

Indirect Polarographic Determination of Carbonyl Compounds Based on Their Reaction with Hydroxylamine

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Summary: Methods for the determination of carbonyl compounds based on their ability to diminish the hydroxylamine anodic wave are described. The necessity of adding a proton acceptor in the determination of ketones is illustrated. The rapid direct current (d.c.) and the alternating current (a.c.) polarographic techniques were applied for the determination of 2.8×10^{-4} M and 1.6×10^{-5} M carbonyl compounds, respectively, with a reproducibility of $\pm 1.4\%$. These methods are shown to be suitable for total carbonyl group determination.

Introduction:

The most common methods for determining carbonyl compounds are based upon the reaction with a hydroxylamine salt in the presence of a base in order to convert the salt to free hydroxylamine which reacts with the carbonyl compound to form the corresponding oxime¹⁻⁴. The amount of hydroxylamine consumed, which is usually obtained by either an acid-base or redox titration, is a measure of the carbonyl compound present. Generally the serious limitations of the acid-base titration are that the end-point leaves something to be desired and that numerous interferences are obtained from strong inorganic and organic acids and bases. On the other hand the main problem inherent in the redox titration is that the reactions of hydroxylamine with many common oxidants are slow and stoichiometrically complicated.

The direct polarographic determination of carbonyl compounds is limited in general to aliphatic aldehydes^{5,6} which are readily reduced at voltages just below the reduction voltages of the more common supporting electrolytes. Ketones on the other hand are reduced at potentials much more negative than those obtainable in the usual supporting electrolytes⁵⁻⁷. Moreover, the direct polarographic determination of carbonyl compounds is frequently complicated by interfering side-reactions such as hydration or acetal formation.

It has been shown that this class of compound can be converted to either hydrazones^{8,9} or semicarbazones¹⁰ these then measured polarographically.

The bisulphite method used by Strand¹¹ is based upon the extent to which the presence of carbonyl compound decreases the bisulphite polarographic wave. This method suffers from some equilibrium difficulties such as incomplete reaction; moreover, most ketones form rather unstable addition products.

Iversen and Lund^{12,13} have shown that hydroxylamine gives a well-defined anodic d.c. polarographic wave with $E_{1/2} = -0.32$ (vs. saturated calomel electrode). They reported that in the presence of oxygen hydroxylamine gives irreproducible anodic double-waves. The first wave, which occurs at the same potential (-0.14 V) as the oxygen reduction wave, could not be removed by flushing with nitrogen. They suggested incorporating sulphite in the supporting electrolyte (0.16 M KOH – 0.16 M Na_2SO_3) for removing dissolved oxygen and elimination of the first wave. The wave height at -0.32 V was proportional to the hydroxylamine concentration in the range 10^{-4} – 10^{-2} M.

Canterford¹⁴ has described an a.c. polarographic method for the determination of 3.20×10^{-5} M hydroxylamine sulphate based on anodic wave measurement at -0.32 V (vs. Ag/AgCl electrode) in 1 M NaOH – 0.1 M Na_2SO_3 . He mentioned that the hydroxylamine peak potential shifts to more negative potentials with increasing NaOH concentration. The contribution of the residual current due to NaOH – Na_2SO_3 solution was negligible.

In the present work indirect d.c. and a.c. polarogra-

phic methods for the determination of the carbonyl compounds are described which are based on the measurement of the diminution of the anodic wave of hydroxylamine due to the formation of the corresponding oxime.

Experimental

Apparatus

A Metrohm Polaricord 506 Model polarograph was used for recording all d.c. and a.c. polarograms. The apparatus is supplied with drop life time control facility. Drop life times of 1 sec and 0.6 sec. were used with d.c. and a.c. polarographic measurements, respectively, with 6×10^{-8} A/mm sensitivity. All potentials quoted were in reference to Ag/AgCl (sat. KCl) electrode. The scan rates employed were 3 and 5 mV/sec. for d.c. and a.c. polarography respectively. The ohmic voltage drop iR complication was solved by using a tungsten electrode as an auxiliary electrode.

