Phenol Product Stewardship Summary (CAS number 108-95-2)

Chemical Formula for Phenol C6H5OH

What is Phenol? Phenol, also known has hydroxybenzene, monohydroxy benzene and carbolic acid, is derived from the basic raw materials of benzene and propylene. These materials are first used to produce cumene, which is then oxidised to become cumene hydroperoxide, before being split into phenol and its co-product, acetone. Phenol is typically a solid at room temperature as it solidifies at 41°C (106 °F). How is Phenol used? Phenol plays an unseen, but major role, in our everyday lives. Plywood, window glazing, DVDs and CDs, computers and sports equipment are some of the many items that rely on this important raw material. Phenol is a major component of the phenolic adhesives used in wood products such as plywood and oriented strand board. It is also used to produce phenolic resins, which are used in the moulding of heat-resistant components for household appliances, counter-top and flooring laminates, and foundry castings. In addition, it is a valuable intermediate in the manufacture of detergents, agricultural chemicals, medicines, plasticisers, and dyes. The largest single market for phenol is in the production of Bisphenol A (BPA), which is manufactured from phenol and acetone. BPA is, in turn, used to manufacture polycarbonate (the largest and fastest growing use for BPA) and epoxy resins. Both polycarbonate and epoxy resins are used in many different industries and in countless items which we encounter every day like CDs, circuit boards and fibre glass boats. When reacted with bromine, BPA forms the fire retardant tetrabromobisphenol A. BPA is also used to manufacture engineering thermoplastics such as polysulfones and polyarylates. Health, Safety and Environmental considerations Phenol is toxic and corrosive. It is classified by the US Department of Transportation (DOT), IMDG, and IATA as Class 6.1/poison. Phenol is also classified as combustible in the US with a flash point of 175º F/79.4º C. Phenol Product Stewardship Summary October, 2012 Most exposure to phenol is through skin contact; it can be fatal if absorbed through the skin or if swallowed. Phenol vapours will cause severe eye, respiratory and digestive tract burns. Even moderate exposure might be fatal since phenol deadens the feeling in exposed areas. Although phenol is classified as a mutagen - and such chemicals may have a cancer risk - there is inadequate evidence in experimental animals for the carcinogenicity of phenol. Phenol has been assigned a class 3, classification not possible from currently available data[, by the International Agency for Research on Cancer (IARC). Phenol has been tested and has not been shown to affect reproduction. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned an eighthour occupational exposure limit of 5 parts per million (ppm) for phenol. Phenol is toxic to aquatic organisms. It is readily biodegradable and has a low potential to bioaccumulate. Storing and transporting Phenol Phenol should be stored in stainless steel or Carbozinc II lined tanks. The transport of phenol is carefully managed and storage containers are normally kept at temperatures above 41º C to maintain the product as a liquid. If transported by rail, only top loaded cars are used. Transport by truck is contracted by Shell or by customer pick up and only if the truck meets an on-site inspection. Risk Characterization Summary Risks associated with exposure to this product have been evaluated for the following “chain-ofcommerce” activities: manufacture, storage, product transfer, transportation, and customers/markets. Due to health, safety and environmental considerations, it is only manufactured, stored and transported to customers in closed systems. Likewise, customers are limited to those who only use the product in closed systems as an intermediate for the manufacture of other chemicals. Proper equipment design and handling procedures maintain low risk from exposure to the product where the product is used as a chemical intermediate. \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ This product stewardship summary is intended to give general information about the chemical or categories of chemicals addressed. It is not intended to provide an in-depth discussion of health and safety information. Additional information is available through the chemical’s applicable Material Safety Data Sheet, which should be consulted before use of the chemical. This product stewardship summary does not supplant or replace required regulatory and/or legal communication documents.

Phenol, a monohydroxy derivative of benzene, occurs naturally in animal waste and by decomposition of organic wastes. It is also produced by man, originally by fractional distillation of coal tar, but more recently by cumene hydroperoxidation and toluene oxidation. As a result of large production volume and natural sources, occupational and environmental exposure to phenol is likely. Phenol poisoning can occur by skin absorption, vapor inhalation, or ingestion, and, regardless of route of exposure, can result in detrimental health effects. Acute toxicity has been observed in man and experimental animals, resulting in muscle weakness, convulsions, and coma. In addition, studies have shown that although teratogenic effects have not been associated with exposure to phenol by either inhalation or oral route, high doses of phenol are fetotoxic. This paper addresses these studies and others in an attempt to determine if human health is at risk to those levels of phenol present in the environment and workplace. However, because data are limited, further research is necessary to analyze the mutagenic and carcinogenic potential of this chemical.

