

Full Paper

An Electrode Immobilized in a Graphite Matrix with Ion Pair Complex for the Determination of Pentachlorophenol

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Abstract- A simple, precise, rapid and low-cost potentiometric method for the determination of pentachlorophenol is proposed. A new pentachlorophenol-sensitive electrode was constructed by incorporating the pentachlorophenol ion pair complex with rhodamine 6G into graphite matrix. The electrode exhibited a linear response over the concentration range of 1×10^{-5} – 5×10^{-2} mol/L, a detection limit of 1.7×10^{-6} (5.2×10^{-5}) mol/L with a Nernstian slope of 41 ± 1 (68 ± 1) mV/decade. The working pH range is 7.5–10.5. The electrode is easily constructed, has fast response time (3–10 s) and can be used for the period of six months without any considerable deterioration. The proposed sensor displays good sensitivity for pentachlorophenol.

Keywords- Pentachlorophenol, Potentiometry Sensors

1. INTRODUCTION

Pentachlorophenol (PCP) is widely used in industry and agriculture for the treatment of wood and for its protection from mould, rodents and insects. Relatively high volatility of PCP and its insolubility in water leads to its concentration in various industrial and biological

objects thus contaminating the environment. PCP is toxic, and is described in literature as highly carcinogenic of B₂ group that causes mutations in human organism [1-2]. Various techniques were proposed for its determination: spectrophotometry [3], liquid chromatography [4-6], gas chromatography [7], and electrochemical methods [8]. These techniques have certain advantages, though the majority of them require the preliminary derivatization of PCP. The use of simple and fast methods is gaining ever increasing demand. One of these is potentiometry with ion-selective electrodes (ISEs) [9]. They are not practically used for the determination of pentachlorophenolate ion [10].

2. MATERIALS AND METHODS

2.1. Equipment

An I-160 M model pH/mV meter with Ag-AgCl reference electrode was used for the measurements of potential difference at 25.0±0.1 °C.

2.2. Reagents

All chemicals were of analytical-reagent grade. Distilled water was used to prepare all solution and in all experiments. Dibutylphtalate (DBP), dibutylsebacate (DBS), dioctylphtalate (DOP), dinonilphtalate (DNP), tricresylphosphate (TCP) were obtained from Sigma-Aldrich. The 0.04 mol/L buffer solutions of pH 2–12 ranges were freshly prepared.

The freshly prepared aqueous standard solutions (1×10^{-8} – 5×10^{-2} mol/L) of pentachlorophenol (Sigma-Aldrich) were prepared in 0.04 mol/L of buffer solution (for the study of the effect of pH) for analytical purposes. Buffer solutions (pH 2–12) were prepared by mixing corresponding amounts of 0.04 M H₃BO₃, 0.04 mol/L CH₃COOH, 0.04 mol/L H₃PO₄ and 0.2 mol/L NaOH. The ionic strength was adjusted with 0.1 mol/L NaCl.

2.3. Construction of the Ion-Selective Electrode

2.3.1. Preparing of an Electrode Active Substance

An ion pair complex of pentachlorophenol with rhodamine 6G was prepared by mixing equal quantities of 1×10^{-2} mol/L pentachlorophenol and 1×10^{-2} mol/L of rhodamine 6G. The solution was settled for 2 h and the sediment of ion pair complex was filtered (quantitative rapid filter paper). This residue was treated with 50 ml of cold distilled water. The filter paper containing the precipitate was dried for 24 h at room temperature. This ion pair complex was used as an electrode-active substance in the preparation of the ion-selective electrode for pentachlorophenol determination.

The ion-selective electrode was prepared as follows: a PVC tube (5.0 mm×7.0 cm) was cleaned and degreased. A working end was a Wood alloy substrate (2.0 mm thick) to which the lead was soldered that formed a site for the deposition of the active component. Electrode

active substance (an ion pair complex of pentachlorophenol with base coloring agent rhodamine 6G, 0.02 g), DBP (0.02 ml) and pure powdered graphite (0.04 g) were mixed in a mortar until a homogeneous paste was obtained. The paste was then deposited onto the prepared site and dried for 2 h.