Chemicals

The chemicals used were all of analytical-reagent grade. Carbonyl-free ethanol was obtained by refluxing absolute ethanol (2 L) with 5 g of 2,4-dinitrophenylhydrazine and 1.5 ml of concentrated hydrochloric acid for 4 hr. and then redistilling twice. Hydroxylamine hydrochloride, pyridine and all carbonyl compounds were prepared in carbonyl-free ethanol. Sodium hydroxide and sulphite aqueous solution was deoxygenated with nitrogen for 15 min. and stored in polyethylene bottle.

General Procedure

In the direct d.c. polarographic procedure 0.25 ml of hydroxylamine hydrochloride solution (0.1M) was transferred into a 25 ml volumetric flask which had already been flushed with nitrogen. Then 1 ml of the carbonyl compound solution was added. The volume was completed to the mark with oxygen-free solution of 1 M NaOH - 0.1 M Na_2SO_3 and the hydroxylamine polarographic anodic wave recorded exactly after 1 min. while nitrogen was passing over the surface of the solution. The procedure was repeated using 1 ml of ethanol

instead of the carbonyl compound solution and the difference in the wave height was a measure of the concentration of the carbonyl compound present.

For the determination of less reactive carbonyl compounds the above procedure was modified by adding 4 ml of ethanolic pyridine solution (1%) to the reaction mixture which was then heated to 70°C for 30 min. (unless otherwise stated) and then cool to room temperature. The volume was completed to the mark with NaOH- Na_2SO_3 solution and treated as above.

With the a.c. polarographic technique the above procedures were exactly followed except that 0.25 ml of 8×10^{-3} M of hydroxylamine hydrochloride was used.

All quoted measurements were the mean of three replicates.

Results and Discussion

Rapid d.c. polarography: in the development of these method several factors were examined. The hydroxylamine hydrochloride concentration and the instrumental parameters were arranged to give the maximum accuracy and precision in the measurement of the wave height.

Although the reaction of carbonyl compounds with free hydroxylamine, in general, is complete the instability of this reagent due to volatilisation or spontaneous decomposition or atmospheric oxidation discourages its use. The magnitude of this source of error was examined by delaying the recording of the hydroxylamine wave for 5 min. after adding sodium hydroxide solution and it was found that 20% of hydroxylamine has been decomposed as compared to 1 min. delay procedure. Therefore, for reproducible and sensitive results the polarogram should be measured as soon as possible after a fixed time from introducing sodium hydroxide solution.

On the other hand, although the hydroxylamine hydrochloride is relatively stable an equilibrium is involved in its reaction with carbonyl compounds, and special conditions are necessary in many cases to obtain substantially complete reactions. The hydroxylamine hydrochloride in 1% ethanolic pyridine solution was found to be stable for longer than 1 hr at 70°C.

The effect of 15 carbonyl compounds on the hydroxylamine wave height was investigated. The results obtained (Table 1) indicate that for all tested aldehydes the equilibrium was sufficiently favourable for satis-

Table 1. The magnitude of the decrease in 1×10^{-3} M hydroxylamine hydrochloride wave height ($\Delta id, \text{cm}$) by 6×10^{-4} of some carbonyl compounds.

Compound	$\Delta id^{(a)}$	Compound	$\Delta id^{(a)}$	$\Delta id^{(b)}$
Formaldehyde	10.4	Acetone	7.4	10.3
Acetaldehyde	10.0	Methyl ethyl ketone	6.7	10.2
Glyoxal ^c	11.7	Methyl n-propyl ketone	6.5	10.0
Propionaldehyde	9.5	Ethylacetoacetate	4.2	9.0
Furfuraldehyde	10.0	Acetylacetone	5.2	11.3
Benzaldehyde	9.8	Acetophenone	3.0	10.0
Anisaldehyde	10.0	Diacetyl	10.2	10.3
Salisaldehyde	9.8			

a) Direct procedure; id blank = 17.5 cm

$\Delta id = id \text{ blank} - id \text{ sample}$

b) Pyridine procedure; id blank = 17.2 cm

c) Concentration of glyoxal = 3×10^{-4} M

factory results to be obtained without special precautions using the direct procedure. On the other hand ketones, particularly those containing very bulky groups, did not show a complete reaction by the direct procedure probably due to steric hindrance. It was, therefore, necessary to use systems that will force the reaction to completion such as applying elevated temperatures and using an acid acceptor in the oximation system to tie up the liberated acid. The Bryant and Smith² method which has been used for many years is based on the use of pyridine as the acid acceptor. In the present work the pyridine procedure was found to give satisfactory results with all the examined ketones.

