Photoacoustic Spectrometry of Solid Samples. III. Microdetermination of Mercury as Hg Diphenylcarbazone Complex

Seiji KAWAMOTO, Yu YOKOYAMA,* and Shigero IKEDA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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Photoacoustic spectrometry was applied to the determination of michroamount of Hg diphenylcarbazone complex. The photoacoustic spectrum and diffuse reflectance spectrum almost agree with each other, showing an absorption maximum at 560 nm, as in the absorption spectrum of the complex in benzene solution. Determination of Hg was performed by measuring the intensity of photoacoustic signal at 560 nm. The normalized signal intensity increased linearly with the amount of mercury ion up to 100 ng, deviating from linear relationship downwards above 100 ng. The photoacoustic signal saturation caused by strong absorption of radiation was investigated.

Photoacoustic spectrometry of solid substances was applied to the determination of Ni, Cu, and Al as Ni dimethylglyoxime complex, Cu thiooxine complex, and Al quinalizarin lake, respectively.[1,2] The complex or lake was formed on filter paper according to the procedure of spot test and the signal intensity by the photoacoustic effect of colored substances was measured. As the amount of the colored substance increased beyond a certain limit, the relation between the amount of substance and normalized signal intensity was no longer linear and the intensity deviated from linear relationship downwards.

Mercury ion forms a strongly colored insoluble complex with diphenylcarbazone. The complex shows violet to blue color and is contrasted with reagent blank in acidic medium. It has been used as a color reagent of mercury in both extraction spectrophotometric determination and spot test. Dithizone is also a very sensitive color reagent, but the reagent itself is intensely colored. The present work was undertaken for a study on the determination of microamount of mercury with diphenylcarbazone and the photoacoustic signal saturation.

Experimental

Apparatus. The photoacoustic spectrometer assembly for this work was the same as previously reported.[1,2] Absorption spectra and diffuse reflectance spectra were measured with a Hitachi 124 type spectrophotometer and a Hitachi 323 type recording spectrophotometer with integrating sphere, respectively.

Reagent. The stock solution of mercury was prepared by dissolving distilled mercury metal in concentrated nitric acid and by diluting the solution with deionized water. The concentration of mercury and nitric acid were adjusted to 1150 ppm and 0.1 mol dm^{-3}, respectively. Standard solutions were prepared by diluting the stock solution and by adjusting the concentration of nitric acid to 0.02 mol dm^{-3}.

Diphenylcarbazone solution was prepared by dissolving 100 mg of diphenylcarbazone in 10 cm^3 ethanol immediately before use.

Other reagents were of reagent grade and were used without further purification. Water was deionized through ion exchange resin after distillation. Carbon black paper was prepared by smoking benzene soot on filter paper.

Procedure. Diphenylcarbazone test paper was prepared by impregnating filter paper with alcoholic solution of diphenylcarbazone. Hg diphenylcarbazone complex was formed by dropping 5 mm^3 of mercury standard solution on a diphenylcarbazone test paper of 10 mm in diameter. The test paper was immediately mounted on the sample holder by use of transparent double-sided adhensive tape and then photoacoustic signal intensity was measured.

Acidity. The sensitivity of mercury determination with diphenylcarbazone depends on the acidity of solution, decreasing with increasing acidity. However, in neutral or weakly acidic solution, other heavy metals also give colored compounds with diphenylcarbazone. With increasing acidity, interference of other ions decreases, and in 0.2 mol dm^{-3} nitric acid solution the diphenylcarbazone reaction is almost specific for mercury.[3] The acidity of solution should be chosen according to the circumstances, especialy in consideration of foreign ions. In the case of high acidity, Hg diphenylcarbazone complex formed on filter paper gradually decomposed to decolorize because of concentration of acid due to evaporation of water. In addition nitric acid vapor attacks the diaphragm of the microphone. Therefore in the present study, the concentration of nitric acid in mercury solution was adjusted to 0.02 mol dm^{-3} and the signal intensity was measured immediately after complex formation.

When sulfuric acid was used, the photoacoustic signal intensity of blank was higher and Hg diphenylcarbazone complex was less stable than in nitric acid medium.

