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Potentiometric Determination of Some Aliphatic Aldehydes Using the Silver/Sulfide Ion-Selective Electrode

M. Tarek M. Zaki* and M. H. Fawzy
Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

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Synopsis. A simple, selective and reproducible method for the potentiometric determination of some aliphatic aldehydes is described. The method is based on oxidation of the aldehydes with silver oxide packed in a column. The formed silver salts of the fatty acids are eluted with water and the silver ion concentration is determined with a silver/sulfide ion-selective electrode using either a calibration graph or a standard addition technique. The effects of experimental variables and the interference of other organic functional groups are investigated. Samples containing up to 5.0 mg aldehyde are analyzed with an average recovery of 98.5% and 98.4% using the proposed techniques, respectively.

Potentiometric methods for aldehyde determination are based on either condensation or oxidation–reduction reactions. In the methods involving condensation reactions, an excess of hydrazine or hydroxyl amine derivatives is added, and the unreacted reagent is back titrated with a suitable titrant. Siggia and Stahl[1] treated aldehydes with excess 1,1-dimethylhydrazine in methanol or ethylene glycol medium. The unused reagent was titrated with hydrochloric acid in methanol. Berka and Zyka[2,3] used 2,4-dinitrophenylhydrazine. The formed hydrazone was separated and the unreacted reagent was titrated with chloramine T in presence of potassium bromide. Moreover, Langmair[4] utilized hydroxylamine hydrochloride as reagent and sodium hydroxide as titrant. However, the former methods lacks selectivity.

On the other hand, Siggia and Segal[5] reported a macro method based on oxidation with Tollens reagent. The residual silver ions were potentiometrically titrated with potassium iodide solution. However, the reagent is unstable and the method is not suitable for adaptation to the micro scale.[6,7]

Application of ion-selective electrodes for end point detection was also reported. Formaldehyde was determined by reaction with iodine–iodide solution in alkaline medium.[8] After acidification, the mixture was titrated with silver nitrate solution using the iodide ion-selective electrode. Moreover, Ma and Hassan[9] reported that the amperometric method of Ikeda[10] for formaldehyde determination with potassium cyanide may be adapted potentiometrically by titrating the unreacted cyanide ions with silver nitrate solution using the cyanide or silver/sulfide ion-selective electrode.

In the present work, the optimum conditions for aliphatic aldehyde determination based on oxidation with silver(I) ions followed by potentiometric measurement using the silver/sulfide ion-selective electrode were investigated. The reagent, silver oxide-butylamine complex, which was recommended by Siggia et al.[11] for the volumetric determination of aldehydes has been tested. However, an invariably low recovery was obtained. To overcome this problem, a potentiometric study based on prior oxidation with silver oxide[12] packed in a column has been carried out. The eluted silver salts of fatty acids were determined with the silver/sulfide ion-selective electrode using either a calibration graph or a known addition technique.

Experimental

Instrumentation and Reagents. An Orion Model EA 920 pH/ISE meter fitted with Orion silver/sulfide ion-selective electrode (Model 94-16) and Orion double-junction reference electrode (Model 90-02) were used for potential measurements.

Silver oxide of 99% purity (Aldrich Chem.) was used to pack two-thirds of a column (1 cm diam. ×15 cm). The filled column was washed several times with twice-distilled water before introducing the samples.

Potassium nitrate solution, 4 M (1 M=1 mol dm^{-3}), was used as ionic strength adjustor (ISA).

Procedure. Introduce 5 ml of the sample solution, containing up to 5.0 mg of the aldehyde in water or 1,4-dioxane, into the column. Elute with water to make a total volume of 40 ml. Collect the eluent in 250-ml beaker. Add 60 ml water and determine the silver ion concentration using the silver/sulfide-double junction reference electrode system by either of the following techniques:

1-Calibration Graph Technique: The electrode calibration graph was established using 100 ml each of the 10^{-1} to 10^{-5} M silver nitrate solution in water or 5% dioxane-water according to the solvent used for the tested sample. To each solution, 2.0 ml of ISA was added before the potential measurement. A linear calibration graph was obtained over the entire range studied.

To the eluted solution, 2.0 ml of ISA was added and the potential was measured. A blank experiment was carried out under identical conditions. The calibration graph was used to determine the silver ion concentration equivalent to the aldehyde sample.

