Spectrophotometric Determination of Periodate With Salicylaldehyde Guanylhydrazone. Indirect Determination of Some Organic Compounds Using the Malaprade Reaction

Juan Josè Berzas Nevado
Department of Analytical Chemistry, University of Extremadura, Badajoz, Spain

Pablo Valiente Gonzàlez
Department of Analytical Chemistry and Electrochemistry, University of Extremadura, Badajoz, Spain

Salicylaldehyde guanylhydrazone reacts with periodate in ammoniacal buffer (pH 9.2) to give a red colour. The reaction can be used for the spectrophotometric determination of trace amounts of periodate. The maximum molar absorptivity at 495 nm is 3.5×10^3 l mol^{-1} cm^{-1} and Beer's law is obeyed between 10 and 45 p.p.m. of periodate with a relative standard deviation of 0.5%. The determination of periodate can be performed in the presence of a 50-fold (m/m) excess of iodate. The method was applied to the indirect determination of several organic compounds via the Malaprade reaction and good results were obtained.

Keywords: *Periodate determination; spectrophotometry; salicylaldehyde guanylhydrazone; ethylene glycol, glycerol and tartaric acid*

Periodate is used widely to determine a number of organic compounds by means of the Malaprade reaction. However, there are few methods described in the literature for the determination of trace amounts of periodate in the presence of a moderate to large excess of iodate. Callejòn Mochòn and Muñoz Leyva have proposed two methods for the spectrophotometric determination of periodate based on the oxidation reactions of this anion with the bisthiosemicarbazones of dimedone[1] or cyclohexane-1,3-dione.[2]

In both methods, the reaction time must be strictly controlled (3 and 10 min, respectively) in order to measure the absorbance accurately. Recently, Verma *et al.*[3] proposed a spectrophotometric method for the determination of periodate using amodiaquine as reagent. Up to a 100-fold excess of iodate can be tolerated, but it is necessary to perform two consecutive extractions in order to determine between 10 and 60 p.p.m. of periodate.

In this work, a simple, sensitive and rapid spectrophotometric method for the determination of periodate using salicylaldehyde guanylhydrazone as reagent is proposed. Up to a 50-fold excess of iodate can be tolerated and, in consequence, the indirect determination of compounds that are oxidised by periodate (Malaprade reaction) can be performed. The method was applied to the indirect determination of ethylene glycol, glycerol and tartaric acid and good results were obtained.

Experimental

Reagents

All solvents were of analytical-reagent grade.

Salicylaldehyde guanylhydrazone (SAG) solution. Transfer 0.1 g of SAG (prepared by the method of Thiele and Bihan[4]) into a 100-ml calibrated flask, add 23 ml of dimethylformamide and shake until all the SAG is dissolved, then dilute to volume with water. This solution is stable for at least 24 h.

Buffer solution, pH 9.2. Prepared by dissolving 14 g of ammonium chloride and 19 ml of concentrated ammonia in water and diluting to 1 l.

Potassium periodate solution, 0.01 M. Prepared by dissolving an accurately weighed amount of analytical-reagent grade potassium periodate in water and standardising the solution iodimetrically. The solution was diluted as required, just before use.

Stock solutions of ethylene glycol, glycerol and tartaric acid were prepared fresh using analytical-reagent grade chemicals.

Procedures

Determination of periodate

To a solution containing up to 1100 µg of periodate, in a 25-ml calibrated flask, add 6.5 ml of 0.1% SAG solution, 5 ml of pH 9.2 buffer solution and dilute to volume with water. The absorbance must be measured between 15 and 35 min after mixing the reagents at 495 nm against water.

Indirect determination of ethylene glycol and glycerol

A sample aliquot containing 32–200 µg of ethylene glycol or 90–220 µg of glycerol was mixed with 2 ml of 2.64×10^{-3} M (for ethylene glycol) or 2 ml of 3.81×10^{-3} M (for glycerol) periodate solution in a 25-ml calibrated flask and, after allowing the reaction to proceed for 15 min at room temperature, 6.5 ml of SAG solution followed by 5 ml of buffer solution were added and the mixture was diluted to the mark with water. The excess of periodate was determined as described under Determination of periodate.

