FIA of Phenol and Pentachlorophenol at Glassy Carbon Electrode in Oxidative Mode

SHAHID BILAL BUTT* AND MUHAMMAD NASIR MASOOD
Central Analytical facility Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan.

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Summary: Flow injection analysis (FIA) method for phenol and pentachlorophenol (PCP) at glassy carbon electrode has been developed. Effect of supporting electrolyte concentration and its nature, effect of sample and ground electrolyte pH, influence of flow rate and passivation of glassy carbon electrode were studied. It was found that an appropriate concentration of supporting electrolyte is required for a better sensitivity of analyte. Phenol and pentachlorophenol can be efficiently analyzed at pH 7. Flow rate between 0.5 to 1.0 ml/ min is optimum for the analysis. Working electrode activity can be regenerated by keeping it at - 0.8V for ten minutes in the flow stream of ground electrolyte. Detection limits for phenol and pentachlorophenol without a preconcentration step is 40 and 100 μg / L respectively and their relative standard deviation (RSD) is around six (N = 4) and four (N = 4) respectively. The former can be improved by incorporating solid phase extraction/ preconcentration that will lower it to hundred times. The proposed method is simple, sensitive and above all selective.

Introduction

Phenol and its substituted products are well known priority pollutants and are potential carcinogenic [1]. Their quantitative structure activity relationship (QSAR) studies reveal that phenols with electron withdrawing groups can produce toxic free radicals. Presence of nearby 380 types of substituted phenols has been reported in the main stream of cigarette smoke [2]. As phenols are byproducts of many industrial processes such as production of plastics, dyes, weed control agents and coking plants, they may be present in raw and potable water resources via spillage or accidents [3-7]. Phenols and its derivatives are toxic to fish and other aquatic animals and cause bad taste and odor in both water and fish at ppb level [8]. So their presence is of great concern and needs to be addressed regarding public health. Therefore, it is essential to develop accurate and precise methods for analysis of phenols and then to propose their removal strategies. Phenols can be detected in water at 0.01-0.1 mg/ l by its taste and odor [9]. The toxic effect of phenol in water enhances by the formation of chlorophenols by chlorination when chlorine is used for the water disinfection [5]. Due to being potential toxicant the EPA, USA selected eleven phenols on the list of priority pollutants [10]. The maximum admissible concentration of phenol and its derivatives in water is 0.5μg/ l for the individual compound. This limit is in accordance with European Community directives [3, 5-6]. It is therefore crucial to monitor concentration of these pollutants in drinking water, using varieties of analytical techniques. A photometric method based on 4-aminoantipyrene for total phenol content is recommended by EPA, USA. However Para-substituted phenols may not be detected [6-11]. GC is more sensitive and provides detection limits in the range of 0.58 to 2.2μg/ L after appropriate extraction, preconcentration and derivatization as per guidelines of EC [6, 12-13]. HPLC has also been used for the analysis of priority phenols by incorporating UV-VIS [1, 3, 11, 14], fluorescence [15] or electrochemical detection [5-6, 14]. Electrochemical mode is the most sensitive of all these and by an online preconcentration using solid phase extraction along with a glassy carbon electrode and amperometeric detector, detection limits as low as 0.01-0.5 μg/ l can be achieved [5-14]. While using EC detector, the parameters such as pH, ionic strength, flow rate and concentration of organic modifier are investigated for efficient detection of priority phenols [12]. In the present communication we report the optimization of the above mentioned parameters for the monitoring of phenols in waste water using glassy carbon electrode.

Results and Discussion

Different experimental parameters have been studied in order to check the efficiency of the FIA system for the analysis of total phenol content in the

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*To whom all correspondence should be addressed.

solution. This includes magnitude of the blank response of working electrode, effect of supporting electrolyte concentration on sensitivity, influence of ground electrolyte, sample pH and flow rate.

Voltammetry of Pentachlorophenol

The voltammetry of PCP was carried out manually by varying the potential of LC-4B electrochemical detector using glassy carbon as working electrode and Ag/ AgCl as reference electrode. A hydrodynamic Voltammogram is shown in Fig 1. It shows that the oxidation peak potential is in the range of + 0.8 to 0.9 volts. This peak potential matched with the peak potential mentioned in the LC-4B detector manual.

