

## MICRODETERMINATION OF SOME ORGANIC NITRILES USING THE CYANIDE ION SELECTIVE ELECTRODE

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### ABSTRACT

The response characteristics of the solid state cyanide ion selective electrode toward some organic nitriles are investigated. In 10 M KOH solution, the electrode exhibits near Nernstian response over the range of  $10^{-2}$  to  $10^{-5}$ M of various substituted benzylnitriles with an anionic slope of 53 - 59 mV/concentration decade. The response time varies from 2 to 15 minutes depending on both the nature of the substituent group and the concentration of the nitrile compound. Direct potentiometric measurement of some nitriles at the level of 0.01 to 1 mg/ml shows an average recovery of 98.2% and a standard deviation of 2.3%. Many nitrogen functional groups do not interfere.

### INTRODUCTION

Ion selective electrodes have been developed to monitor ionic species. They cannot be used for direct determination of most organic functional groups. Similarly, covalently bound species can be determined only after conversion into their ionic counterparts by decomposition or chemical transformation (Ma and Hassan, 1982). It has been reported, however, that some organically bound sulfur (Hassan and Rechnitz, 1982, Hassan and Rechnitz, 1983), halogen (Rakias, Toth and Pungner, 1980), and fluorine (Zentner, 1973) compounds can directly be determined without prior decomposition using the sulfide, halide and fluoride ion selective electrodes, respectively.

The present work was undertaken to study the response characteristics of the solid state cyanide ion selective electrode for some organic nitriles and to develop a simple method for their potentiometric determination. The choice of these compounds resulted from their action as potential physiological hazards and the absence of simple methods for their determination.

### EXPERIMENTAL

#### Apparatus

The potentiometric measurements were conducted with Orion 701 pH-meter using Orion cyanide ion selective electrode (Model 94-06A) in conjunction with an Orion double junction reference electrode (Model 90-02) with 10%  $\text{KNO}_3$  in the outer compartment (Hassan, 1977).

### Reagents.

Unless otherwise stated, all reagents used were of analytical reagent grade, and deionized water was used throughout. The purity of the nitrile samples was not less than 99% as confirmed by elemental nitrogen analysis. Solutions of  $10^{-1}$  to  $10^{-4}$ M of various substituted benzylnitriles were prepared in 96% ethanol.

### Procedure.

Transfer a 9-ml aliquot of 10 M KOH solution to a 50-ml beaker. Immerse the cyanide electrode and the double junction reference electrode in the solution, and connect to the pH-meter. Switch on the millivolt scale, stir the solution, and record the potential reading after it becomes stable. Add to the solution 1.00 ml aliquot of  $10^{-4}$  to  $10^{-6}$ M of the alcoholic benzylnitrile solution, each in a separate experiment, stir and record the potential reading. Plot a calibration curve between the potential reading in millivolts and the logarithm of the nitrile concentration. Use the curve for subsequent measurements of unknown benzylnitrile solutions.

## RESULTS AND DISCUSSION

The output potential of the cyanide electrode in conjunction with a double junction Ag/AgCl reference electrode was measured at 25°C for  $10^{-2}$  to  $10^{-5}$ M benzylnitriles in KOH solutions of different concentrations. No response was noticed in alkali solutions of  $\text{pH} < 12$ . In alkaline solutions of concentrations 1 M, however, the electrode responded linearly to the logarithm of the nitrile concentration. A tenfold change in the concentration of various benzylnitriles gave rise to a potential change ranging from 31 to 58 mV depending on both the nature of the substituent group (electron attracting or electron repelling groups) and the concentration of alkali (Fig. 1). In 10 M KOH solution, various substituted benzylnitriles displayed a potential change of 58 mV/concentration decade. Typical response curves of benzylnitrile and potassium cyanide in 10 M KOH are in Fig. 2. Under these conditions, the time required for the electrode to reach values within  $\pm 1$  mV of the steady potential varied from 2-5 to 6-15 minutes for  $10^{-2}$  and  $10^{-4}$  M solutions of the organic nitriles, respectively.