2-Known Addition Technique: Add 2.0 ml of ISA to the eluent, place the electrodes and stir thoroughly. Measure the relative millivolt. Set the reading to zero by turning the calibration control or record the potential reading, if the reading cannot be set to zero. Prepare a standard solution about ten folds as concentrated as the sample concentration under investigation. Add 2.0 ml of ISA to each 100 ml standard. Add 10.0 ml of the standard to the sample and stir thoroughly. Record the potential difference (ΔE). If the meter could not be zeroed in the former step, subtract the second reading from the first to get (ΔE). Calculate the silver ion concentration in the sample which is equivalent to the aldehyde using the equation:

$$C_0=\frac{C_sV_s}{V_0+V_s}\left[10^{-\Delta E/S}-\left(\frac{V_0}{V_0+V_s}\right)\right]^{-1}$$

where C_0 and C_s are the molar concentrations of the sample

Table 1. Potentiometric Determination of Some Aliphatic Aldehydes Using The Silver/Sulfide Ion-Selective Electrode

Sample	Carbonyl group(%)				
	Calcd	Electrode calibration method		Standard addition method	
		Found	Recovery	Found	Recovery
Formaldehyde solution (37 wt.%)	93.33	91.56	98.1	91.44	98.0
		91.58	98.1	91.53	98.1
		91.64	98.2	91.55	98.1
Acetaldehyde	63.64	62.79	98.7	62.69	98.1
		62.85	98.8	62.76	98.6
		62.91	98.9	62.80	98.7
Propionaldehyde	48.28	47.67	98.7	47.66	98.7
		47.76	98.9	47.72	98.8
		47.81	99.0	47.74	98.9
Butanal	38.89	38.35	98.6	38.29	98.5
		38.36	98.6	38.34	98.6
		38.38	98.7	38.35	98.6
Pentanal	32.56	32.01	98.3	31.98	98.2
		32.05	98.4	31.99	98.2
		32.08	98.5	32.03	98.4
Hexanal	28.00	27.42	97.9	27.37	97.8
		27.48	98.1	27.40	97.9
		27.51	98.3	27.43	98.0

and the standard, V_0 and V_s the corresponding volumes and S is the electrode slope in mV per ten-fold change in concentration. C_0 may also be calculated using the equation:

$$C_0 = QC_s$$

where Q is the value from the known table.[13]

Results and Discussion

The aim of this work was to accomplish the optimum conditions for aliphatic aldehyde determination by oxidation with silver(I) ions. The low recovery obtained using silver oxide-butylamine complex[11] as reagent and silver/sulfide ion-selective electrode for the end point detection, may be attributed to the presence of free amine which affect the sensor membrane. Therefore, an external column packed with silver oxide was utilized as oxidizing agent.

Selection of Conditions. Aliphatic aldehydes are oxidized with silver oxide to the corresponding silver salt of the fatty acids according to the equation:

$$2\,\mathrm{RCHO} + 3\,\mathrm{Ag_2O_{(s)}} = 2\,\mathrm{RCOOAg} + \mathrm{H_2O} + 4\,\mathrm{Ag_{(s)}}$$

Water, methanol, ethanol, 1-propanol, 2-propanol, and 1,4-dioxane were tested as solvents for aldehyde samples. Water was suitable for aldehydes of low molecular weight. On the other hand, aldehydes of relatively high molecular weight were best dissolved in 1,4-dioxane. Using alcohols as solvents were accompanied by a slight increase in the blank values. This is presumably due to the partial oxidation of this alcohols with silver oxide.

The effect of water volume necessary for eluting the formed fatty acid silver salts was investigated. 20 ml of water was sufficient to elute the formed silver formate or acetate. However, 35 ml of water was required to elute the salts formed by oxidation of higher aldehydes such as pentanal or hexanal. Larger volumes of water than that was accompanied by increasing the blank value due to the solubility of silver oxide. Therefore, 35 ml of water was recommended to elute all samples.

Analysis of Aldehyde. The results obtained for the analysis of some aldehydes using the calibration graph and the standard addition techniques are summarized in Table 1. Average recoveries of 98.49% and 98.37% with a relative standard deviation of 0.32% and 0.33% were obtained, respectively. On the other hand, the analysis of higher aliphatic aldehydes such as octanal and decanal, in addition to aromatic aldehydes gave low recoveries. This may be due to a nonstoichiometric oxidation with silver oxide or incomplete elution of the formed fatty acid silver salts.

Interferences. The extent of interference from other organic functional groups was investigated. Alcohols (methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol), ketones (acetone, 2-butanone, 3-pentanone, 2-hexanone, and 4-methyl-2-pentanone), amides (formamide, acetamide, and *N,N*-dimethylformamide), imides (succinimide), and hydrogen peroxide did not interfere.

However, acids and esters interfered. Esters undergo partial hydrolysis to form the corresponding fatty acid silver salts. Therefore, a preliminary separation of these compounds was required before aldehyde determination.

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