All tested aldehydes reacted quantitatively with hydroxylamine at room temperature while sterically hindered ketones generally required elevated temperature for quantitative reaction. However, temperatures in excess of 70°C are not recommended, for the losses by volatility would be too great on the μM - scale.

The oximation reaction of all examined aldehydes was found to be complete in 1 min. which is the time required for recording the polarogram whereas the reaction of ketones needed 30 min. for completion except acetophenone which required a reaction time of 1 hr.

Calibration graphs for the determination of some carbonyl compounds are shown in Fig. 1. The relative

standard deviation for 7 replicate determinations of 6×10^{-4} M acetone is $\pm 1.4\%$.

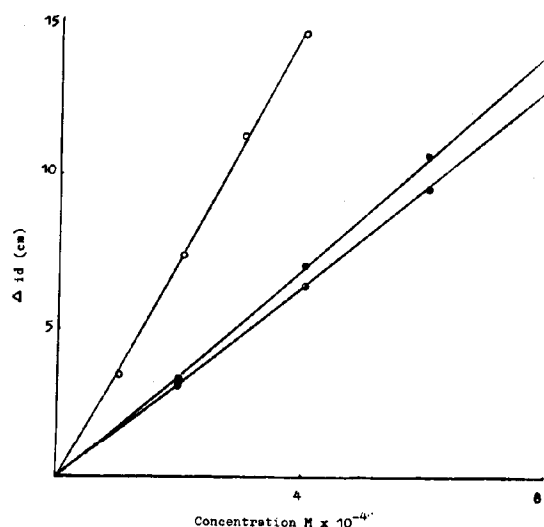


Fig. 1: Rapid d.c. calibration graphs for the determination of Glyoxal (o); acetaldehyde; formaldehyde (o); diacetyl (direct procedure) and acetophenone and acetone (ϕ) (pyridine procedure).

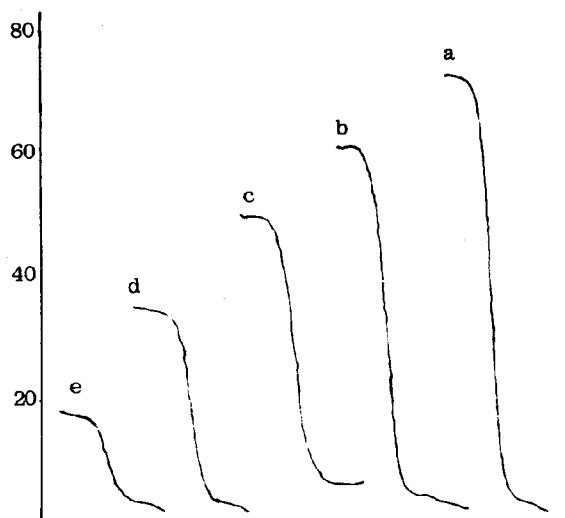


Fig. 2: Effect of acetaldehyde on the rapid d.c. wave of 1.0×10^{-3} M hydroxylamine (a) 0.0; (b) 2×10^{-4} M; (c) 4×10^{-4} M; (d) 6×10^{-4} M; (e) 8×10^{-4} M.

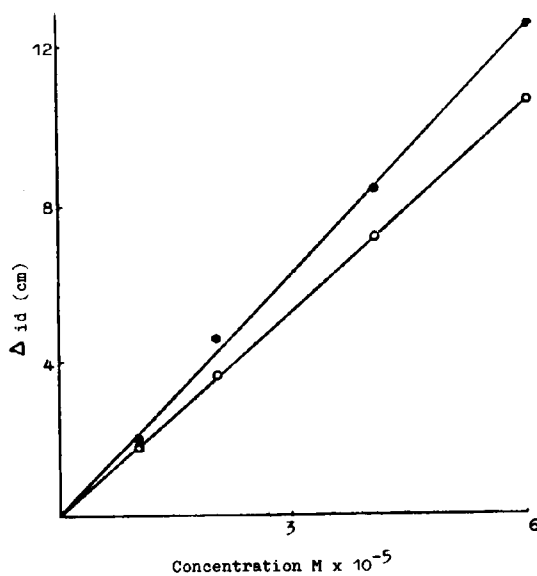


Fig. 3: Rapid a.c. calibration graphs for the determination of formaldehyde, acetaldehyde (.) (direct procedure) and acetone (o) (pyridine procedure).