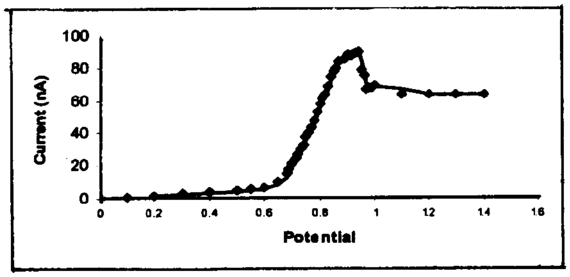


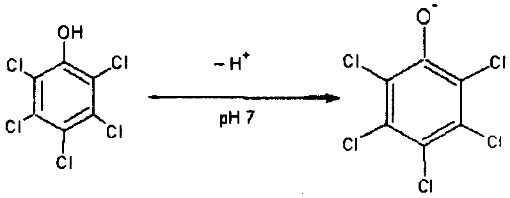
Fig. 1: Hydrodynamic Voltammogram for PCP in 1mM trisodium citrate and 4mM $NaClO_4$ buffer pH-7 at glassy carbon electrode vs Ag/ AgCl reference electrode, flow rate 1ml/ min.

Effect of Supporting Electrolyte Concentration

Ground electrolytes having varied concentrations were investigated. The buffer 0.2M sodium per chlorate and 5mM tri-sodium citrate in 40 % methanol-water [12] of pH 3.7 exhibited high background non-faradic current. Therefore, diluted buffers of pH 4 were prepared having electrolytic concentrations (2.5, 10), (1, 4) and (0.5, 2) mML^{-1} sodium citrate and sodium perchlorate respectively. High non faradic current was observed except with buffer concentration 1mM tri-sodium citrate and 4 mM sodium perchlorate. It gave adequate response and sensitivity for phenols at glassy carbon electrode at + 0.8V. It is due to the appropriate activities of citrate and perchlorate anions which may behave as ion pair for the oxidative products and net ionic strength of the solution remains same [16]. In addition, appropriate concentration of carboxylic compounds such as citrate anion may take part in intermediate oxidation reaction with the analyte. As a result a species that can be oxidized more easily and efficiently is produced [17]. Buffer with concentration 0.5, 2 mM of sodium citrate and sodium perchlorate respectively caused high uncompensated resistance R_u, as a result there was large iR drop. Thus, high concentration of supporting electrolyte reduces the sensitivity of the PCP and phenol oxidation peak where as the appropriate concentration improved the response.

Effect of pH

Electrochemical oxidation of phenol and pentachlorophenol was studied at pH 4 and 7. It was observed that at the applied voltage + 0.8V, current response increases from acidic to basic pH for both pentachlorophenol and phenol. Plots were drawn between the oxidative current nano ampere (nA) and concentration at pH 4 and 7. It showed that oxidation of pentachlorophenol and phenol was more feasible at pH 7. It is mainly because of the ease with which pentachlorophenolate and phenolate anions exist in solution at relatively higher pH and can be readily oxidized. The pKa values for PCP and phenol are 4.7 and 10 respectively. Nearly two units Shift in pH from pKa 4.7 to 7 for PCP ionize most of PCP and it exists as pentachlorophenolate anions. Similarly, there is effect of pH shifting on phenol response due to increase in concentration of phenolate anions [18-19]. It is clear from the Fig. 2 and Fig. 3 that pH has significant effect on detection efficiency and slope for phenol as compared to that of PCP. It is because of oxygen atom of phenol which is electron rich and probably making electron transfer kinetics more feasible as compare to oxygen atom of PCP which is electron lean due to the presence of five electron withdrawing chloro groups as shown in equation 1.