Results and Discussion

Photoacoustic Spectrum of Hg Diphenylcarbazone Complex. The photoacoustic spectrum was obtained by calculating the normalized intensity (I_n) at each wavelength and by plotting the value against wavelength.[1,2] The photoacoustic spectrum of Hg diphenylcarbazone complex thus obtained is shown in Fig. 1. The absorption maximum appears at *ca.* 560 nm and the photoacoustic spectrum of benzene solution of the complex except for broadening of the absorption band. It also agrees with

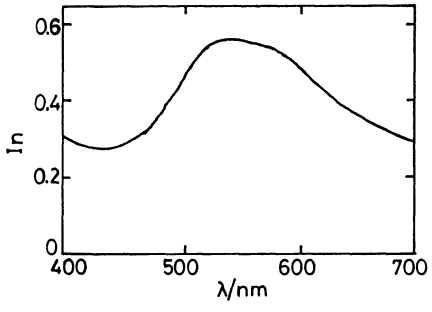

Fig. 1. Photoacoustic spectrum of Hg diphenylcarbazone complex.

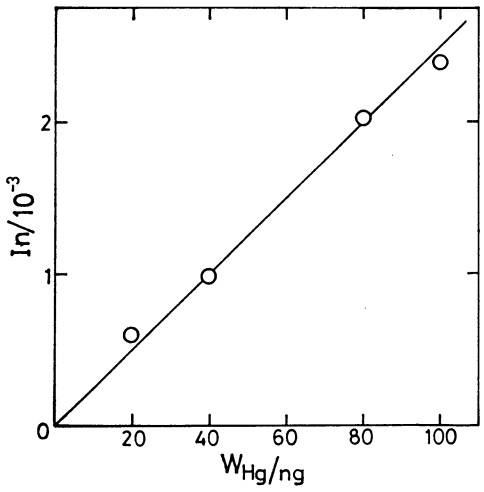

Fig. 2. Calibration curve for mercury. Wavelength: 560 nm.

the diffuse reflectance spectrum.

Determination of Microamounts of Mercury by Photoacoustic Spectrometry. Hg diphenylcarbazone complex was formed by the analytical procedure on diphenylcarbazone test paper. A blank diphenylcarbazone test paper was prepared by dropping 5 mm^3 of 0.02 mol dm^{-3} nitric acid. The photoacoustic signal intensity of sample, blank and carbon black were measured at 560 nm, and the normalized signal intensity was calculated. The calibration curve obtained by plotting the normalized signal intensity against mercury amount was linear from 20 to 100 ng as shown in Fig. 2. The detection limit for mercury (20 ng) was lower than for diffuse reflectance spectrometry of the complex (40 ng),[4] and that for extraction photometry of the complex in benzene (5 μg).[5]

TABLE 1. DETERMINATION OF Hg

Taken W_{Hg}/ng	Found W_{Hg}/ng		
20	26	22	26
40	38	37	42
80	84	84	76
100	100	92	92

By use of the calibration curve, determination of Hg was carried out. The results are summarized in Table 1. Samples containing 20 ng of Hg showed comparatively higher results. The error was within ±8% for samples containing Hg from 40 to 100 ng.

Saturation of Photoacoustic Signal. The photoacoustic effect of solid sample was analyzed theoretically by Rosencwaig and Gersho.[6] The expression giving the amplitude of pressure fluctuation by photoacoustic effect in a cell is simplified, when the thermal diffusion length of the sample (μ_s) and the optical absorption length ($\mu_\beta = 1/\beta$) are appreciably larger than the sample thickness (l). Thus the amplitude of pressure fluctuation in the cell is given by

$$Q = A[1-\exp(-\beta l)], \quad (1)$$

where A is a constant which depends on thermal property of the sample cell and of the filler gas, geometrical structure of the cell, intensity of the incident monochromatic light and the ambient pressure and volume, and β denotes the optical absorption coefficient of the solid sample (in cm^{-1}) for the wavelength λ, and is $2.3\times\varepsilon C$ where ε is the molar extinction coefficient of the sample and C is the sample concentration. Since the exponential term of Eq. 1 is approximated by $1-\beta l$ for a very small value of βl, Eq. 1 becomes

$$Q \cong A\beta l = 2.3A\varepsilon Cl. \quad (2)$$

It is obvious from Eq. 2 that the calibration curve obtained by plotting the signal intensity against sample amount is linear for a small amount of sample. For a higher value of βl, however, the higher order terms of expantion terms of $\exp(-\beta l)$ can be ignored. When $\exp(-\beta l)$ is developed up to the second order term, Eq. 1 becomes

$$Q = A\beta l\left(1-\frac{\beta l}{4}\right). \quad (3)$$

When βl increases infinitely and the sample absorbs most part of the incident light, $\exp(-\beta l)$ nearly equals zero and therefore Eq. 1 becomes

$$Q = A. \quad (4)$$

It is obvious from Eqs. 3 and 4 that, as the absorption coefficient increases or sample thickness becomes larger, saturation of the signal intensity occures. As a result, the signal intensity approaches gradually to a constant value independent of the absorption coefficient and the sample thickness.

