DETERMINATION OF PHENONES IN A PERFUME COMPOSITION

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ABSTRACT

Direct Current Polarography (DCP) and Differential Pulse Polarography (DPP) methods have been developed for the qualitative as well as quantitative analysis of acetophenone and benzophenone in perfume samples.

Acetophenone produces well defined waves in 0.05 M LiCl over a wide range of pH from 1.3 to 11.3 with $E_{1/2}$ values ranging from –1.1 to –1.6 V and E_p = –1.16 V to –1.68 vs SCE. Benzophenone produces well defined waves in 0.05 M LiCl at pH range from 1.3 to 8.5 with $E_{1/2}$ values ranging from –0.9 V to –1.3 V and E_p = –0.96 to –1.34 V vs SCE.

Both the compounds under study are reversibly reduced at the electrode surface. The number of electrons involved in the electrode process for both acetophenone and benzophenone was one in each case. This has been confirmed by the measurement of $E_{3/4} - E_{1/4}$ values and also from the log plot slopes for the reduction waves. The wave height of the polarogram was found to be proportional to the concentration of the compound in each case.

The developed methods have been standardized for the determination of these compounds in perfume compositions. The concentration of acetophenone and benzophenone in 1 ml of perfume composition (the name has not been disclosed for reasons of secrecy) has been reported in the paper.

The observed data has been subjected to statistical analysis which revealed high reliability and precision.

INTRODUCTION

Acetophenone has a persistent and powerful odour which is taken advantage of by perfumers in the preparation of perfumes of the type of new

mown hay, syringa, and the like /1/. The powerful odour and relative stability of acetophenone is desirable in many perfume compositions like gardenia and hawthorn, etc. /2/. Acetophenone is used in perfumery to impart an orange blossom-like odour /3/. It is also used as a modifier and to produce compounding notes /4/.

Benzophenone possesses a mild, sweet, rosaceous odour which is very persistent. It is therefore useful in many types of perfumes. It also serves as a fixative and it has the advantage of blending well with many types of perfumery aromatics, at the same time adding a sweet note to the perfume.

Its fixative property is due to its high boiling point (306°C) and low volatility at room temperature. Benzophenone is a stable compound in perfumes /2/. It is a valuable crystalline fixative of pleasant odour that can be used in almost any sweet floral bouquet of perfumes, especially gardenia and new-mown hay /3/.

A survey of the literature reveals that determination of acetophenone and benzophenone has been carried out by liquid chromatography /5/, gas chromatography /6/, UV /7/, reversed phase liquid chromatography /8/, spot test analysis /9/, etc. Interestingly, many organic compounds with the ketone group produce reasonable polarographic / voltammetric responses, and can be qualitatively and quantitatively determined voltammetrically /10/.

Voltammetric methods are far better than these conventional methods, as they are non-destructive, rapid and very sensitive. The minimum detection limit of direct current polarography (DCP) is 10^{-5}M, whereas for differential pulse polarography (DPP), it is 10^{-7}M.

The authors have used DCP and DPP methods for the analysis of acetophenone and benzophenone and used the said procedure for analysis of these compounds in perfume compositions, the results of which have been reported in the paper.

EXPERIMENTAL

Instrumentation

The DCP and DPP studies were carried out on an Elico (India) DC polarograph, Model CL-357, and an Elico pulse polarograph, Model CL-90, respectively. A Systronic digital pH metre-35 was used for the pH measurements. The polarographic cell consisted of a three electrode assembly with a calomel electrode (reference electrode) and platinum electrode

(auxiliary electrode). The working electrode was dropping mercury electrode. The capillary characteristics of the DME had a $m^{2/3}$ $t^{1/6}$ value of 2.5 $mg^{2/3}$ $sec^{-1/2}$ at 60 cm effective height of mercury column.

Chemicals and reagents

The chemicals used were of Analar/BDH grade. Doubly distilled water was used to prepare the solutions. 0.05 M LiCl, 0.01M solution of benzophenone and acetophenone were prepared by dissolving their requisite quantity in 70:30 v/v alcohol:water. 0.1% gelatin was prepared by dissolving a requisite quantity in warm distilled water. pH adjustments were made using dilute solutions of HCl/NaOH. The solutions were deaerated by bubbling purified hydrogen gas for 10 minutes before recording the polarograms/ voltammogram.