Equation – 1

Blank Response due to mismatch of ionic strength

Blank response level of glassy carbon electrode in FIA system is important in order to measure the accurate lower detection limit. It is

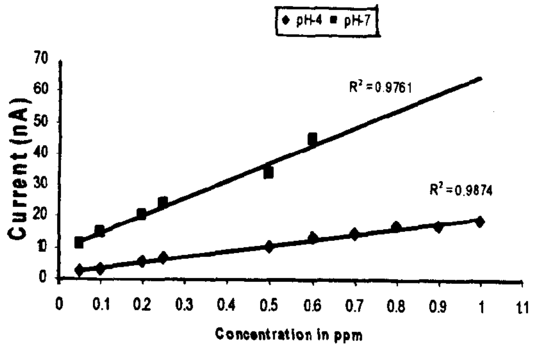


Fig. 2: Calibration curve for Phenol at 0+0.8V glassy carbon electrode using 40 % methanol/ water buffer pH 4 and 7 as ground electrolyte, flow rate 1ml/ min.

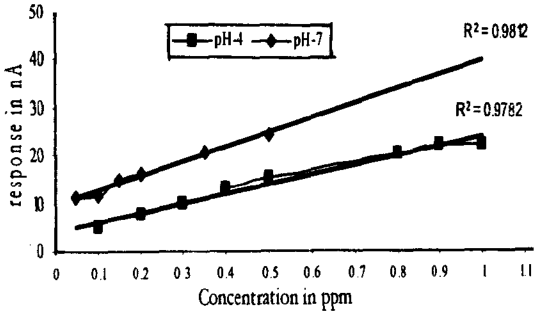


Fig. 3: Calibration curves for PCP at pH 4 and 7. Experimental conditions as per Fig 2.

composed of a transient component, which further composed of faradaic and nonfaradaic components of the response [20]. The amperometeric response varies with change in ionic strength of the injected blank. Therefore, electrode response as a function of ionic strength was studied. The pure methanol having no ionic strength without supporting electrolyte shows a sharp dip and then anodic rise in the response as shown in Fig. 4. Same behavior was observed when phenol was taken in the methanol. However, blank response was reduced when standard phenol solution was prepared in ground electrolyte. The transient component of the negative blank response is due to a compositional change in the electrical double layer which causes a change in the capacitance. Transient component also have some current contributed by oxidation-reduction of the electro active species. This is mainly due to a shift in redox formal potential $E^0$of a couple. The magnitude of the faradaic component of the blank response in the case of ionic strength mismatch mainly depends on pKa value and proton stoichiometries [20].

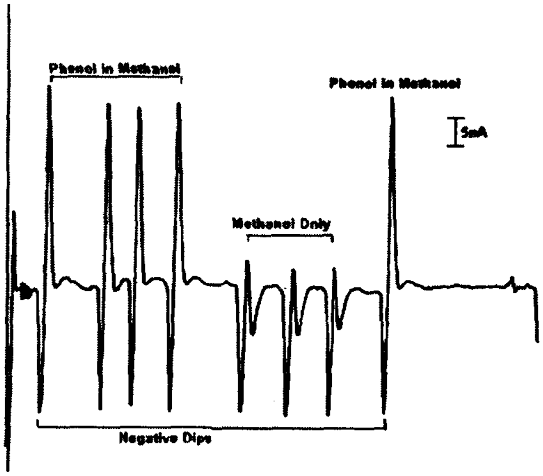


Fig. 4: Amperometeric response of one ppm phenol at pH-7. Experimental conditions as per Fig 2 except pH.

Efficiency of Glassy Carbon Electrode

A decrease in amperometeric response and fouling of glassy carbon electrode was observed after repeated injections of the analyte for its higher concentrations *i.e.* 2 ppm as shown in Fig. 5. Electrode passivation and fouling was more pronounced for pentachlorophenol as compared to phenol. It is mainly because of deposition of oxidative products via polymerization in free radical rich environment. Oxidation process may be a primary oxidation of molecules at the electrode surface or a secondary oxidation produced by free radicals generated in the primary process [18]. The latter is the main cause of polymerization. Three approaches are mostly employed to prolong the sensitivity and stability of electrode. A preventive approach is to suppress secondary oxidation by scavenging the phenoxy free radicals produced in the primary process. It was observed that perchlorate and citrate system have had better scavenging effect as compared to phosphate. That is why, relatively less passivation and fouling of glassy carbon electrode were observed in the currently employed perchlorate-citrate buffer system. Another approach is to remove deposited matter from the electrode surface by attempting its reduction or oxidation at different voltages. An in situ treatment of electrode by setting a negative potential of - 0.8V across working and reference electrode for at least ten minutes has much improved the efficiency of glassy carbon as shown