Since carbon black might be assumed to be an approximately black body absorbing visible light perfectly, the normalized signal intensity (I_n) obtained by taking the ratio of the signal intensity of the sample to that of carbon black is given as follows by means of Eqs. 1 and 4.

$$I_n = \frac{S_s}{S_b}[1-\exp(-\beta l)], \quad (5)$$

where the coefficient S_s/S_b is a correction term introduced by considering that the photoacoustic signal intensity is proportional to surface area of the substance, and S_s and S_b are surface areas of samples and carbon black, respectively.

Since Eq. 5 was derived on the assumption that $\mu_s > l$, it is necessary to examine the validity of assumption. Experiments were carried out with Hg diphenylcarbazone complex formed on filter paper. Rosencwaig and Gersho[6] showed that in the case of $\mu_s > l$ and $\mu_\beta > l$, the photoacoustic signal intensity (I) is proportional to the reciprocal of chopping frequency of the incident light (ω^{-1}), but the signal intensity is proportional to $\omega^{-3/2}$ in the case of $\mu_s < l$ and $\mu_\beta > l$. Thus the dependence of the photoacoustic signal intensity of Hg diphenylcarbazone complex on the chopping frequency was investigated. The relation between photoacoustic signal intensity (in μV) and ω^{-1} is shown for the range of the chopping frequency from 17—125 Hz in Fig. 3. In this chopping frequency range the signal intensity is proportional to ω^{-1}. It is concluded that Hg diphenylcarbazone complex prepared in this way satisfies $\mu_s > l$.

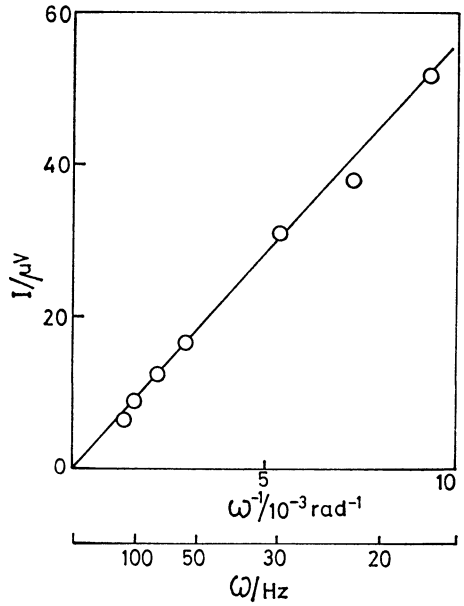

Fig. 3. Photoacoustic signal intensity of Hg diphenylcarbazone complex *versus* reciprocal of the chopping frequency.

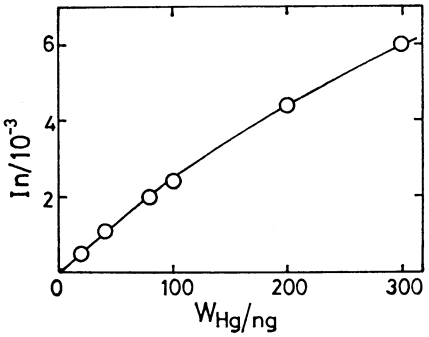

Fig. 4. Observed normalized signal intensity of Hg diphenylcarbazone complex *versus* weight of Hg in complex.

