

Determination of Trace Amounts of Acetic Acid in Ethanol by Fluoride Isoconcentration Using the Method of Standard Additions

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The large and systematic change in cell potential resulting from the addition of 0–1% *m/m* of acetic acid to a solution of ethanol containing 1×10^{-3} M tetraethylammonium fluoride (TEAF) as background electrolyte, using a fluoride ion-selective electrode and a calomel reference electrode filled with lithium chloride, provides a graphical method for the rapid determination of acetic acid in ethanol. Readings obtained by direct potentiometry show good reproducibility and stability. The method, characterised by its accuracy and simplicity of operation, compares favourably with gas chromatographic methods and can be used for the determination of acetic acid in vinegar.

Keywords: Acetic acid determination; acetic acid - ethanol mixtures; fluoride ion-selective electrode; acetic acid determination in vinegar; fluoride isoconcentration

In cells having ion-selective electrodes many aqueous solvent mixtures show a systematic change in cell potential with a variation in the concentration of organic solvent under ion isoconcentration conditions.^{1,2} The use of this effect for the determination of solvents in binary solvent - water mixtures, first reported in 1975,¹ has been applied to the direct potentiometry of methanol in methanol - water mixtures.² Ethanol was determined in spirits by the fluoride ion isoconcentration technique (FICT) using fluoride ion-selective and reference electrodes.³ A study of binary acetic acid - water and acetic acid - methanol mixtures under fluoride isoconcentration conditions undertaken by Kakabadse and Ake revealed a hypersensitivity of the fluoride electrode towards small changes in the acetic acid concentration at high methanol concentrations.⁴ They proposed the use of the fluoride electrode for monitoring the production of vinegar from ethanol by FICT.⁵ For the FICT the preparation of standard solutions and measurement of potential are time consuming steps requiring a large amount of pure solvent, which might be difficult to obtain. For this study, the standard additions method based on the FICT was applied to the determination of trace amounts of acetic acid in ethanol (acetic acid being an impurity in ethanol).⁶ This method can be used for the determination of acetic acid in vinegar after mixing with ethanol.

Experimental

Reagents

Ethanol and acetic acid were obtained from Fluka and purified as described elsewhere.⁷ All other chemicals were of analytical-reagent grade. A stock solution of 10^{-2} M tetraethylammonium fluoride (TEAF) in ethanol was prepared. Vinegar was obtained from the Kербала Canning Company and the Albadawy Factory.

Apparatus

Measurements were made on magnetically stirred solutions at $25 \pm 0.1^\circ\text{C}$ using a Radiometer PHM 64 Research pH - millivoltmeter with a potential range of ± 1500 mV and a discrimination of ± 0.1 mV. A Hewlett-Packard 9862 A calculator - plotter was used and a Radiometer Model 1002 F fluoride ion-selective electrode and calomel (K 701) or silver-silver chloride (K 801) reference electrodes were also used. A Schott Geräte TR 156 automatic titrator was employed for the addition of acetic acid. For comparison a Pye Unicam Model 28852 GCD chromatograph (column packing, Porapak Q) was also used for the determination of acetic acid in ethanol. Nitrogen was used as carrier gas at a flow-rate of 60 ml min^{-1} .

Preparation of Calibration Graphs

Procedure I, for the determination of acetic acid in ethanol

The cell consisted of a 100-ml Nalgene polyethylene beaker fitted with a rubber stopper in which holes were bored for the insertion of the electrodes and the titrator tip. The cell was charged with 50 ml of ethanol containing 1×10^{-3} M TEAF. Known increments (0–0.5 ml) of acetic acid were added using the automatic titrator and potentials were measured immediately after each addition. Potentials were plotted against percentage of acetic acid (Fig. 1, A). For the determination of acetic acid in ethanol 5 ml of 1×10^{-2} M TEAF in ethanol were pipetted into a 50-ml calibrated flask and the solution was diluted to the mark with the sample. The potential of this solution was measured after washing the surface of the electrode with ethanol. The percentage of acetic acid in the sample was then obtained directly from the calibration graph.