When not in use, the electrode was kept immersed in a small volume of 0.05 mol/L pentachlorophenol solution.

3. RESULTS AND DISCUSSION

3.1. Electrode Response

The effect of solvent mediators on the potentiometric response characteristics of the pentachlorophenol ion-selective electrode based on the pentachlorophenol ion pair complex with rhodamine 6G was investigated, and the results are summarized in Table 1 – 2. The corresponding EMF responses are shown in Fig.1. Significant difference in the potential response of the electrodes was found among the five different solvent mediators that were used.

Table 1. Characteristics of different electrode active substances with different solvent mediators of pentachlorophenol ion-selective electrodes

Plasticizer	Slope (mV)	Linearity range (mol/L)	Detection limit (mol/L)	Response time (s)
DBP	50	$9 \times 10^{-5} - 5 \times 10^{-2}$	5.2×10^{-5}	3–5
DBS	-	-	-	-
TCP	68	$9 \times 10^{-5} - 5 \times 10^{-2}$	5.2×10^{-5}	3–5
DOP	65	$9 \times 10^{-4} - 5 \times 10^{-2}$	1.8×10^{-4}	3–7
DNP	41	$9 \times 10^{-5} - 5 \times 10^{-2}$	1.7×10^{-6}	4–10

Note: Average of five determinations.

The pentachlorophenol ion-selective electrode made using DBP exhibited a calibration plot of a very good Nernstian slope for pentachlorophenol concentrations between 1×10^{-8} and 5×10^{-2} mol/L with detection limit of 1.7×10^{-6} mol/L. Consequently, the electrode made using DNP was selected for the remaining studies.

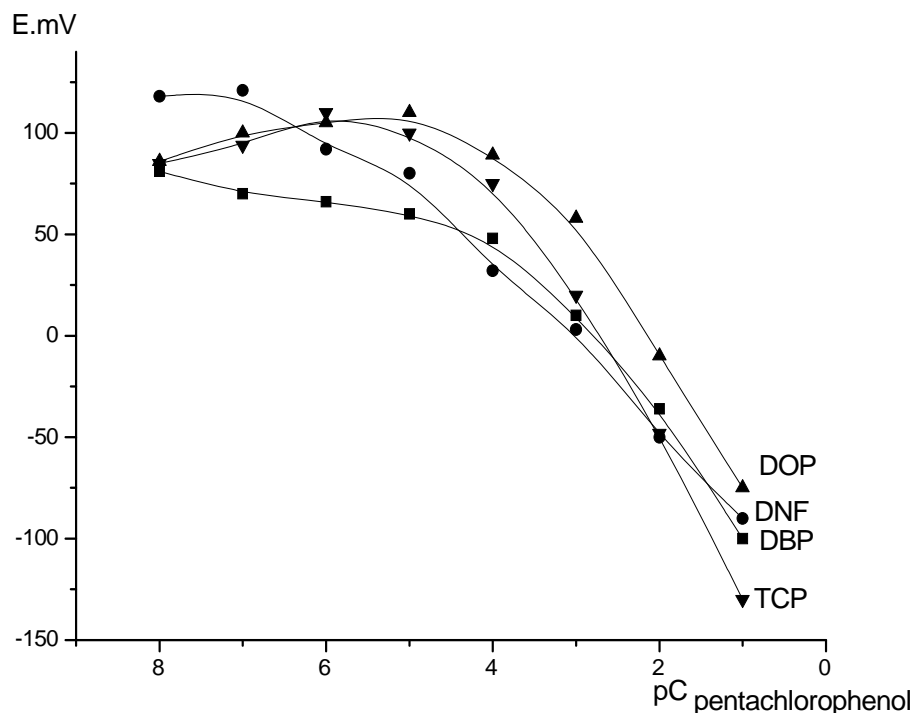


Fig. 1. Effect of the nature of the plasticizers on the electrode response

Table 2. Characteristics of ion-selective electrodes with different content of electrode solvent mediator

Content of electrode solvent mediator, DNP %	Slope (mv)	Linear range (mol/L)	Detection limit (mol/L)	Response time (s)
38	35	$9 \times 10^{-5} - 5 \times 10^{-2}$	3.6×10^{-4}	3–5
48	43	$9 \times 10^{-5} - 5 \times 10^{-2}$	1.8×10^{-6}	4–10
58	41	$9 \times 10^{-5} - 5 \times 10^{-2}$	1.7×10^{-6}	4–10
74	40	$9 \times 10^{-4} - 5 \times 10^{-2}$	3.5×10^{-5}	4–10

Note: Average of five determinations.

