Journal of Pharmaceutical & Biomedical Analysis
Vol. 9, No. 9, pp. 769–771, 1991
Printed in Great Britain

0731–7085/91 $3.00 + 0.00

Short Communication

Determination of phenylmercury(II) by photometric titration with dithizone in a mixed organic medium

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Keywords: *Phenylmercury(II) determination; photometric titration; dithizone.*

Introduction

The potent biocidal activity of the phenylmercury(II) cation has been exploited, among others, in the agricultural, paint and paper industries and in the formulation of pharmaceutical preparations such as solutions, antiseptic creams and ophthalmic solutions.

Dithizone has been by far the most frequently used photometric reagent in the determination of phenylmercury(II) since the early studies by Irving *et al.* [1, 2] on the interaction between the cation and dithizone in liquid–liquid systems and on the spectroscopic features of the resulting complexes. Most of the procedures developed to this end have been reported by Miller *et al.* [3] and are based on the formation of a 1:1 complex (i.e. the primary dithizonate PhHgHDz) by liquid–liquid extraction and on the subsequent absorbance measurement on the organic phase. Howorka and Howorka [4] and Kassebaum [5] reported semi-quantitative methods for the determination of phenylmercury(II) in ophthalmic solutions using dithizone as reagent. Other procedures are simpler and less laborious but either require expensive instrumentation (e.g. a gas chromatograph [6] or a non-flame atomic absorption spectrometer [7]) or cannot be applied to the low concentrations at which phenylmercury(II) usually occurs in pharmaceutical preparations (e.g. volumetric titration with thiocyanate [8]).

The high sensitivity of dithizone can be combined with the simplicity and affordability of single-phase photometric titrations. So far this advantageous association has scarcely been exploited [9–11].

The present paper reports on the photometric determination of phenylmercury(II) with dithizone in a mixed medium of water, chloroform and ethanol. This medium allows in many instances the determination of phenylmercury without any previous treatment of the sample, as in ophthalmic or in topical fungicidal preparations that are simple aqueous or organic solutions of the active compound.

Experimental

Apparatus

Visible spectra were recorded on a Perkin–Elmer 554 UV–vis spectrophotometer. Photometric titrations were carried out with a Vitatron UC-200 S photititrator fitted with a modified titration cell (2-cm light-path) capable of holding larger than normal volumes (25 ml), and with an interference filter allowing the passage of light wavelengths longer than 580 nm. Glass burettes fitted with Teflon stopcocks and of a precision of ±0.01 ml were also used.

Reagents

Phenylmercury(II) solutions were prepared by weighing the required amounts of the nitrate ($PhHgNO_3PhHgOH$, Ventron) (recrystallized twice in water) and were stored in glass flasks in the dark.

Stock solutions of dithizone in chloroform were made from the solid reagent (Merck p.a. or Carlo Erba RPE), which was purified by the

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method of Iwantscheff [12]. The purity of solutions was evaluated according to the criterion involving the ratio of absorbances at 605 and 440 nm [13]. Only those solutions with an absorbance ratio $R_A \geq 2.64 \pm 0.02$ (consistent with the theoretical value, $R_A = 2.66$ [14]) were accepted for use. These solutions were stored in non-actinic flasks in a refrigerator under a 1-cm thick layer of 1 M sulphuric acid. The titrant solutions ($5–10 \times 10^{-5}$ M) were standardized by spectrophotometric titration by a method developed in the authors' laboratory [11].

The mixed medium was prepared from deionized, double-distilled water, perchloric acid, ethanol and analytical reagent-grade chloroform which had been distilled and stabilized with 0.5% (v/v) of ethanol.

Titration procedures

Procedure A. Place 5.00 ml of standard solution of dithizone (5×10^{-5} M in chloroform), 15 ml of ethanol and 2 ml of 0.5 M perchloric acid into the titration cell (2-cm light-path) of a photometer provided with an interference filter of 580 nm. Titrate with the aqueous solution of the sample (phenylmercury(II) content, 10–230 ppm) with continuous stirring under subdued room lighting. Record the absorbance (corrected for the dilution effect) as a function of the titrant volume added until a constant absorbance value is obtained. On the graph obtained, extrapolate the linear segments and calculate the titration end-point from their intercept.

Procedure B. Similarly, place 3.00 ml of the aqueous solution of the sample (phenylmercury(II) content lower than 16 ppm in this case), 15 ml of ethanol and 2 ml of 0.5 M perchloric acid into the titration cell. Titrate the mixture with a standard solution of dithizone in chloroform (10^{-4} M) until the absorbance reaches a value close to unity. Determine the titration end-point as in Procedure A.

Results and Discussion

Titration medium

Water was used in the titration medium because the analyte occurs chiefly in aqueous solutions. On the other hand, chloroform is one of the two solvents in which dithizone is usually employed; solutions in chloroform possess a high molar absorptivity and are stable enough for analytical purposes [15]. Although Le Goff and Trémillon [9] used a mixture of acetone and water as solvent for their photometric titrations with dithizone, the practice is inadvisable since, as acknowledged by its proponents, the reagent is unstable in acetone and in aqueous basic media [15]. Chloroform, on the other hand, allows potential metal interferents to be removed by liquid–liquid extraction in the presence of a high concentration of chloride [3, 10]. Finally, ethanol is the ideal solvent to enable mixtures of chloroform and water to be prepared.