Procedure II, for the determination of acetic acid in vinegar

A calibration graph was constructed for potential *versus* the amount of acetic acid added to 50 ml of an ethanol solution containing 10% *m/m* of water in the presence of 1×10^{-3} M TEAF (Fig. 1, B). For the determination of acetic acid in

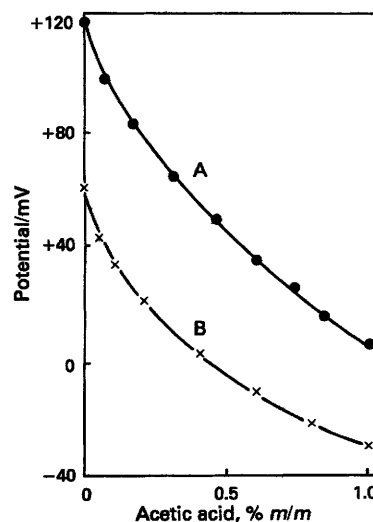


Fig. 1. Calibration graphs showing the variation in potential with the addition of 0–1% *m/m* of acetic acid to (A) ethanol and (B) a mixture of ethanol, water (10% *m/m*) and TEAF (1×10^{-3} M). A Radiometer fluoride ion-selective electrode and a calomel (LiCl) reference electrode were used

Table 1. Change in cell potential, ΔE , standard deviation, σ , and coefficient of variation, δ , with the addition of 0–1% *m/m* of acetic acid to ethanol containing different concentrations of TEAF. A Radiometer fluoride ion-selective electrode and different reference electrodes were used

Reference electrode	Fluoride ion concentration/ <i>m</i>	Mean ΔE /mV	σ /mV*	Acetic acid, % <i>m/m</i>	δ †
Calomel (LiCl) ..	10 ⁻⁴	94.3	0.86	1.00	—
		—	0.67	0.05	1.16
	10 ⁻³	100.7	0.87	1.00	—
		—	0.63	0.05	1.07
10 ⁻²	10 ⁻²	103.8	1.03	1.00	1.25
		—	0.79	0.05	1.25
	10 ⁻⁴	88.3	0.93	1.00	—
		—	0.57	0.05	1.23
Ag - AgCl (LiCl) ..	10 ⁻²	95.1	0.98	1.00	—
		—	0.65	0.05	1.24
	10 ⁻³	85.1	0.88	1.00	—
		—	0.73	0.05	1.34

* σ = standard deviation for seven measurements of potential.

† $\delta = 100 \sqrt{\sigma_1^2 + \sigma_2^2} / \Delta E$.

Table 2. Accuracy of the determination of acetic acid by direct potentiometry for the addition of 0–1% *m/m* of acetic acid to ethanol containing 1×10^{-3} M TEAF. A Radiometer fluoride ion-selective electrode and a calomel (LiCl) reference electrode were used

Sample	Acetic acid, % <i>m/m</i>		Procedure	Relative error, %	
	Prepared by accurate weighing	Found by standard additions technique		Standard additions technique	Gas chromatography
Ethanol	0.941	0.903	I	-4.0	+2.1
	0.675	0.637	I	-5.6	-4.0
	0.243	0.235	I	-3.3	+1.5
	0.102	0.104	I	+2.0	+3.3
	0.054	0.057	I	+5.6	-1.9
Vinegar	3.91*,†	3.84	II	-1.8	—
	3.67*,‡	3.52	II	-4.3	—

* Results obtained by gas chromatography.

† Acetic acid in vinegar from Kerbala Canning Co.

‡ Acetic acid in vinegar from Albadahy Factory.

vinegar, samples (5 ml) of vinegar were added by pipette to a 50-ml calibrated flask containing 5 ml of 1×10^{-2} M TEAF in ethanol and the mixture was diluted to the mark with pure ethanol. The potential of this solution was measured and the percentage of acetic acid in the vinegar mixture was obtained from the calibration graph. The mass of acetic acid in the vinegar, was then calculated by considering the dilution involved.

Results and Discussion

There might be several reasons for the large and systematic change in the cell potential with the addition of 0–1% *m/m* of acetic acid to ethanol containing 1×10^{-3} M TEAF as a background electrolyte (Fig. 1). Such reasons might include changes in the activity of the fluoride ions,² strong adsorption of fluoride ions on the electrode surface in the organic solvent,⁷ the formation of HF_2^- on the surface film of the electrode⁷ and changes in the liquid junction potential at the reference electrode.²

The following requirements must be met if the solvent effect on the cell potential is to be useful analytically: a large change of potential (ΔE) for a given change in the acetic acid concentration; a systematic and reproducible change in the potential, which must be stable; and a rapid electrode response.³ The relevant experimental parameters in this work are the nature of the background electrolyte and its concentration and the type of reference and fluoride electrodes used.

