The metal ions chelating with PAN under the experimental conditions were copper, iron, nickel and cobalt. These were added to 1.0 ppb cobalt sample solutions at various concentrations. Copper ions showed a decrease of 15% in the photoacoustic signal at 1000 ppb. At 1000 ppb of iron there was an increase in the signal of about 15%. Nickel did not significantly interfere with the photoacoustic signal up to 500 ppb. In the case of marine water, although a large amount of salt exists as the matrix for cobalt ions, the 3.5% existence of sodium chloride has no significant effect on the photoacoustic intensity. This superior characteristic of the method for the interference of other metal ions is thought to be due to the following reasons: the first is based on the selection (by extraction) of metal-PAN chelates with chloroform; the second is based on the chromatographic separation of metal-PAN complexes through the TLC plate to the depth direction.

The eluent is usually developed parallel to the stationary phase. The direction of development of the proposed method is at right angles to the stationary phase. Since cobalt-PAN complexes do not migrate from the origin in conventional TLC, the chelate is expected to stay at the surface of the Empore plate. Other metal-PAN complexes and excessive PAN are eluted through the Empore TLC plate. By continuing with this idea, if a weak eluent is used, these samples
would be separated from each other in the Empore TLC plate. Studies of stepwise elution using this method and photoacoustic determination are now in progress in our laboratory.

References