**INTRODUCTION**

**PHENOLS**

In chemical terminology, a phenol is a single aromatic ring organic compound with an -OH group. An alkyl, straight chain or ring, organic compound with an -OH group is an alcohol. A double aromatic ring organic compound with an -OH group is a naphthol.

Phenol, formerly called carbolic acid, is an aromatic organic compound, C6H5OH. It is weakly acidic and resembles an alcohol in structure. The colourless, needlelike crystals of purified phenol melt at 43°C (109°F) and boil at 182°C (360°F). Phenol is soluble in organic solvents and slightly soluble in water at room temperature, and completely soluble above 66°C (150.8°F). It is a constituent of coal tar.

Phenol was first used as a disinfectant in 1867 by the British surgeon Joseph Lister for sterilizing wounds, surgical dressings, and instruments. Dilute solutions are useful antiseptics, but strong solutions are corrosive and scarring to tissue. Less irritating and more efficient germicides have replaced phenol, but it is widely used in the manufacture of resins, plastics, insecticides, explosives, dyes, and detergents. It is also used as a raw material for the production of medicinal drugs such as aspirin.

The term phenol is also used for any of a group of related acidic compounds that are hydroxyl derivatives of aromatic hydrocarbons. These include such substances as cresol, catechol, quinol, xylenol, guaiacol and resorcinol. For consistency and clarity these are all named as substituted phenols in this document. See[Appendix 1](http://www.env.gov.bc.ca/wat/wq/BCguidelines/phenol/phenol.html#appendix1) for a partial list of some phenol compounds.

The latest CCME document combines all of the 1- and 2-hydric phenols together into one group for setting guidelines based on toxicity. We have followed the same procedure for establishing these working guidelines with the exception of setting separate guidelines for 4-hydroxyphenol (hydroquinone) and 3-hydroxyphenol (resorcinol). There are several reasons for this.

There can be large differences in the toxicity of the various distinct phenol compounds, particularly when the substituents are strong electron donors or sinks. This can lead to over-protection for some of these compounds because the guideline is established to accommodate the most toxic phenol.

There is a paucity of existing reliable data that can be used to set guidelines for individual compounds. The guidelines are set to account for the most toxic phenols. If circumstances warrant, it is recommended that dischargers carry out Water Effect Ratio trials with their specific effluent and their ambient water to determine an acceptable site-specific phenol concentration.

Toluene and the xylenes are not phenols in their un-substituted form. Toluene is 1-methyl benzene and the xylenes are: 1, 2-dimethyl benzene, 1, 3-dimethyl benzene or 1, 4-dimethyl benzene. However, if one of the other substitutions on the benzene ring is a hydroxy group, then they become a phenol, cresol or xylenol. Therefore, for example: 4-hydroxy toluene, 4-methyl phenol, 1-methyl-4-hydroxy benzene, and 1-hydroxy-4-methyl benzene are all the same compound, as are 3, 4-dimethyl phenol, 3, 4-dimethyl xylenol, 1-hydroxy-3, 4-dimethyl benzene and 2-methyl-4-hydroxy toluene.

One must be aware of all these alternate names when looking up data on phenol compounds. It is best to try to find one name in the Chemical Abstracts Service (CAS) registry that has a bewildering variety of alternate names listed. Using the substituted benzene or phenol nomenclature can reduce the ambiguity and confusion. In this document, we try to use only a few alternate names.

There are, in theory, an infinite number of phenols since up to 5 'R' groups (long-chain aliphatics) can be substituted and each of these can be very complex and substituted itself. In practice, there are far too many phenols to deal with individually but the toxic properties of many long-chain aliphatic substituted compounds will be quite similar. It is the toxicity of the phenols with simple substituents like methyl (-CH3), hydroxyl (-OH), amino (-NH2), nitro (-NO2), methoxy (-CH3O) and the halogens (-Cl, -Br, -I, -F) that are of most toxicological concern. Most phenols are used as bactericides, fungicides and herbicides; particularly the halogenated phenols, and especially the chlorinated halophenols.