The effect of various concentrations of acetaldehyde on the height of the d.c. polarographic wave of hydroxylamine hydrochloride (10^{-3} M) is shown in Fig. 2. The half-wave potential of hydroxylamine wave (-0.32 V) was unaffected by adding acetaldehyde. This indicates that the wave measured is that of the unreacted hydroxylamine. No other waves were observed in the potential range -0.2 to -0.5 V.

Rapid a.c. polarography

As previously mentioned the feasibility of using the rapid a.c. polarographic technique for the determination of hydroxylamine has been shown by Canterford¹⁴. In the present work, the determination of the 15 carbonyl compounds via the rapid a.c. polarographic recording of the unconsumed hydroxylamine anodic wave was investigated. The result obtained showed 10-fold improvement in sensitivity as compared with the d.c. technique for all the carbonyl compounds reported in Table 1. Fig. 3 illustrates examples of some of the calibration graphs constructed. The relative standard deviation for 7 replicate measurements of 4×10^{-5} M of acetone is $\pm 1.6\%$. The effect of different concentrations of acetaldehyde on the hydroxylamine rapid a.c. polarographic wave is shown in Fig. 4.

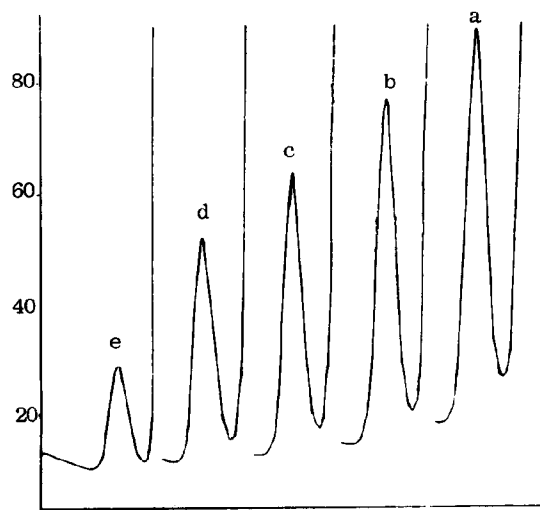


Fig. 4: Effect of acetaldehyde on the rapid a.c. wave of 8.0×10^{-5} M hydroxylamine (a) 0.0; (b) 1×10^{-5} M; (c) 2×10^{-5} M; (d) 4×10^{-5} M; (e) 6×10^{-5} M.

Table 2. Analysis for total carbonyl group.

Mixture, M x 10 ⁻⁵	Total carbonyl group taken M x 10 ⁻⁵	Total carbonyl group found M x 10 ⁻⁵
Formaldehyde (1), glyoxal (1), acetone (1) and acetophenone (1)	5	4.7
Methylethyl ketone (1), methyl-n-propyl ketone (0.5), benzaldehyde (1) and propionaldehyde (0.5).	3	3
Formaldehyde (0.5), acetaldehyde (0.5), propionaldehyde (0.5) and salicylaldehyde (0.5).	2	1.9
Acetone (1), methylethyl ketone (0.5), methyl-n-propyl ketone (0.5) and acetophenone (1).	3	2.8

The fact that the decrease in the hydroxylamine wave height per carbonyl group is the same for all carbonyl compounds which were investigated indicates the applicability of these methods to functional group analysis for a wide range of aliphatic and aromatic aldehydes and ketones. The pyridine procedure with a.c. measurement was applied for the determination of total carbonyl function. The results obtained (Table 2) by referring to acetaldehyde calibration graph indicate an error of the order of 5%. This error in total carbonyl group measurement could be minimized by referring to a ketone calibration on one hand and to an aldehyde calibration on the other and then calculating the average.

To conclude, the d.c. and a.c. polarographic techniques have proved to be simple, rapid, fairly sensitive and acceptably precise methods for an indirect determination of carbonyl compounds.

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