Indirect determination of tartaric acid

A sample aliquot containing 150–500 µg of tartaric acid in a 25-ml calibrated flask was cooled in ice, mixed with 1.5 ml of a 4.10×10^{-3} M periodate solution and kept at the same temperature (*ca.* 0 °C) for 30–40 min. Then, 6.5 ml of SAG solution followed by 5 ml of buffer solution were added and the mixture was diluted to the mark with water. The excess of periodate was determined as described under Determination of periodate.

Results and Discussion

Absorption Spectrum

Periodate oxidises SAG in basic medium to give a red species (a precipitate is formed in the total absence of organic solvents), which has a maximum absorption at 495 nm, whereas the reagent blank has a negligible absorption at this wavelength. The absorption spectrum of the reaction product is shown in Fig. 1; it is similar to the absorption spectrum of the product formed after catalytic oxidation of SAG with
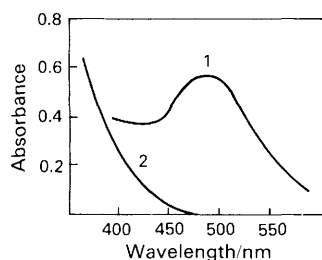
Fig. 1. Absorption spectra of (1) the product from the reaction of SAG with periodate (1.5×10^{-4} M) and (2) the reagent blank

Table 1. Indirect determination of ethylene glycol, glycerol and tartaric acid

Organic compound	Added, p.p.m.	Found,* p.p.m.	RSD, % ($n = 4$)
Ethylene glycol	6.57	6.65	0.4
	4.38	4.51	0.6
	2.64	2.68	1.3
Glycerol	8.23	8.41	0.2
	6.17	5.96	0.4
	4.12	4.23	0.7
Tartaric acid	24.6	25.7	0.2
	18.5	19.6	0.4
	10.6	11.1	1.0

* Mean of four determinations.

hydrogen peroxide and Mn^{II}.[5] All subsequent measurements were carried out at 495 nm.

Effect of Reaction Variables

The optimum pH range for full colour development is between 8.7 and 9.7; both below and above this pH range the intensity of the colour decreases. Ammoniacal buffer solution was used for adjustment of the pH.

The influence of the reagent concentration was investigated for samples containing 25 p.p.m. of periodate in a final volume of 25 ml. The maximum absorbance was obtained with $0.66–1.16 \times 10^{-3}$ M SAG solutions. A 1.08×10^{-3} M SAG solution was selected as the optimum. This concentration is obtained when 6.5 ml of 0.1% SAG solution are added to the 25-ml calibrated flasks.

To keep the oxidised product in solution, the presence of dimethylformamide (6%) is necessary.

The stability of the red colour obtained was studied using samples containing different periodate concentrations. The

samples remained stable for between 15 and 35 min. Measurements were therefore performed after 20 min.

Spectrophotometric Characteristics

Beer's law is obeyed over the range 10–45 p.p.m. of periodate in 25 ml of the final solution. The equation of the calibration graph is $y = -0.0005 + 0.0186x$ (where y = absorbance and x = periodate concentration in p.p.m.) with values for the standard deviations of the slope and intercept of 0.0007 and 0.02, respectively. The correlation coefficient was calculated to be 0.9974. The molar absorptivity at 495 nm is 3.5×10^3 $1 \, mol^{-1} \, cm^{-1}$ and the relative error (95% confidence level) of the method is $\pm 0.5\%$.

Indirect Determination of 1,2-Diols

The determination of periodate with SAG was investigated in the presence of different amounts of iodate. The results obtained showed that up to a 50-fold excess of iodate with respect to periodate could be tolerated.

The spectrophotometric method can also be applied to the indirect determination of 1,2-diols and related compounds, using the Malaprade reaction. The results obtained for ethylene glycol, glycerol and tartaric acid are summarised in Table 1. These results were calculated using the calibration graph for periodate and by assuming that the oxidation reactions between periodate and ethylene glycol, glycerol or tartaric acid are quantitative (100%) and that the stoicheiometry of the reaction is 1:1 (periodate to organic compound) for ethylene glycol and tartaric acid and 2:1 for glycerol.

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