The environmental half-lives of most phenols are short, rarely as long as a month. Some are photo-degraded, especially in air. The microbial half-life is short, typically measured in days under aerobic conditions. Once a discharge ceases, environmental levels will drop rapidly due to bacterial breakdown. The half-life of phenols in fish is less than one day and phenols do not accumulate. Hence the existence of high levels in fish tissues indicates chronic or current exposure.

Microorganisms will alter their metabolic processes to utilize phenols. If they have not previously been exposed there will be an initial adaptation period until a large microbial population has been established. Any subsequent additions of phenols will be quickly degraded.

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**RECOMMENDED GUIDELINES**

The following guidelines are based on readily available existing information which is summarized in tables in [Appendix 2](http://www.env.gov.bc.ca/wat/wq/BCguidelines/phenol/phenol.html#appendix2). The Canadian Council of Ministers of the Environment (CCME) has set guidelines for all mono- and di-hydric phenols.

**FRESHWATER AQUATIC LIFE**

Aquatic Life is the only water use for which guidelines are being set in this document. They are working guidelines subject to revision when more complete data become available. The maximum concentration of 4-hydroxyphenol (quinol, hydroquinone, 1,4-benzenediol) should not exceed 4.5 micrograms/L. The maximum concentration of 3-hydroxyphenol (resorcinol, 1,3-benzenediol) should not exceed 12.5 micrograms/L, and the maximum concentration of the total of all other non-halogenated phenols should not exceed 50 micrograms/L.

**RATIONALE**

The lowest LC50 data found for many phenols is presented in [Table 2](http://www.env.gov.bc.ca/wat/wq/BCguidelines/phenol/phenol.html#table2). The lowest effect for 4-hydroxyphenol (hydroquinone) was for *Daphnia magna*, at 0.09 mg/L. For 3-hydroxyphenol (resorcinol), the lowest effect level measured was at 0.25 mg/L, also for*Daphnia magna*. These were divided by a safety factor of 20:1 in order to estimate a safe minimal, or no effect, level for other freshwater species.

The next most toxic form of phenol was reported for fathead minnows, *Pimphales promelas* using 4-phenylazophenol at 1.17 mg/L. We have assumed that the sum of all other phenols present (non-chlorinated) should not exceed this level since there are many phenol compounds with similar toxicity (see [Table 2](http://www.env.gov.bc.ca/wat/wq/BCguidelines/phenol/phenol.html#table2)).Therefore, for all other phenols, we divided this level by a factor of 20 to estimate the safe level.

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**APPLICATION OF GUIDELINES**

Chlorophenols, hydroquinone and resorcinol should be measured separately and compared to their respective proposed guideline values. A measurement of total phenols minus the sum of total chlorophenols, hydroquinone, and resorcinol allows one to determine if the guideline for total phenols is met.