Table 1 summarized the performance characteristics of the cyanide electrode toward some substituted benzylnitriles. Determination of some of these compounds at the concentration level of 0.01 to 1 mg/ml using the calibration curve method (Ma and Hassan, 1982) show an average recovery of 98.2% and a mean standard deviation of 2.3%. Amines, amides, anilides and hydrazines (e.g., aminophenol, benzamide, acetanilide and hydrazine sulfate) at a concentration as high as 100-fold molar excess over benzylnitriles do not interfere. This procedure offers many advantages in term of sensitivity, simplicity and selectivity over many of the commonly used methods involving measurement of the total nitrogen content or reduction into ammonia or amide (Whitehurst and Johnson, 1958).

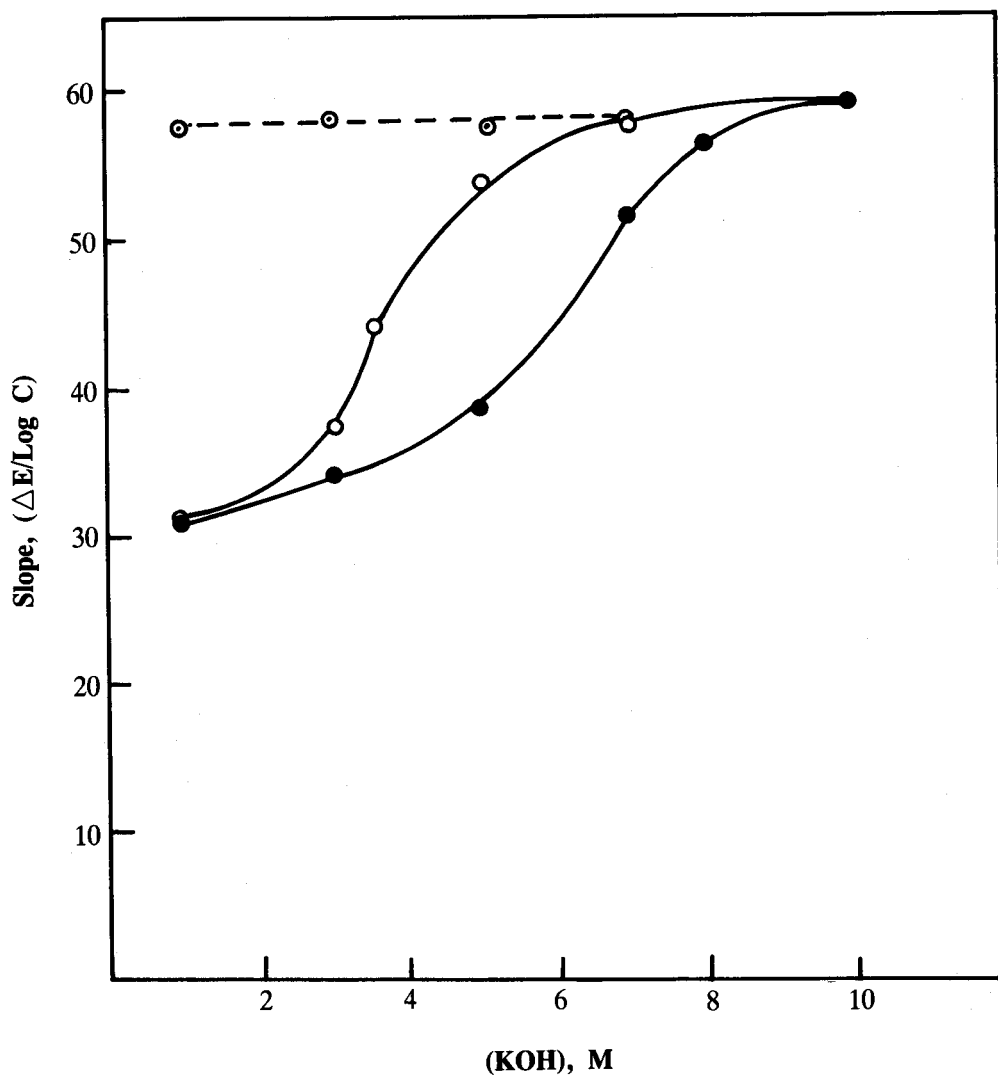


Figure 1. Effect of alkali concentration on the response of the cyanide electrode for : . KCN, ○ p-methyl-benzonitrile; and ● p-fluorobenzonitrile.

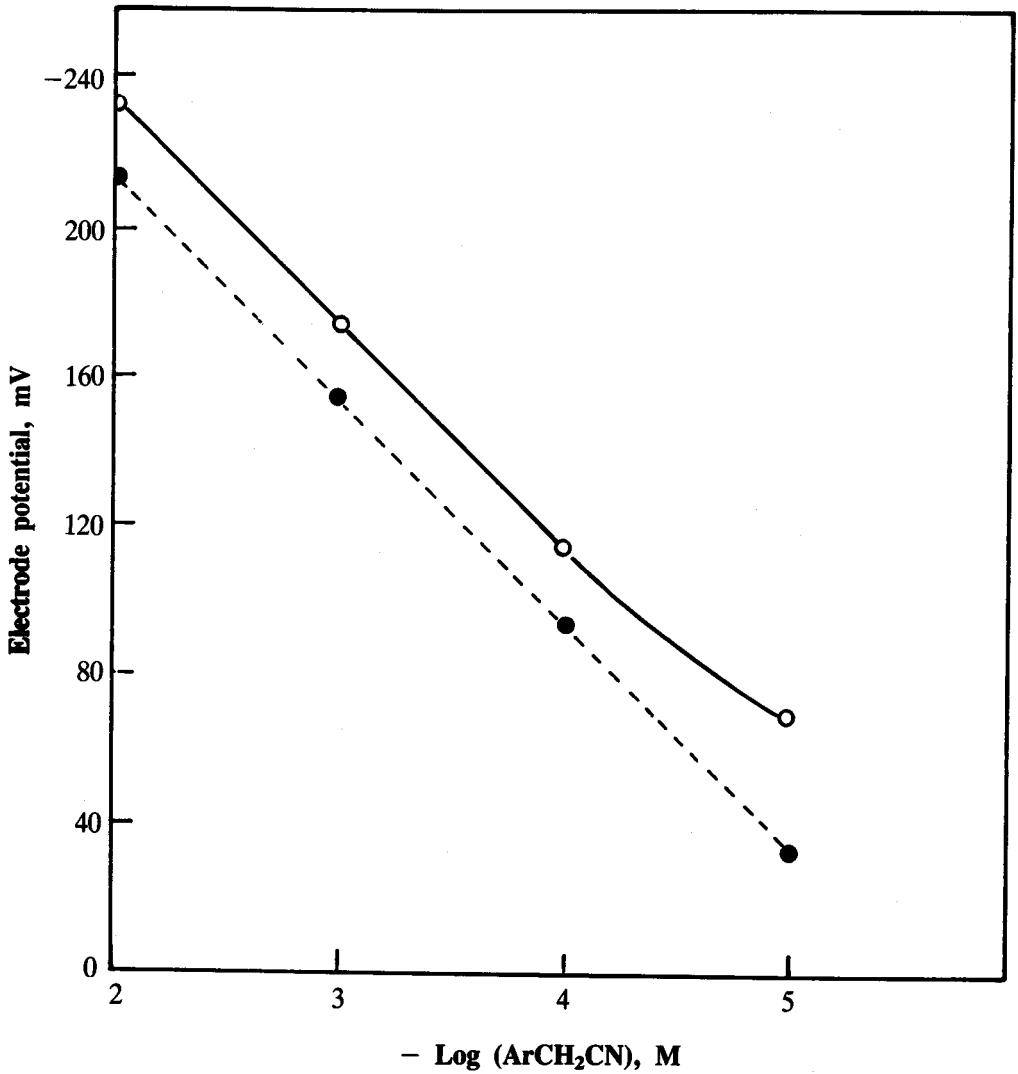


Figure 2. Typical calibration graphs for: ● KCN; and ○ benzonitrile in 10 M KOH using the cyanide ion selective electrode.

