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Determination of water in ascorbic acid by the proton isoconcentration technique using the standard addition method

M.R.O. KARIM,* Th.M. KARADAGHI and S.O. ISMAIL

Chemistry Department, College of Science, Salahaddin University, Arbil, Iraq

Abstract: Water has been extracted from ascorbic acid into a dry mixture of equal volumes of methanol–organic solvents (*n*-propanol, ethylene glycol or propylene carbonate) and was determined potentiometrically, using the calibration graph based on the large and systematic change in cell potential for addition of 0–1%, m/m water into a dry mixture of the above mentioned mixture containing 2×10^{-3} M trifluoromethanesulphonic acid (TFMSA) using a combination pH glass electrode with silver–silver chloride reference electrode having tetraethylammonium chloride (TEACl) in methanol as a filling electrolyte. The method is fast, accurate, reproducible and simple for operation.

Keywords: *Water determination; ascorbic acid; proton isoconcentration technique; direct potentiometry.*

Introduction

The application of direct potentiometry to the determination of residual water in organic solvents using a pH glass electrode under proton isoconcentration conditions was first reported in 1977 independently by Kakabadse [1] and Schwabe and Quick [2]. This technique was subsequently applied to various solvents as a batch method [3–10] and recently in online monitoring [11, 12]. The addition method in the proton isoconcentration technique (PICT) has recently been employed for water determinations in organic solvents, acetic or formic acids [9].

The stability of ascorbic acid depends on protection against hydrolysis which forms L-diketogulonic acid and then oxalic acid [13]. The instability of the vitamin C in blanching water causes the loss of vitamin activity during blanching of many foods [13]. Ascorbic acid is oxidized by iodine so that a direct titration by the Karl Fischer (KF) method is not possible [14]. Johansson recommended a two-component technique for water determination in ascorbic acid [14]. In the present work the water content in solid ascorbic acid has been extracted by equal volumes of dry methanol–organic solvent mixtures and determined potentiometrically using addition method in the PICT.

Experimental

Reagent

The organic solvents were obtained from Fluka and were dried as described elsewhere [7, 15]. The water contents after drying, as determined by KF titration were 0.03, 0.01, 0.05 and 0.05% (m/m) in methanol, *n*-propanol, ethylene glycol (EG) and propylene carbonate (PC), respectively — Aldrich trifluoromethansulphonic acid (0.1 M) was prepared in dry *n*-propanol or in PC; the preparation was done in a dry box under nitrogen and used as a stock solution. Ascorbic acid was obtained from Riedel-De Haen AG and dried under vacuum.

Apparatus

Measurements were made on magnetically stirred solutions at 25 ± 0.1°C using an Orion Model 811 digital pH-millivoltmeter with a potential range of ±1000 mV and discrimination of ±0.1 mV. A Hewlett Packard 9862 calculator–plotter was used for drawing the graphs. An Orion 910–100 combination pH glass electrode with a silver–silver chloride reference electrode having a saturated TEACl in methanol as a filling electrolyte was used. A Schott Gerate TR 156 automatic titrator was used for addition of water.

Preparation of calibration graph

A dried two-necked round-bottomed flask

* Author to whom correspondence should be addressed.

(100 ml) fitted with a combination pH glass electrode in a dry box under a blanket of dry nitrogen to prevent absorption of atmospheric moisture, was charged with 50 ml dry mixture consisting of 25 ml methanol, 24 ml *n*-propanol, EG or PC, and 1 ml 0.1 M TFMSA. Known increments of 0–0.5 ml water were added using the automatic titrator and the potential was recorded 1 min after each addition. The potential was plotted against percentage of water. For the water determination in solid ascorbic acid; 0.5 g of the solid sample was added to 50 ml of the above mentioned dry mixture containing 2×10^{-3} M TFMSA and was stirred for 20 min on the magnetic stirrer. Potential of the suspension was measured and water content of the sample was obtained directly from the calibration graph (Fig. 1).