Determination of benzophenone and acetophenone

A known concentration of benzophenone was taken into a polarographic cell having 10 ml of 0.05 M LiCl and 1 ml of 0.1% gelatin. The volume of the test solution was made up to 100 ml with 70:30 v/v alcohol:water. The polarogram was recorded keeping the initial emf set to–0.95 V.

The polarogram of acetophenone was also recorded in the same manner, keeping the initial emf set to –1.3 V.

Calibration curves were obtained by taking varying concentrations of benzophenone / acetophenone. The polarograms were recorded under the above-mentioned experimental conditions.

Acetophenone and benzophenone were also determined simultaneously in one run. 5 ml of 0.01M acetophenone and 5 ml of 0.01M benzophenone were taken into a polarographic cell having 10 ml of 0.05M LiCl. The volume of the test solution was made up to 100 ml with 70:30 v/v alcohol:water. 1 ml of 0.1% gelatin was added as maximum suppressor. The pH of the analyte was adjusted to 2.9 with dilute NaOH/HCl solution. The polarogram was recorded as described earlier, keeping the initial emf set to –0.90V.

Determination of benzophenone and acetophenone in perfume composition

For the determination of acetophenone and benzophenone in an unknown sample, 1 ml of perfume composition was transferred to a polarographic cell

containing 10 ml of LiCl solution. Polarograms were recorded in exactly the same manner as described earlier.

Acetophenone and benzophenone content of the perfumes were determined with the help of the calibration curves and with the standard addition method.

RESULTS AND DISCUSSION

Under the aforesaid experimental conditions acetophenone and benzophenone are easily reducible at the DME surface. Acetophenone gives a well defined wave with $E_{1/2} = -1.40$ V and $E_p = -1.46$ V (Fig. 1) vs SCE at pH 2.9. The electrode process was found to be reversible. The number of electrons involved in the electrode process was found to be one as calculated by measuring $E_{3/4} - E_{1/4}$ values. This has been confirmed by the log plot slopes /11/. Benzophenone produced a distinct reversible reduction wave with $E_{1/2} = -1.10$ V and $E_p = -1.12$ V (Fig. 2) vs SCE at pH 2.9. The number of electrons involved in the electrode process was found to be one /11/. Figure 3 shows the DC and DP polarograms of a mixture of acetophenone and benzophenone. The standardised methods were found to be very accurate for the determination of these compounds in perfume compositions. The DC and DP polarograms of perfume samples have been shown in Figs. 4 and 5.

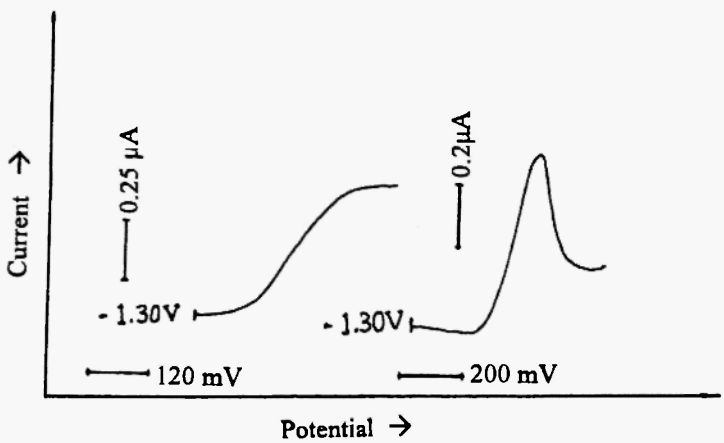

Fig. 1: A typical DC and DP polarogram of acetophenone in 0.05 M LiCl at pH 2.9.