For analytical applications, the response time of a sensor is an important factor. The static response time of the electrode, tested by measuring the average required to achieve a potential within ± 1 mV of the final steady-state potential upon successive immersion of a series of pentachlorophenol solutions, each having a ten-fold difference in concentration, was within 10 s for pentachlorophenol concentrations $< 10^{-3}$ mol/L. The potential stayed constant for about 5 min, after which a very low divergence within the resolution of the millivoltmeter was observed.

3.2. Effect of content of electrode-active substance

The influence of the content of electrode active-substance electrodes on the potential response was tested in the 5–25 % range (adjusted with 0.1 mol/L NaCl). The results are shown in Table 3. Thus, the content of electrode active substance does not significantly modify the potential response.

3.3. Effect of pH

The most important factor of the functioning of the most all ion-selective electrodes is the acidity of the medium expressed as pH value. The reason for this is chemical processes involving the membrane components, the determined substance, and H_3O^+ or OH^- ions. Wide application of an ISE requires the knowledge of the operating pH range of the given electrode. This is especially important for the electrodes sensitive to organic anions. The acidity of the medium affects the state of an ion associate and other membrane components. A number of parallel protolytic processes take place at the membrane-solution interface that can be quite complicated. We have investigated the effect of pH on main electrode characteristics of our ISE based on the ion associate with a basic dye. Generally, the operating pH range of an ISE with an ion associate is determined by the protolytic properties of the ion associate components [11].

Table 3. Characteristics of ion-selective electrodes with different content of electrode-active substance (plasticizer – 65% DNP)

Content of electrode-active substance, %	Slope (mV)	Linearity range (mol/L)	Detection limit (mol/L)	Response time (s)
5	51	1×10^{-5} – 5×10^{-2}	2.8×10^{-5}	3–5
10	41	9×10^{-5} – 5×10^{-2}	1.7×10^{-6}	4–10
15	50	1×10^{-5} – 5×10^{-2}	1.4×10^{-5}	3–5
20	74	1×10^{-5} – 5×10^{-2}	5.0×10^{-5}	3–5
25	61	1×10^{-4} – 5×10^{-2}	3.1×10^{-5}	4–10