1. Introduction

Phenol (C6H6O) is a common pollutant present in the wastewaters of industries, such as efineries, coal processors, olive mills, and the manufacturers of pet-rochemicals, fabrics, plastics, wood products, paints, papers and resins, among others. Phenol may have harmful effects on both public health and aquatic life; for example, it has been found that the metabolism, survival, growth and reproductive system of fish are affected when they live in phenolic-polluted water [1].In humans, the effects of repeated oral exposure to phenol include diarrhoea, mouth sores and dark urine2]. Furthermore, the ingestion of 1 g of phenol is fatal 3]. Consequently, the treatment of phenol-containing wastewater is required prior to its discharge. Adsorption onto activated carbon is widely recog-nised as one of the most efficient methods for phenol removal at low concentrations from wastewater. How-ever, the use of commercial activated carbon as adsor-bents is often limited due to economic reasons; thus, the use of low-cost precursors, such as agro-waste materials, for the production of activated carbon and its use on phenol removal from aqueous solutions have been investigated in several studies [4–12]. In Mexico, the INEGI reported that 8.2×106 L of beer were produced in 2008 [13]. This industrial activity generated large quantities of barley husk as a by-prod-uct, and this waste was previously used as a precursor for the activated carbon [14]. This material was used as an adsorbent in this research due to its physico-chemical properties, which includes high surface area and surface functional groups. In addition to the high cost, the main drawback of the use of activated carbon as an adsorbent is the sec-ondary pollution generated by the disposal of the spent adsorbent. To overcome this disadvantage, there are numerous adsorbent regeneration techniques used to re-establish the maximum adsorbent capacity and to preserve, as much as possible, the initial weight and pore structure of the adsorbent. Thermal regeneration is one of the desorption methods most widely employed. In this method, the adsorbates are desorbed by means of volatilisation and oxidation at high tem-perature. However, this method has disadvantages, such as the loss of activated carbon by attrition (5–10%), due to excessive burn off and washout during each cycle [15]. Chemical regeneration of adsorbents is a feasible alternative because it has some advantages; for instance, it can be performed in situ, there are no losses of activated carbon (unlike in thermal desorp-tion), it is possible to recover valuable adsorbates and the chemical reagents can be reused [16]. Commonly, the process of adsorption in the liquid phase has been carried out mostly in the fixed-bed col-umns in a continuous flow operation. Nevertheless, the operational complexity and the limitation of the removal efficiency have led to a search of new and efficient equipment that can provide better removal efficiency without additional mechanical complica-tions. Airlift reactors have drawn increased attention as possible alternatives to fixed-bed columns because of their advantages such as a simple construction without moving parts, a high liquid phase content, a low operational shear stress and good mixing proper-ties with minimal energy consumption [17]. Addition-ally, airlift reactors allow the use of powdered adsorbents, which is not possible in fixed-bed columns due to high pressure drops, and the use of adsorbents with low hardness values, due to the low shear stress in the reactor. Therefore, the objective of this study is to investigate the effect of a number of variables on the batch, and continuous operations (of an airlift reactor) of phenol adsorption onto barley husk-acti-vated carbon (BHAC) and the regeneration of theadsorbent with four different eluents.