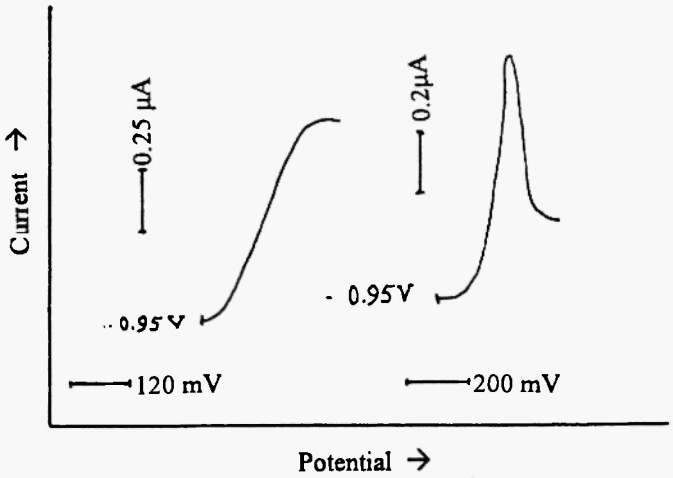

Fig. 2: A typical DC and DP polarogram of benzophenone in 0.05 M LiCl at pH 2.9.

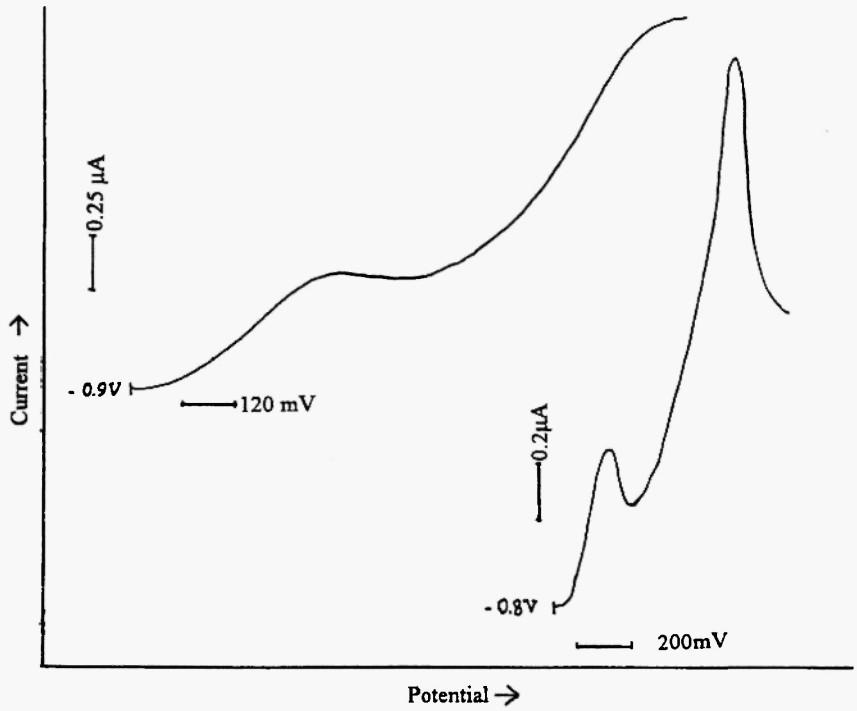

Fig. 3: DC and DP polarograms of a mixture of 9.0 mg benzophenone and 5.8 mg acetophenone in 0.05 M LiCl at pH 2.9.

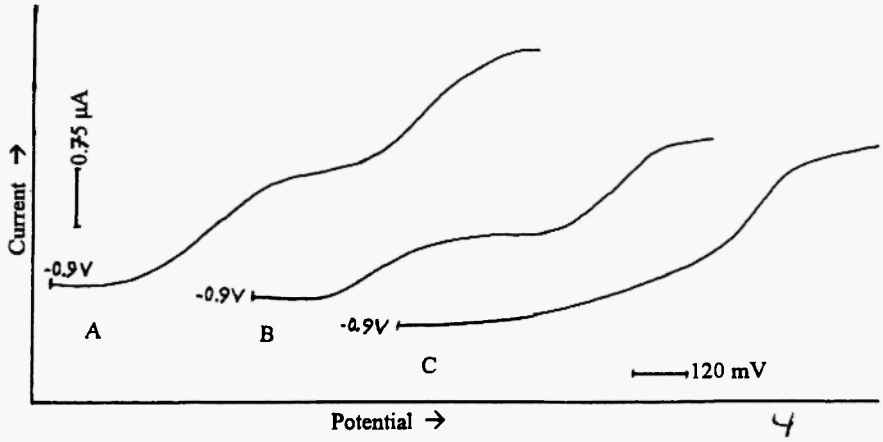

Fig. 4: DC polarograms of perfume samples in 0.05 M LiCl at pH 2.9. (A) Sample 1, (B) Sample 2, (C) Sample (3) (1 ml perfume per 100 ml of analyte).