Spectroscopic features

Variations in the proportions in which the three solvents were used in the mixed medium did not significantly affect the visible spectrum of the species PhHgHDz. However, an increasing proportion of chloroform in the medium resulted in a linear increase in the absorbance and a significant shift of the absorption maximum to longer wavelengths. This effect appears to be related not only to the influence of the dielectric constant of the medium on the dissociation equilibrium of dithizone but also to the preferential solvation of dithizone in chloroform, as suggested by Bag and Freiser [16]. Figure 1 shows the visible spectra of dithizone, the PhHgHDz complex and the HDz^- anion in the medium of water–chloroform–ethanol (10:35:55, v/v).

The absorption maximum of dithizone ($\lambda_{max} = 597$ mm, $\epsilon_{max} \simeq 40{,}800$) and PhHgHDz ($\lambda_{max} = 473$ mm, $\epsilon_{max} \simeq 31{,}000$) are two potentially useful wavelengths. The

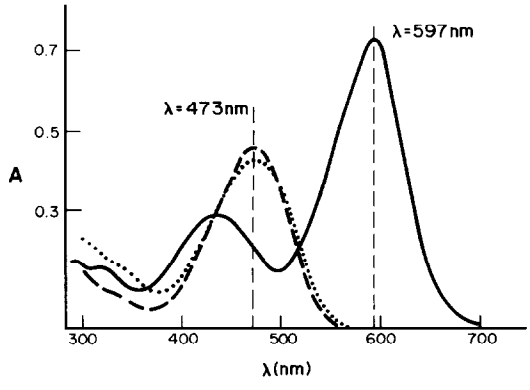

Figure 1
Absorption spectra of dithizone (——), ammonium dithizone (. . . . . .) and phenylmercury(II) dithizonate (– – – – –) in water–chloroform–ethanol (10:35:55, v/v). Concentration of each species was about 2×10 M.

Table 1
Photometric titration of phenylmercury(II) nitrate with dithizone in a water–chloroform–ethanol medium*

		Phenylmercury(II) (ppm)				
	n	Added	Found	Error (%)	SD (ppm)	RSD (%)
Procedure A	3	123.3	123.9	0.5	0.7	0.6
Procedure B	3	2.50	2.39	−4.5	0.08	3.4

* For details of the solvent medium, see Experimental.

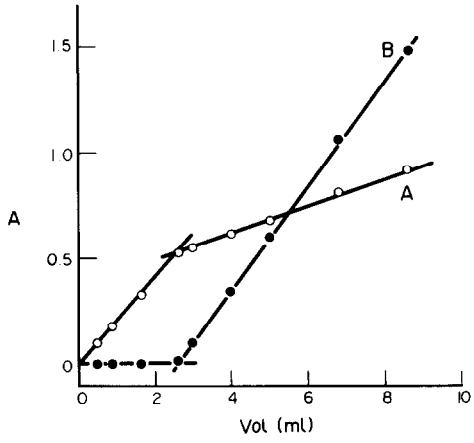

Figure 2
Curves obtained in the photometric titration of phenylmercury(II) nitrate with dithizone in water–chloroform–ethanol (10:35:55, v/v). Wavelength: (A) 473 nm; (B) 597 nm.

latter wavelength is somewhat less convenient as it results in a less abrupt variation of the absorbance at the end-point. Figure 2 shows the photometric titration curves obtained at these two wavelengths.

None of the typical photochromic effects of dithizone and some of its complexes was observed under the working conditions, probably as a result of the presence of water and ethanol [15]. The reproducibility of the results was considerably improved by working under subdued room light.

Optimal pH-range

The titration medium should have an acidity of less than 1 M in order to ensure the stability of the C—Hg bond [3]. A mineral acidity of about 0.05 M was found to be optimal in this respect as it efficiently hindered all side equilibria potentially interfering with the formation of the main complex (PhHgHDz–$(PhHg)_2Dz$) [2] or with the photometric detection of the end-points [PhHgHDz (yellow)–$PhHgDz^-$ (magenta) and, especially, H_2Dz (blue)–HDz^- (orange)] [13]. Nitric acid proved to be inadequate on account of its oxidizing character; in fact, perchloric acid solutions were found to be more stable.

Accuracy and precision

The two analytical procedures are applicable to different concentrations of phenylmercury(II). Thus, Procedure A, which involves the titration of a dithizone standard solution with the phenylmercury(II) sample solution, allows 10–230 ppm of this cation to be determined with commendable accuracy and precision (Table 1). On the other hand, Procedure B, in which the phenylmercury(II) sample solution is titrated with a dithizone standard solution, allows cation concentrations lower than 16 ppm to be determined with a precision (RSD) of 3.4% and an error of 4.5% for 2.5 ppm of $PhHg^+$.

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[*Received for review 5 December 1990; revised manuscript received 11 April 1991*]