Determination of Phenols in Drinking Water with Agilent Bond Elut Plexa SPE and HPLC Author Andy Zhai Agilent Technologies, Inc. 412 Yinglun Road Waigaoqiao Free Trade Zone Shanghai 200131 China Application Note Environmental Abstract A method for simultaneous determination of 11 phenols in drinking water was developed and validated. The analytes were extracted by solid phase extraction (SPE) with an Agilent Bond Elut Plexa cartridge, and separated by HPLC using an Agilent Poroshell 120 column. Overall recoveries ranged from 87% to 108%, with RSD values between 1.4% and 6.7%. The method was simple and effective for the extraction, enrichment, and analysis of multiple phenol compounds in drinking water. Introduction Phenols are harmful to people, dangerous to the environment, and can impart a metallic taste and odor to water when it is chlorinated. Frequently, these compounds find their way into the environment as water pollutants, making analytical determination of phenols necessary. This application note describes the development of a sample extraction, cleanup, and enrichment method with an Agilent Bond Elut Plexa cartridge and a separation method using an Agilent Poroshell 120 column, with quantification by HPLC [1]. In line with EPA 604, 11 phenol compounds were chosen [2]. The structures and pKa for the compounds used in this study are shown in Table 1. 2 Table 1. Phenols Used in This Study No. Name pKa Structure 1 Phenol 9.89 2 4-nitrophenol 7.08 3 2-chlorophenol 8.56 4 2-nitrophenol 7.22 5 2,4-dinitrophenol 4.09 6 2,4-dimethylphenol 10.6 7 4-chloro-3-methylphenol 9.56 8 2,4-dichlorophenol 7.68 9 4,6-dinitro-2-methylphenol 10 2,4,6-trichlorophenol 7.41 11 pentachlorophenol 4.92 OH OH O2N Cl OH OH NO2 NO2 NO2 HO CH3 OH CH3 CH3 OH Cl OH Cl Cl NO2 OH O2N CH3 Cl OH Cl Cl Cl OH Cl Cl Cl Cl Experimental Reagents and chemicals The standards solution and other chemicals were purchased from Sigma-Aldrich (Saint Louis, MO, USA). All reagents and solvents were HPLC or analytical grade. Methanol, acetonitrile, water, and tetrahydrofuran were from Honeywell (Muskegon, MI, USA). Formic acid (FA) was from Fluka (Sleinheim, Germany). Standard solutions The standard solution (500 μg/mL for phenol, 2-nitrophenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4-dimethylphenol; 1500 μg/mL for 2,4-dinitrophenol and 2,4,6-trichlorophenol; 2500 μg/mL for 4-chloro-3-methylphenol, 4,6-dintrophenol-2-methylphenol, 4-nitrophenol, and pentachlorophenol) was made in methanol. The QC spiking solutions were made fresh daily in 1:1 acetonitrile:water with 0.1% formic acid. Equipment and materials Instrument Agilent 1200 series HPLC system Column Agilent Poroshell 120 SB-C18, 2.1 x 100 mm, 2.7 μm (p/n 685775-902) Solid phase extraction Agilent Bond Elut Plexa cartridge, 60 mg, 3 mL (p/n 12109603) Vacuum manifold Agilent Vac Elut 20 Manifold Tall Glass Basin (p/n 12234104) HPLC conditions Mobile phase A: 0.1% Formic acid in water B: 0.1% Formic acid in acetonitrile Gradient time (min) B (%) 0 15 10 50 11 90 12 90 12.5 15 14 15 Flow rate 0.4 mL/min Detection UV, 280 nm Injection 40 μL Sample preparation Drinking water was purchased from a local supermarket. A 250 mL water sample was prepared by adjusting the pH to 2.0 with phosphoric acid solution (0.1 mol/L). The Agilent Bond Elut Plexa cartridge was preconditioned with 3 mL tetrahydrofuran and 3 mL methanol, then equilibrated with 3 mL water. 