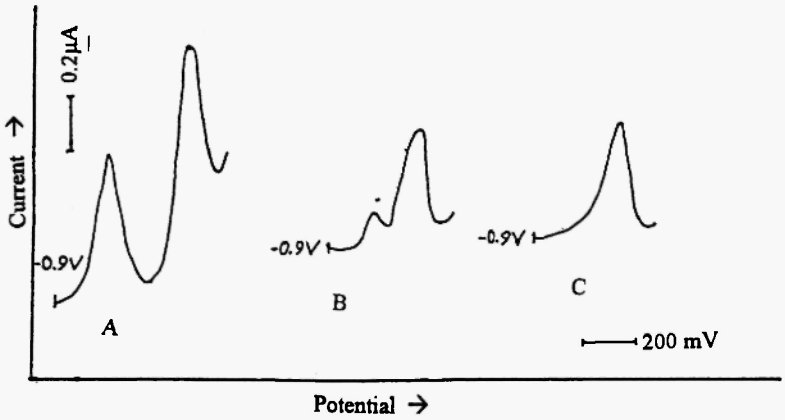

Fig. 5: DP polarograms of perfume samples in 0.05 M LiCl at pH 2.9. (A) Sample 1, (B) Sample 2, (C) Sample (3) (1 ml perfume per 100 ml of analyte).

Quantitative analysis of the samples for their benzophenone / acetophenone content has been done by wave height method and the statistical analysis of the results by an external spiking method. The percentage recovery in all the cases was found to be more than 99.7% (Table 1). The final analysis results (Table 2) have been compared with those claimed by the manufacturer and

Table 1

Results* on perfume compositions for their acetophenone and benzophenone contents (mg/ml)

Perfume	Compound	Parameter	DCP		DPP	
			Added	Found	Added	Found
Sample 1	Benzophenone	Amount	-	3.02	-	3.01
			2.70	5.70	2.70	5.70
		% R	99.6		99.8	
		RMD	0.06		0.019	
		SD	0.13		0.1	
		% CV	4.4		3.32	
	Acetophenone	Amount	-	4.01	-	3.99
			3.60	7.60	3.60	7.57
		% R	99.8		99.7	
		RMD	0.016		0.15	
		SD	0.1		0.1	
		% CV	2.4		2.50	
Sample 2	Benzophenone	Amount	-	1.98	-	1.96
			1.82	3.75	1.82	3.75
		% R	98.6		99.4	
		RMD	0.006		0.004	
		SD	0.01		0.01	
		% CV	0.50		0.51	
	Acetophenone	Amount	-	Nil	-	Nil
			Nil	Nil	Nil	Nil
		% R	Nil		Nil	
		RMD	Nil		Nil	
		SD	Nil		Nil	
		% CV	Nil		Nil	
Sample 3	Benzophenone	Amount	-	2.44	-	2.47
			1.82	4.20	1.82	4.27
		% R	98.5		99.15	
		RMD	0.01		0.008	
		SD	0.03		0.01	
		% CV	1.96		0.6	
	Acetophenone	Amount	-	10.15	-	10.00
			10.8	20.85	10.8	20.76
		% R	99.5		99.8	
		RMD	0.002		0.06	
		SD	0.03		0.07	
		% CV	0.29		0.79	

*Average of four determinations.

% R = Percentage recovery RMD = Relative Mean Deviation

SD = Standard Deviation CV = Coefficient of variance

Table 2

Final analysis results on perfume compositions for their benzophenone and acetophenone contents

Perfume	Compound	Found		Reported by the Manufacturer
		DCP	DPP	
Sample 1	Benzophenone	3.02	3.01	3.00
	Acetophenone	4.01	3.99	4.00
Sample 2	Benzophenone	1.98	1.96	1.95
	Acetophenone	Nil	Nil	Nil
Sample 3	Benzophenone	2.44	2.47	2.48
	Acetophenone	10.15	10.00	10.00

were found to be in good agreement. A comparison of the results with literature /4/ also reveals the reliability of the observed data. The standardized method can thus be recommended for such an analysis and also for the purpose of quality control in the perfume industry.

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