Note: Average of five determinations

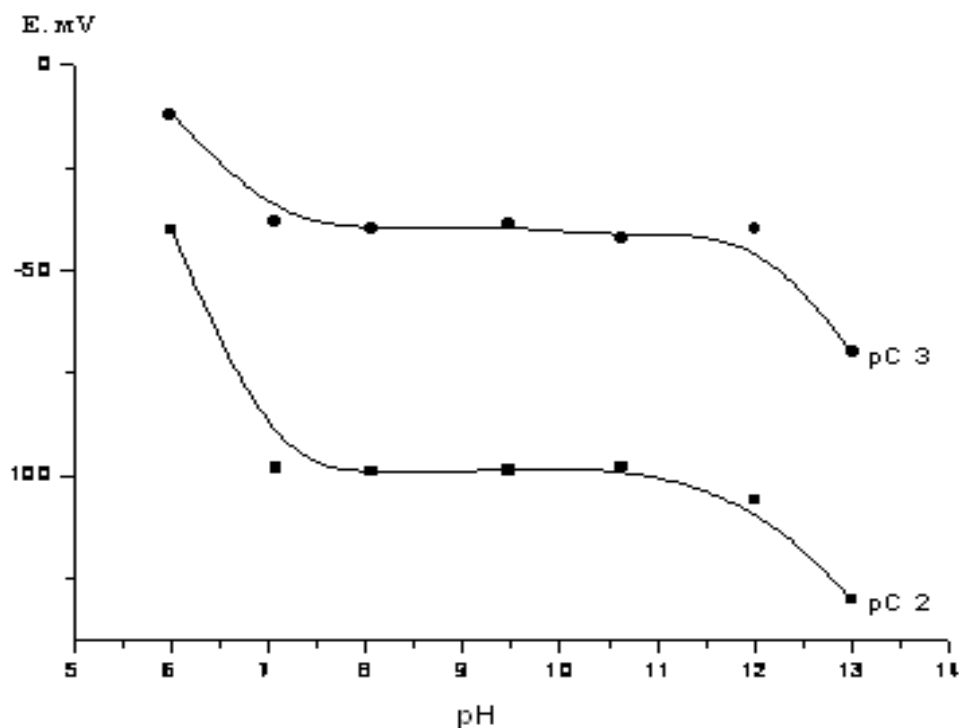


Fig. 2. Effect of the solution pH on the electrode potential of pentachlorophenol-selective sensor

The effect of pH on the potential response of pentachlorophenol ISE was tested using 1×10^{-8} – 5×10^{-2} mol/L pentachlorophenol solutions over the pH range of 7.5–10.5 (Fig. 2). The pH was adjusted using universal buffer solutions. It is apparent from pH-potential profiles that there is no change in potential response. So this entire range of pH can be taken as the operating pH range of the electrode. It is one of the main and very important advantages of this pentachlorophenol ISE.

3.4. Potentiometric selectivity coefficients

An important characteristic of any ion-selective sensor is its response to the primary ion in the presence of other ions present in solution, which is expressed in terms of the potentiometric selectivity coefficient [12]. The potentiometric selectivity coefficient of the pentachlorophenolate sensor was determined by the “separate solutions” method. The developed sensors exhibit satisfactory selectivity toward common anions: SO_4^{2-} , HPO_4^{2-} , Cl^- , Br^- , I^- , IO_3^- , ClO_3^- (≥ 4), NO_3^- (2), $\text{C}_6\text{H}_5\text{COO}^-$ (1.5), ClO_4^- (1). One can see that the potentiometric selectivity coefficient correlates to the hydration energy of the respective ion.

3.5. Applications

Table 4 shows the results of proposed method that was successfully applied for the determination of pentachlorophenol in its solutions. The content of these solutions was then determined by the proposed electrode using the “added-found” method.

Table 4. Potentiometric determination of pentachlorophenol

Probe	Added, mg	Found, mg	
1	75	74.8	$\bar{X} = 74.8$; RSD = 1.2 %; $\Delta X = \pm 1.1$; $\varepsilon = 0.26$ %
2	100	98.8	$\bar{X} = 98.8$; RSD = 1.3 %; $\Delta X = \pm 1.6$; $\varepsilon = 1.2$ %

$n=5$, Confidence level of 95 %. Note: RSD = relative standard deviation

The proposed electrode exhibits long lifetime, good stability, sensitivity, precision, and selectivity. It had rather good metrological characteristics, high sensitivity; it is low-cost, easy to prepare and to use. An electrode was developed by us is superior (especially in wide pH range of the determination of pentachlorophenol and lifetime) compared to pentachlorophenol ion-selective electrodes described in other methodologies of its potentiometric determination.

4. CONCLUSION

A simple, precise, rapid and low-cost potentiometric method for the determination of pentachlorophenol is reported. The pentachlorophenol-sensitive electrode was constructed by incorporating the pentachlorophenol ion pair complex with rhodamine 6G into graphite matrix. The electrode exhibited a linear response over the concentration range of 1×10^{-5} – 5×10^{-2} (9×10^{-5} – 5×10^{-2}) mol/L, a detection limit of 1.7×10^{-6} (5.2×10^{-5}) mol/L with a Nernstian slope of 74 ± 1 mV/decade. The working pH range is 7.5–10.5. The electrode is easily constructed, has fast response time (3–10 s) and can be used for the period of six months without any considerable deterioration. The proposed sensor displays good selectivity for pentachlorophenol.

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