3 The 250 mL sample was passed through the cartridge at a rate of 5 mL/min under vacuum. After the sample passed completely through the cartridge, the cartridge was washed with 2 mL water and discarded. The cartridge was then dried under negative pressure below 2.0 kPa for 3 minutes. Finally, the cartridge was eluted with 3 mL tetrahydrofuran. The collected eluent was reduced to about 0.2 mL under nitrogen at room temperature. The resulting solution was brought up to 0.5 mL accurately with water. Then the solution was filtered through a 0.45-μm filter membrane (p/n 5185-5836) and analyzed by HPLC. The procedure used for the SPE extraction is shown in Figure 1. Results and Discussion Matrix blank material was prepared by taking the drinking water through the entire extraction and sample cleanup procedure. External-standard calibration curves were made by spiking matrix blanks at respective concentrations. Linear regressions were calculated for the phenols using the areas under the peaks and the spiked concentrations. The precision of the method was determined as recoveries of spiked phenols in drinking water after the SPE procedure, and the analysis was performed with six replicates at each level. The chromatograms of the blank, the spiked standard, and the standard are shown in Figure 2. The linearity, recovery and reproducibility data are shown in Table 2. Condition 1 3 mL tetrahydrofuran Condition 2 3 mL methanol Equilibration 3 mL water Load 3 mL sample Wash 2 mL water Elute 3 mL tetrahydrofuran Evaporate to 0.2 mL under nitrogen Reconstitute to 0.5 mL with water Dry cartridge under vacuum 3 minutes Figure 1. SPE procedure for phenols in water. Compound Regression equation Correlation coefficient Spiked level (μg/L) Recovery (%) RSD (n=6, %) Phenol Y = 75.621 x -0.1425 0.9995 2.5 96.7 5.1 4-Nitrophenol Y = 82.313 x -0.0897 0.9992 12.5 98.2 1.4 2-Chlorophenol Y = 103.267 x -0.2578 0.9986 2.5 93.7 5.6 2-Nitrophenol Y = 68.304 x 0.0752 0.9993 2.5 92.6 4.8 2,4-Dinitrophenol Y = 75.366 x -0.2335 0.9997 7.5 99.3 2.8 2,4-Dimethylphenol Y = 66.689 x -0.1226 0.9984 2.5 99.5 6.2 4-Chloro-3-methylphenol Y = 76.407 x 0.0571 0.9991 12.5 87.3 3.7 2,4-Dichlorophenol Y = 59.018 x -0.2639 0.9979 2.5 91.5 2.3 4,6-Dinitro-2-methylphenol Y = 125.735 x 0.3428 0.9996 12.5 90.6 1.9 2,4,6-Trichlorophenol Y = 70.028 x -0.1112 0.9989 7.5 96.4 2.9 Pentachlorophenol Y = 62.135 x 0.1457 0.9991 12.5 108.2 6.7 Table 2. Linearity, Recoveries and RSDs of Phenols in Drinking Water with SPE www.agilent.com/chem Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material. Information, descriptions, and specifications in this publication are subject to change without notice. © Agilent Technologies, Inc., 2012 Printed in the USA January 6, 2012 5990-9730EN Conclusion Agilent Bond Elut Plexa provides a simple and effective single cartridge method for the extraction and enrichment of multiple phenol compounds in drinking water. The recovery and reproducibility results based on solution standards are acceptable for phenol residues determination in drinking water. The impurities from water were minimal and did not interfere with any of the phenols analyzed. References 1. William J. Long and Anne E Mack (2010) Fast Analysis of Environmental Phenols with Agilent Poroshell 120 EC-C18 columns. Agilent Technologies, Inc. Publication 5990-6156EN. 2. US Environmental Protection Agency. Method 604 – Phenols. For More Information These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem. 8 6 4 2 0 ×102 ×102 ×102 8 6 4 2 0 8 6 4 2 0 01234567 Acquisition time (min) Response units 8 9 10 11 12 13 14 A B C 1 2 3 4 5 6 7 8 9 10 11 Figure 2. Chromatograms: A- Standard solution with matrix blank; B- Spiked standards in drinking water with SPE procedure; C-Drinking water blank sample with SPE procedure. 1) Phenol, 2) 4-Nitrophenol, 3) 2-Chlorophenol, 4) 2-Nitrophenol, 5) 2,4-Dinitrophenol, 6) 2,4-Dimethylphenol, 7) 4-Chloro-3- methylphenol, 8) 2,4-Dichlorophenol, 9) 4,6-Dinitro-2-methylphenol, 10) 2,4,6-Trichlorophenol, 11) Pentachlorophenol