The relation between the photoacoustic signal intensity and mercury amount dropped onto filter paper was linear for 20—100 ng of Hg, as shown in Fig. 2. In order to examine the relation above 100 ng of Hg, measurements were extended up to 300 ng of Hg. The results are shown in Fig. 4. The normarized signal intensity of sample containing Hg above 100 ng deviates from linear relationship downwards. The normalized signal intensity was calculated from Eq. 5 by substituting the following values; the molar extinction coefficient ($\varepsilon=4.5\times10^4$), which was determined on benzene extract of the Hg complex, S_s which was measured on the spot of complex, $S_b=0.785$ cm^2, the concentration of complex in filter paper (C), which was calculated from mercury amount dropped onto test paper and the volume of spot [$S_s\times$thickness of filter paper (l)]. The normalized signal intensity calculated by use of these parameters is plotted against the mercury amount in Fig. 5. Figures 4 and 5 almost agree with each other except for the scale of the ordinate. And it is understood that the saturation of normalized signal

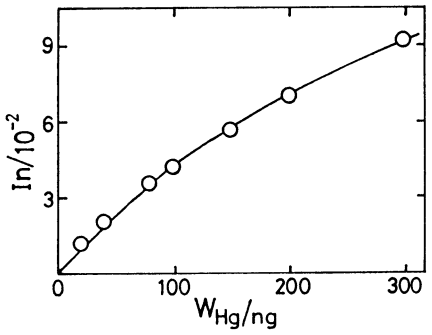

Fig. 5. Calculated normalized signal intensity of Hg diphenylcarbazone complex *versus* weight of Hg

intensity is mainly due to the terms of higher order of $[1-\exp(-\beta l)]$ in Eq. 5.

Disagreement between the calculated and the observed intensities might be explained by some of the following factors: 1) Validity of the assumption that carbon black paper used is a black body, 2) estimation of the term βl, and 3) estimation of the effective particle size of solid samples.

When the black standard is not a perfectly black body, it is expected that the observed value is larger than the calculated value. Since this is not the case, the experimental results can not be explained by this factor. A light absorber having a microscopically heterogeneous distribution in a dispersed system should show apparently a smaller absorption coefficient than that shown in a homogeneous system. The value of ε measured in homogeneous solution would be too high to used in Eq. 5, giving a higher calculated photoacoustic intensity. In fact the calculated intensity is one order higher than the observed one. On the other hand, since the incident beam reflects repeatedly within texture of filter paper before passing through it, the effective optical path length would be greater than the sample thickness (l). Therefore lowering of I_n caused by decrease in apparent absorption coefficient would be cancelled partially by increase in effective optical path length.

Absorption by particles is largely affected by particle size, the smaller the particle size, the higher the photoacoustic intensity. Usually the particle size of soot produsd by burning is approximately 50—500 nm. Crystals (approximately 1—30 μm) of Hg diphenylcarbazone complex formed in filter paper can be observed by microscopy. Effective surface area of benzene soot seems to be at least one order larger than that of the complex. This might be the principal cause for the difference between the observed and the calculated intensities.

Saturation of the photoacoustic signal should influence the shape of photoacoustic spectrum as well as calibration curve. As is obvious from Eq. 2, the photoacoustic spectrum can reflect wavelength dependency of β for a small value of βl. However, when the photoacoustic intensity is beyond the range of proportionality around the absorption maximum, the center of the absorption band should be flattened for saturation of absorption. Therefore in measurement of the photoacoustic spec-

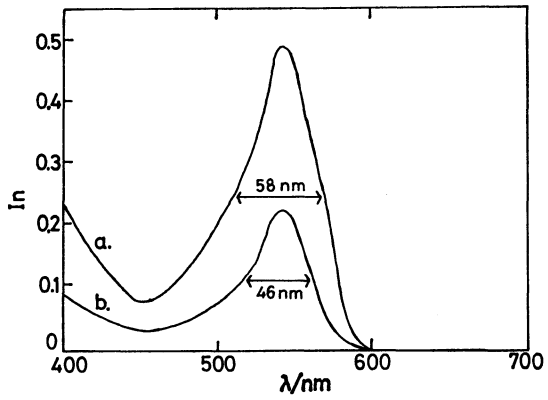

Fig. 6. Photoacoustic spectra of Ni dimethylglyoxime complex.
(a) $W_{Ni}=3$ μg, (b) $W_{Ni}=0.7$ μg.

trum, it is desirable to restrict the value of βl within the proportionality range by reducing the concentration of absorber and/or the thickness of samples. The phenomenon of saturation could easily be demonstrated by photoacoustic spectra of Ni dimethylglyoxime complex. Figure 6 show the spectra of samples containing 0.7 and 3 μg of Ni. The former belongs to the linear part of calibration curve for nickel and the latter to the saturation part. The half maximum width of the absorption band at 545 nm was 46 and 58 nm for the former and the latter samples, respectively. The absorption band is broadened due to saturation of photoacoustic signal.

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