Effect of Fluoride Ions

Potassium, ammonium and tetraethylammonium fluorides were each used as the background electrolyte and tested for

their effect on the value of ΔE in the system (ethanol - 1×10^{-3} M F⁻ - 0–1% *m/m* acetic acid) using fluoride ion-selective and calomel (LiCl) reference electrodes. The values obtained for ΔE were 87, 88.1 and 100.7 mV for potassium, ammonium and tetraethylammonium fluorides, respectively. The higher ΔE obtained for TEAF may arise from the complete ionisation of this salt in ethanol - acetic acid mixtures.⁷

The fluoride concentration and the magnitude of ΔE appear to follow the same trend (see Table 1). Measurements of potential were more reproducible at low acetic acid concentrations in ethanol. The coefficient of variation, δ , is a useful guide for optimisation of the experimental conditions.³ The lowest value of δ was obtained for 1×10^{-3} M TEAF in ethanol. Hence, this was chosen as the background electrolyte.

Effect of Reference Electrode

Calomel reference or silver - silver chloride electrodes with saturated lithium chloride as electrolyte and the Radiometer fluoride ion-selective electrode were tested for their sensitivity and reproducibility of measurements of potential for the addition of 0–1% *m/m* of acetic acid to ethanol containing 1×10^{-3} M TEAF. The lowest value of δ was achieved when the calomel (LiCl) electrode was used (see Table 1). Lithium, rather than potassium, chloride was used as the filling electrolyte so as to increase the stability of the measurements.³

Effect of Fluoride Ion-selective Electrode

Only the Radiometer fluoride ion-selective electrode was used in this investigation. The advantage of this technique is that

Table 3. Limit of detection of acetic acid in ethanol containing 1×10^{-3} M TEAF using a Radiometer Model 1002 F fluoride ion-selective electrode and a calomel reference electrode with saturated lithium chloride as a filling electrolyte. Measurements performed at $25 \pm 0.1^\circ\text{C}$

Acetic acid present in ethanol, % m/m	Sensitivity/ mg kg^{-1} per 2 mV
0	40
0.5	72
1.0	98

better conditioning of the electrode is achieved during use compared with the FICT.² This electrode behaves as an acetic acid selective electrode in ethanol and in an ethanol - 10% m/m water mixture. The electrode must be washed with ethanol after use in acetic acid - ethanol mixtures.

Accuracy of Acetic Acid Determination

The results obtained for samples of acetic acid in ethanol (prepared by accurate weighing) are shown in Table 2. In general, the accuracy is satisfactory and compares favourably with that achieved by a gas chromatographic method. The interference by water in the acetic acid determination (0–2% m/m) was studied by adding 0, 0.5 or 1 ml of water to 50 ml of ethanol containing 0, 0.5 or 1% m/m of acetic acid in the presence of 1×10^{-3} M TEAF. No significant change in cell potential was observed (less than 0.4 mV, which is within the range of reproducibility for the potential measurements). The relative errors obtained for the determination of acetic acid in vinegar by direct potentiometry were in agreement with the gas chromatographic values, e.g., –1.8 and –4.3% for vinegar from the Kerbala Canning Company and the Albadawy Factory, respectively.

Limit of Detection of Acetic Acid in Ethanol

The sensitivity of the fluoride ion-selective electrode towards changes in the acetic acid concentration in ethanol depends on the amount of residual acetic acid present in the ethanol (Table 3). The limit of detection for acetic acid was based on the amount of acetic acid that had to be added to ethanol in order to produce a change in cell potential of 2 mV for a solution of ethanol containing 1×10^{-3} M TEAF, i.e., corresponding to twice the value of the standard deviation.

Conclusion

The proposed method can be used for the determination of acetic acid in ethanol. It is characterised by its accuracy and simplicity. The method can also be used for the determination of acetic acid in vinegar⁵ and is comparable to a gas chromatographic method.

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