**2.1 Sources** of phenols Phenols mainly occur in nature as a product of coal tar or crude petroleum. However, phenols are formed as natural decay of organic compounds. Phenols present in nature include tyrosine found in proteins which belong to the class of amino acid. Epinephrine is an adrenaline that produces hormone. Serotonin is a neurotransmitter found in the brain 7 and urushiol, which causes irritation generated by poison ivy to prevent animals from doing certain things. Some phenol can be gotten from plant like thymol, separated from thyme and eugenol, extracted from cloves. (Wade 2009.) 2.2 Uses of phenols Phenol is used as raw material in the manufacture of a wide range of important chemicals including phenolic resins, bisphenol-A, caprolactam, alkylphenols and adipic acid. Phenol is widely used for the treatment of injuries. It is suitable for making aspirin drug also antiseptics and local anaesthetics (Wade 2009). Phenol is used in the manufacture of paints and varnish removers, lacquers, rubber, ink, and illuminating gases, tanning dyes, perfumes, toys and soaps (Wade 2009). Phenol is used as an industrial chemical in the manufacturing of certain products such as “resins, plastics, fibers, adhesives, iron, steel, aluminum, leather, and rubber”, also phenol is present in disinfectants, cigarette smoke, and emissions from vehicles (EHC 161, 1994). Phenols have a wide range of applications in household products and industrial synthesis. They are used as disinfectants in household cleaners, lotions, salves, ointments and in mouth wash. However, compounds of phenols are used in dye industries to make colored azo dyes and used as components in making wood preservatives such as creosote. Industrial applications of phenols are used in making plastics, explosives like picric acid, and drugs such as aspirin. (Wade 1999.) 2.3 Physical properties of phenols Phenols which are identical to alcohols having a hydroxyl group attach to an aromatic ring which enables them to undergo intermolecular hydrogen bonding. They have the ability to form stronger hydrogen bond than alcohols. Nevertheless, the presence of hydrogen bonds in phenols makes them to be more soluble in water. Hence, the occurrence of hydrogen bonds in phenols results in higher melting and boiling points. (Wade 2009.) 8 Table 5 summarizes the physical and chemical data of eleven phenols specified by certain environmental agencies in their priority pollutants lists. The eleven groups of phenols are determined in water to ensure that the concentration does not exceed the limit provided by the environmental agencies. TABLE 5. Physical and chemical data of Phenols (Merck chemicals 2010) Formula Molar mass (g/mol) Melting point (°C) Boiling point (oC) Density (g/cm3 ) Phenol C6H5OH 94.11 40.8 181.8 1.06 (20 °C) 2-nitrophenol 2-(NO2)C6H4OH 139.11 43 - 45 215 - 216 1.26 (20 °C) 2-chlorophenol 2-(Cl)C6H4OH 128.55 7 174 1.26 g (20 °C) 2,4-dinitrophenol 2,4-DNP 184.11 114 - 115 1.68 (20 °C) 2-methyl-4,6- dinitrophenol C7H6N2O5 198.14 82 - 85 312 4-nitrophenol O2NC6H4OH 139.11 110 - 115 279 1.48 (20 °C) 2,4- dimethylphenol 2,4- (CH3)2C6H3OH 122.16 25 211 1.016 (25 °C) 4-chloro-3- methylphenol 4-(Cl)-3- (CH3)C6H3OH 142.58 63 - 65 235 - 239 1.37 (20 °C) 2,4,6- trichlorophenol C6H3Cl3O 197.44 65 - 68 244 - 246 1.675 (25 °C) 2,4-dichlorophenol 2,4- (Cl)2C6H3OH 163 40 - 43 209 - 211 Pentachlorophenol C6HCl5O 266.34 190-191 309-310 1.978 (22 °C) 9 3 METHODS FOR DETERMINING OF PHENOLS IN WATER There are methods which have been developed over the years for the determination of phenolic compounds in water and waste water. Some of these methods are spectrophotometry, electrochemical methods, capillary electrophoresis, the gas chromatographic (GC) method using liquid-liquid extraction and either using flame ionization detection (FID) or derivatization and electron capture detection (ECD) to analyze different phenols at a low concentration. In determination of phenol at high concentration, the gas chromatography/mass spectrometric (GC/MS) method with liquidliquid extraction is employed. (Eaton, Clesceri, Rice & Greenberg 2005, 79-80.) In water treatment plant, chlorine applications have resulted in producing chlorophenol. The method which can be applied in analyzing phenol, ortho- and meta- substituted phenols is known as 4-aminoantipyrine colorimetric method. However, para-substituted phenol with sub group known as carboxyl, halogen, methoxyl or sulfonic acid group cannot be determine using 4-aminoantipyrine method under certain pH ranges. Thus, 4- aminoantipyrine method is suitable for water samples with high sensitivity. The disadvantage of this method is that any color produced by the reaction of any phenolic compounds is proved to be phenol. (Eaton et al. 2005, 43-44.) Chemiluminescence (CL) is an analytical detection method suitable for very low detection limit, fast and large linear working range that can be obtained using simple instrumentation. Chemiluminescence method is applied for the determination of phenol, including luminal CL system and acidic KMnO4CL system. However, due to lack of selectivity for phenol, chemiluminescence systems cannot determine phenol in water samples directly. Phenol can be determined only when the CL system is combined with some separation precession like per-distillation, liquid chromatography and capillary chromatography. (Huili, Jiagen, & Baoxin 2006.) Liquid-liquid extraction gas chromatographic method is applied in analyzing phenols and some substituted phenols in water either in municipal or industrial released. During confirmation of an unknown compound, the use of derivatization, cleanup and electron capture detector gas chromatography (ECD/GC) are used to determine results obtained by 10 flame ionization detector gas chromatographic (FID/GC) method. (Eaton