Results and Discussion

The following requirements must be met if the effect of a solvent on cell potential is to be useful analytically: (i) a large change in potential (ΔE) for a given change in water concentration; (ii) a systematic and reproducible change in potential; (iii) a rapid electrode response [3]. The experimental parameters examined in this work were nature of solvent and recovery of water, nature of acid and its concentration and type of reference and pH glass electrodes.

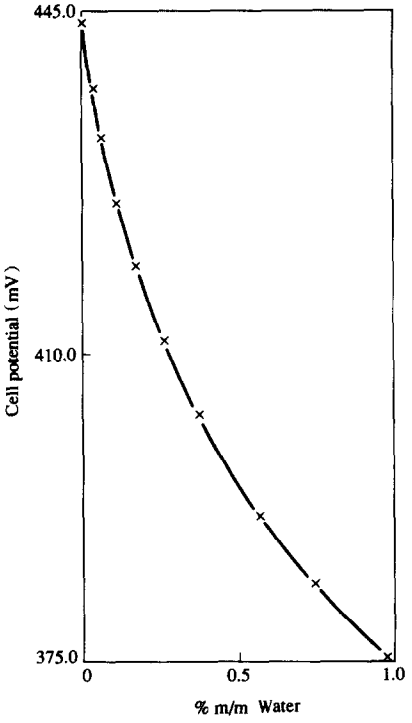

Figure 1
Calibration graph showing the change in potential on addition of 0–1% (m/m) water to a dry mixture of equal volumes of methanol–*n*-propanol in the presence of 2×10^{-3} M trifluoromethanesulphonic acid, using combination pH glass electrode.

Effect of solvent and recovery of water

Methanol was used for water extraction from sugars [16] and dry food materials [17] and determined by Karl Fischer titrations [16, 17]. The change in cell potential for addition of 0–1% (m/m) water into dry methanol was not large enough (i.e. 34.9 mV) for a sensitive method for water determination. The large and systematic change in cell potential was observed when methanol was mixed with dry *n*-propanol, PC or EG (Table 1). There may be several reasons for hypersensitivity of the cell potential at high solvent concentrations to small change in water content, e.g. liquid junction potential at the reference electrode, medium effect, gradual dehydration of the gel layer at the outer surface of the glass electrode, or increase in the proton activity in the outer swelling layer of the glass [6].

The recovery of water was studied by adding 0.05 or 0.1 ml water on 0.5 g of dry milled ascorbic acid and left for 24 h. The wet ascorbic acid was mixed with 50 ml of dry equal volumes methanol–solvent mixture in the presence 2×10^{-3} M TFMSA; the potential of the suspension was recorded after stirring for 5, 10, 15, 20 and 30 min. The same amounts of water were added to the dry extractant solvents in the presence of 2×10^{-3} M TFMSA (in the absence of the solid ascorbic acid); the potential of each solution was measured after 5 min and compared with the potential of the suspensions in the above procedure (Table 2). It can be seen from Tables 1 and 2 that the equal volumes of dry methanol–*n*-propanol mixture is the best solvent for complete extraction of water from solid ascorbic acid and the time of stirring was found to be 20 min at 25°C. The capacity of this super dry extractant solvent is 4 mg water ml^{-1}.

It was found that for a given concentration of water, ΔE value is higher in equal volume of methanol–*n*-propanol than in methanol–EG. This may be because EG is closest to water in the permitivity (i.e. 37.7) than *n*-propanol (20.3) [5]; whilst PC (64.4) is an aprotic solvent

Table 1
Change in potential, ΔE, and standard deviation (n = 7) for the addition of 0–1% (m/m) of water to equal volumes of methanol–solvent mixtures in the presence of 2 × 10^{-3} M trifluoromethanesulphonic acid, using combination pH glass electrode

Solvent	Mean ΔE (mV)	Standard deviation, σ (mV)
Methanol + propylene carbonate	56.3	0.86
Methanol + ethylene glycol	46.2	0.80
Methanol + n-propanol	68.7	0.58
Methanol	34.9	0.48

σ = Standard deviation for seven potential measurements for a solvent mixture containing 0.1% (m/m) water.