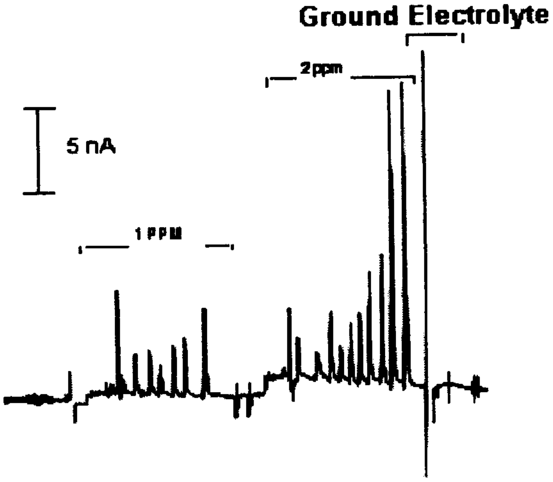


Fig. 5: Deteriorated response of PCP at glassy carbon electrode after around 80 injections. Experimental conditions as per Fig 2 except pH7

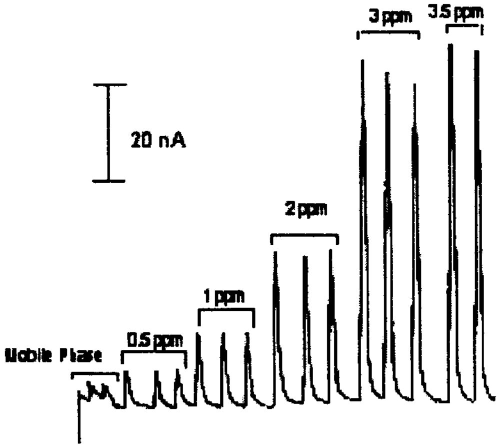


Fig. 6: Change in response of Glassy Carbon electrode after in situ treatment at -0.8V for ten minutes. Experimental conditions as per Fig 2.

in Fig. 6. As third option, polishing of working electrode is recommended from time to time [21] practically after two to three working days or after around 100 injections. A freshly polished glassy carbon electrode showed a transcendent improvement in response as shown in Fig. 7.

Flow Rate Effect

Flow rate affects peak shape rather than peak area or peak height. At flow rates lower than 0.5ml/min, peak broadening and tailing took place. At flow rates between 0.7-1.0 ml/ min peak shape improves to a regular Gaussian peak. At further higher rates, tailing, skewing and splitting of peak was observed.

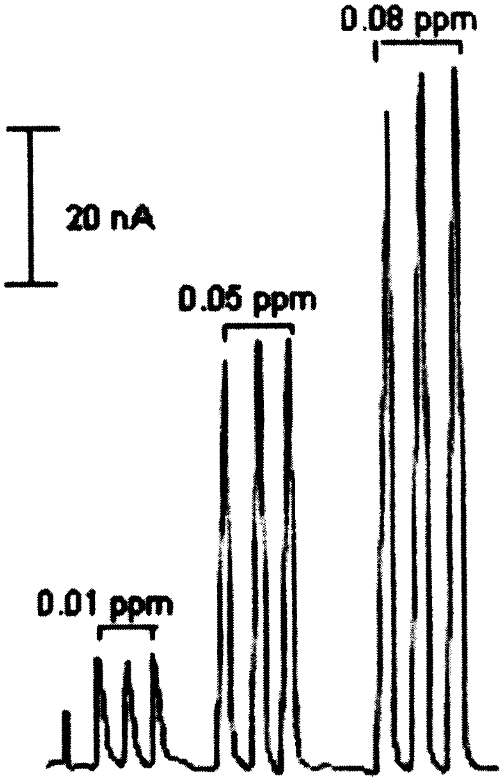


Fig. 7: Improved response of glassy carbon electrode at pH 7 after mechanical polishing with Alumina. Experimental conditions as per Fig 2.