et al. 2005, 79- 80.) Method 8041 gives a wide number of options for the determination of phenols in water and soil samples. Phenols are separated from water at pH < 2 with methylene chloride using liquid-liquid or continuous liquid extraction. Phenols is analyzed by FID using one column or double column procedure after solvent evaporation and replacing the solvent to 2- propanol. Thus, sensitivity may not be suitable for the underivatized phenols. Phenols can be derivatized with diazomethane to produce methyl ester of phenol and can be determined by FID. A suitable approach for sensitivity and selectivity can be achieved by derivatizing the analyte extracts with pentafluorobenzylbromide (PFBBr) and detecting the derivatized phenols using electron capture detector (ECD). Hence, three phenols: 2, 4-dinitrophenol, 2- methyl-4, 6-dinitrophenol and dinoseb are not derivatized by PFBBr. During cleanup process, a silica gel is used after the derivatization. (Grob & Barry 2004.) Another method for derivatization is the use of acetic anhydride (C4H6O3). The sample is adjusted to pH≈7 using sodium hydroxide or phosphoric acid and adding potassium carbonate and acetic anhydride to the sample. After mixing, hexane is used to extract the derivatives then the extract is injected into gas chromatography column. This method is not suitable for nitrophenols because of the poor effectiveness of the derivatization reaction. (Dmitruk, Zbiec & Dojlido 2006.) The characteristics of high performance liquid chromatography (HPLC) are proved to be an effective method for the separation of phenols. However, improvements have been made in HPLC analysis of compounds. In recent years, devices for detection and identification coupled to HPLC have been developed to make separation, qualification and quantification of compounds possible. HPLC methods for analysis of compound avoid the difficulties and time-consuming separation of compounds for the subsequent individual identification of each compound. Thus, in this research, information of the analysis of phenols by HPLC is provided. 11 4 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY In our present time, there is a rising interest in applying high performance liquid chromatography (HPLC) which is not subject to temperature dependence to the determination of not just volatile organic compounds like aliphatic and polyaromatic hydrocarbons, saturated and unsaturated aliphatic halogen compounds, haloforms and some esters, phenols unlike the gas chromatography, but for all organic and inorganic matter present in water samples. Hence, in liquid chromatography, a liquid passes through a porous solid stationary phase and the elute flows through a detector. In HPLC, the mobile phase is pumped at high pressure (Crompton 1999, 57.) The essential parts of liquid chromatography include the mobile phase of solvent, high pressure and low pressure gradient programmers, pumps (piston and diaphragm pumps, syringe and rapid refill pumps), valves and oven column. The detectors used in high performance liquid chromatography include UV detector which can be fixed or variable wavelength, the fluorescence detector and the refractive index detector. An HPLC stationary phase includes irregular and spherical silica gel. (Scott 2008.) Graph 1 gives a clear illustration of the essential parts of liquid chromatography from one component part to another. GRAPH 1. The essential parts of liquid chromatography copyright by Scott 2008 12 The mobile phase which is a solvent is contained in a bottle. A high pressure pump is needed to deliver the mobile phase at a certain flow rate apparently in milliliters per minute. Also, an injector known as auto-sampler passes samples into a constant moving mobile phase stream that moves the sample into the HPLC column. The stationary phase is a chromatographic material packed in a column and it is needed to effectively carry out the sample separation. Furthermore, a detector helps to visualize the separated sample bands eluting the HPLC column and the mobile phase leaves the detector which is collected by waste system. However, the detector is connected to a data collection system that stores the electrical signal that produces the chromatogram on its screen. The end results are seen as chromatogram appearing as peaks of various heights depending on the concentration of the sample constituents. (Waters Corporation 2010.) Graph 2 gives a concise picture on the operation of high performance liquid chromatography (HPLC) system. Computer data device HPLC column Mobile phase solvent GRAPH 2. Operation of HPLC system copyright by Waters Corporation 2010 Pump Waste system Detector Sample Autosampler Result 13 4.1 Types of chromatography column High performance liquid chromatography (HPLC) have been created so as it can perform to a very high level by combining selective stationary phases of different material sizes with it, also with adequate columns with big amount of plates per liter. There are different types of chromatography column used in high performance liquid chromatography which are reversed-phase chromatography, reversed-phase ion-pairing chromatography, ionsuspension chromatography and ion-exclusion chromatography. Reversed phase chromatography (RPC) column are mostly used in all HPLC applications. (Crompton 1999, 57.) 4.1.1 Reversed phase chromatography This is the most commonly used chromatographic mode in HPLC. It is used for the analysis of wide range of neutral compound which are carbohydrates and polar organic compounds. Reversed phase chromatography is mostly performed by using bonded silicabased columns by limiting the pH range to 2.0 - 7.5. (Crompton1999, 57.) GRAPH 3. Reversed-phase chromatography column copyright by Dong 2010

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