Table 2
Cell potentials for addition of water on 0.5 g of dry ascorbic acid and mixed with 50 ml equal volumes of dry methanol–solvent mixtures (indirectly) or directly into the mixture in the presence of 2 × 10^{-3} M trifluoromethanesulphonic acid, using combination pH glass electrode

Extractant solvent	Water added (%, m/m)	Cell potential for indirect water addition (mV)	Cell potential for direct water addition (mV)
Methanol + n-propanol	0.09	434.0	434.0
	0.20	416.8	416.0
Methanol + ethylene glycol	0.09	357.0	357.4
	0.20	348.2	348.0
Methanol + propylene carbonate	0.09	421.2	418.3
	0.20	410.0	406.2

Ascorbic acid was left for 24 h after water addition.

which is quite different from water and alcohols.

Effect of acid

The following strong acids 2 × 10^{-3} M perchloric, hydroiodic [7] or TFMSA were used as background electrolytes in the dry methanol–n-propanol for pH glass electrode in the presence of dry ascorbic acid. A decrease of 3 mV was observed after 15 min when perchloric acid was used; this may be due to oxidation of ascorbic acid, while, formation of iodine in the stock solution of hydroiodic acid 0.1 M in n-propanol was observed, this is not acceptable [14]. TFMSA 2 × 10^{-3} M was used as background electrolyte in the present work. The interference of ascorbic acid in the determination of water was studied by adding 0.5 g of the dry acid to 50 ml dry methanol n-propanol mixture in the presence of 2 × 10^{-3} TFMSA; potential of each solution was measured; there was no change in the potential. An increase of 3 mV was observed when 0.5 g dry ascorbic acid was added to the equal volume of methanol–ethylene glycol mixture. This may be due to ionization of ascorbic acid in methanol–EG mixture.

Effect of pH glass and reference electrodes

The Orion 910-100 combination pH glass electrode was used in the present work and conditioned in methanol–propanol mixture in the presence 2 × 10^{-3} M TFMSA. The reference electrode was a silver–silver chloride electrode having TEACl in methanol as a filling electrolyte. It was found that the leakage of water from the reference electrode into standard solution was negligible [9].

Accuracy of water determination

The results obtained for samples containing various amounts of water are shown in Table 3. In general, the accuracy of the method was satisfactory. Water content (0–200 mg) in 0.5 g ascorbic acid was completely extracted by 50 ml of equal volumes of dry methanol–n-propanol as can be seen from Table 3.

Limit of detection of water in ascorbic acid

The detection limit is based on the amount of added water on 0.5 g of ascorbic acid which was extracted by 50 ml of dry equal volumes of methanol–n-propanol and produced a change of 1 mV, i.e. corresponding twice the standard deviation (Table 1). The detection limit of

Table 3
Accuracy of the water determination in ascorbic acid by indirect potentiometry for the addition of 0–1% (m/m) water to equal volumes of methanol–*n*-propanol containing 2×10^{-3} M trifluoromethanesulphonic acid using combination pH glass electrode

Water added on 0.5 g of ascorbic acid (mg)	Water found (mg) by PICT	Standard deviation, σ ($n = 7$)	Relative error (%)
52.0	53.0	0.021	+1.92
100.3	100.8	0.015	+0.50
200.5	198.3	0.020	−1.10

water was found to be 60 mg kg^{-1} of extractant solvent.

It can be seen from Fig. 1, the sensitivity of the method depends on the amount of residual water present in methanol–propanol mixture. The sensitivity decreased as the water content was increased [6, 7]. This may be due to the complete dehydration of the gel layer at the outer surface of the glass electrode in a completely dry solvent [6, 7].

Conclusion

The proposed method can be used for the water determination in ascorbic acid. The method can be suggested for water determination in strong solid acids like citric or tartaric acids which can shift the pH of Karl Fischer reagent far enough into acidic region and direct titration of water is not successful [18].

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