Interference study

The influence of various cations and anions normally present in water and waste water on the amperometric response was studied. It was observed that 500 ppm of calcium, magnesium, chloride, sulphate and nitrates did not interfere. Moreover 100 ppm of potassium hydrogen phthalate, para hydroxy benzoic acid, 1,4-dibenzoic acid and salicylic acid also did not much affect amperometric response of phenol. This indicates the selectivity of the FIA system that is mainly due to the selective oxidative potential of phenols at the glassy carbon electrode which rarely overlaps with other analytes. It is a distinct advantage of electrochemical technique over a photometric method where interferences are expected due to sample matrix. This indicates that the FIA is quick, simple, sensitive and selective method.

Monitoring of Phenols in Waste Water

The developed FIA method was used to monitor total phenols in waste water samples. The samples were diluted as per requirement in the ground electrolyte. These were filtered using syringe filter of 0.45 micron. The presence of phenols was confirmed by standard addition of phenol in the sample. The results are summarized in Table-1. It may be mentioned that generally employed Million's test [22] for phenols require dissolution of mercury for preparation of fresh mercuric nitrate. Therefore, the proposed FIA is simple, sensitive, selective and environment friendly.

Table-1: Total Phenol concentrations in waste water measured by FIA method (µg/ L)

Serial No.	Phenol µg/ L[a]	Standard deviation	RSD
1	49	2.2	4.4
2	62	2.9	4.6
3	72	2.9	4.0
4	51	2.2	4.5

a: Average of quadruplicate values.

Experimental

Instrumentation

The HPLC solvent delivery system consisted of quaternary gradient pump K-1001 and solvent organizer K-1500 were from Knauer, Germany. The standards and samples were injected using a injection loop of 20 µl that was used in combination with Rheodyne injector 7725i. Detection of the phenols in flow injection analysis system was carried out with the help of an electrochemical detector LC-4B BAS, USA. The electrochemical cell consists of a glassy carbon as working electrode fitted in a 20 µl flow through cell and reference electrode Ag| AgCl/ in three M NaCl. Alumina powder CF 1050, BAS, USA was used for polishing glassy carbon electrode when desired. Polishing was repeated almost after every hundred injections. For loading of sample, a glass syringe by Innovative labour system ILS, Stuetzerbads, Germany was used. For signal recording a strip chart recorder, model: 561-0219, Hittachi, was used in addition to a printer / plotter Varian 4710, USA.

Chemicals and Reagents

Phenol, trisodiumcitrate, sodiumperchlorate and potassium hydrogen phthalate, 1, 4-dibenzoic acid, salicyclic acid and para hydroxy benzoic acid were purchased from MERCK, Germany. Pentachlorophenol from Janssen Chemie (Geel, Belgium). Glacial acetic acid, potassium dihydrogen phosphate and disodium hydrogen phosphate were purchased from Fluka, Switzerland. All experiments were preformed by using deionized and doubly distilled water. The reagents were of analytical grade and were used as received.

Standards and Buffer Solution Preparation

A pH-7 buffer for pH calibration was prepared by mixing 0.025M potassium di-hydrogen phosphate and 0.025M di-sodium hydrogen phosphate. pH 4 buffer was prepared having 5mM of tri-sodium citrate and 20 mM of sodium perchlorate. pH-4 was set with the help of glacial acetic acid. The stock solution of 100 ppm for phenol, pentachlorophenol, potassium hydrogen phthalate, 1,4-dibenzoic acid, para hydroxy benzoic acid and salicylic acid were prepared. They were kept under darkness when not in use. Standard solutions of required concentration to be analyzed were prepared daily. Wastewater samples were filtered through disposable 0.45 micron syringe filters MFS Inc, Japan.

Conclusions

It is observed that appropriate concentration of supporting electrolyte 1mM sodium citrate and 4mM sodium per chlorate buffer pH 7 plays important role for the ease of electron transfer reaction and response stability. pH also has an important role in redox reaction and for the case of phenols, lower potentials are required for oxidation at optimum pH. Calibration curves for different phenols were fairly linear in the range 0.01-1.0 mg/ L and in routine concentration up to five ng (20µL, 50µg| L) can be detected. Moreover, the know-how of phenols oxidation may be needed in designing electrochemical cell for the degradation removal of phenols from waste water in a waste treatment plant. The proposed method is capable of efficiently monitoring the trace level of total phenols in potable and in wastewater.

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