Table 1

Response Characteristics of the Cyanide Ion Selective Electrode Toward Some Benzyl nitrile Derivatives in 10 M KOH.

Substituent group	Slope (mV/log C)	Standard dev. mV	Response time, min	Lower limit of linear range, M
—	59	1.3	4 - 10	$3 \times 10^{-5}$
<u>o</u> -Cl	53	1.1	6 - 15	$5 \times 10^{-4}$
<u>m</u> -Cl	58	1.3	4 - 10	$10^{-4}$
<u>p</u> -F	58	1.5	5 - 10	$10^{-4}$
<u>o</u> -F	53	1.4	8 - 15	$10^{-4}$
<u>m</u> -F	58	1.6	4 - 8	$2 \times 10^{-5}$
<u>p</u> -CH <sub>3</sub>	59	1.4	3 - 8	$6 \times 10^{-5}$
<u>o</u> -CH <sub>3</sub>	58	1.4	5 - 10	$5 \times 10^{-5}$
<u>m</u> -CH <sub>3</sub>	59	1.4	2 - 6	$4 \times 10^{-5}$

The response of the cyanide electrode for benzyl nitriles is not due to any free cyanide ion present as contaminant. Moreover, no cyanide ion is split off on treatment with alkali. This is based on the finding that some nitriles are extracted unchanged from 10 M KOH solution as verified by elemental analysis and infrared data. Furthermore, no cyanide ion is detected in the aqueous alkali test solution as confirmed by negative Prussian blue test. It is worthy to mention that hydrolysis of organic nitriles does not yield cyanide ion, but under controlled conditions it gives ammonia. Few nitriles give cyanide ion only upon enzymatic hydrolysis (Hassan, 1982). It seems, however, that the high polarising power of the  $C \equiv N$  group in strong alkali solutions imparts an appreciable dipole moment ( $D = 3.5$ ) to the organic moiety (Shaw, 1965) and allows the non-ionized but strongly polar organic molecules to be absorbed and sensed at the membrane of the electrode.

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## التقدير الكمي الميكروئي لبعض النيتريلات العضوية باستخدام القطب الاختياري لأيون السيانيد

سعد السيد محمد حسن

درست استجابة القطب الاختياري لأيون السيانيد تجاه بعض النيتريلات العضوية ، ووجد أن هذا القطب يستجيب إستجابة تتفق مع معادلة نرنست لعدد من مركبات النيتريل العضوية المستبدلة بمجموعات طاردة أو ساحبة للاليكترونات . وبإذابة هذه المركبات في محلول ١٠ ملاري من إيدروكسيد البوتاسيوم فإن هذه المحاليل تظهر علاقة خطية بين جهدا وتركيز المركبات ويبلغ ميل الحظ ٥٣ - ٥٩ ميليفولت لكل وحدة لوغاريتمية من التركيز . ويبلغ وقت الاستجابة لهذا القطب ٢ - ١٥ دقيقة معتمداً على تركيز النيتريل وطبيعة المجموعة المستبدلة فيه . وقدرت كميات تبلغ ٠١ ر إلى ١ ميليجرام/سم<sup>٢</sup> من هذه المركبات بالطريقة الجهدية المباشرة ، وبلغت دقة النتائج ٩٨٢٪ بتفاوت قياس مقداره ٢ر٢٪ ولا تتداخل كثير من المركبات النيتروجينية العضوية .