

Differential spectrophotometric determination of phenylephrine in eye-drops: the ΔAr method

In the classical spectrophotometric method for the determination of phenylephrine, the absorbance A in 0.1N sodium hydroxide is related to the concentration C by an equation $A = a_1 + b_1C$, where a_1 is the 'blank' absorbance and b_1 is the absorptivity. In the relative absorbance method (Pall, Svehla & Erdey, 1964; Svehla, 1966; Belevov, 1970), in which the absorbance of the solution of unknown concentration C is compared with that of a reference solution of known concentration C_r and similar composition, the relative absorbance Ar is related to C and C_r by an equation $Ar = b_2(C - C_r) = a_2 + b_2C$. Another modification, which also partially compensates for interference by other components of the eye-drops, is to measure the difference between the absorbance of two solutions of the same concentration, one in 0.1N sodium hydroxide and the other in 0.1N sulphuric acid. The absorbance difference ΔA is attributed solely to the phenylephrine and it is assumed that the irrelevant absorption is independent of the pH (Aulin-Erdtman, 1955; Junejo & Glenn, 1956). This leads to an equation $\Delta A = a_3 + b_3C$.

It is now proposed to use a combination of the Ar and ΔA methods, so as to gain the benefits of both methods. The relative absorbance difference ΔAr is related to C by an equation $\Delta Ar = a_4 + b_4C$.

Experiments were made with concentrations of phenylephrine leading to absorbances or absorbance differences in the range 0.15 to 0.9, and with a reference solution giving an absorbance of about 0.4. The measurements were made in 0.1N sodium hydroxide at the maximum at 238 nm, and in 0.1N sulphuric acid at the maximum at 274 nm. The relation between absorbance or absorbance difference and concentration (C , μg per ml) were found to be as follows:

$$\begin{aligned} A &= -0.0076 + 0.0534C \\ Ar &= -0.4293 + 0.0530C \\ \Delta A &= 0.0028 + 0.0421C \\ \Delta Ar &= -0.3344 + 0.0419C \end{aligned}$$

Recovery experiments by the four methods, with 12 determinations by each method, showed the following mean result and coefficient of variation: A , $105.31 \pm 2.64\%$; Ar , $101.21 \pm 1.73\%$; ΔA , $101.90 \pm 3.18\%$; ΔAr , $100.96 \pm 1.48\%$. It is seen that both the Ar method and the ΔA method lead to better accuracy because of compensation for irrelevant absorption, but use of the ΔAr method gives both better accuracy and better reproducibility.

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