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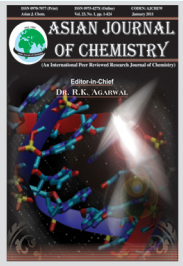

Solid-Phase Extraction Method for the Analysis of Eleven Phenolic Pollutants in Water Samples

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An analytical protocol for the determination of priority phenolic compounds: phenol, 2-methyl 4,6-dinitrophenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachloro-phenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4-chloro-3-methylphenol, 2,4,6-tribromophenol and 2,4-dimethylphenol, in water samples using strata C_{18} cartridge is presented. Different parameters affecting extraction and peak separation were optimized. Recoveries using spiking of the test compounds varied in the ranged between 69.43 ± 1.76 % and 101.87 ± 0.45 %. The high recoveries obtained validated the method. Detection limits obtained ranged from 4 μg L^{-1} for 2,4-dimethylphenol to 166 μg L^{-1} for 4-nitrophenol, using LC-UV. The results obtained by applying the developed method to real environmental water sample containing 2,4-dichlorophenol, 2-methyl, 4,6-dinitrophenol, pentachlorophenol and 2,4,6-tribromophenol indicated the following concentration levels: 5.129, 0.561, 4.788 and 0.868 ng μL^{-1}, respectively.

Key Words: Solid phase extraction, Phenolic compounds, Pollutants.

INTRODUCTION

Phenol and phenolic substances are aromatic hydroxyl compounds classified as monodric, dihydric or polyhydric depending on the number of hydroxyl groups on the aromatic benzene ring[1,2]. They are synthetic organic compounds which are produced industrially for their use as plant protecting agents (pentachlorophenol and tetrachlorophenols) and wood preservatives (mixture of chlorophenols) because of their fungicidal or antiseptic properties[3-5]. They may also be formed as by-products during disinfection of drinking water by chlorination, production of paper, cooking process during wood pulp bleaching or distillation of wood[5-7].

They may occur naturally in aquatic environments from the decomposition of aquatic vegetation. The major anthropogenic sources are industrial effluents, domestic sewage and wastewater treatment plants. Some possible routes of these compounds into the environment are shown in Table-1. Investigations across the world have shown the contamination of many environmental matrices such as surface water and groundwater by chlorophenols[8-11], bottom sediments, leachates and soil[3,12-14] and atmospheric air[5,15]. They are also present in wastes from cooking plants, gas works and are reported as intermediates in the production of plastics, dyes, antioxidants and pesticides[4,6,16].

Phenols and their substituted compounds have been reported to be toxic to aquatic organisms and humans and to bioaccumulate in food chains[17-19]. They may also act as substrates for the formation of polychlorinated biphenyls and dioxins[20].

Due to their toxicity on drinking and surface waters, aquatic and human lives, the European Commission (EC) and United States Environmental Protection Agency (USEPA) have classified some of them as endocrine disrupting chemicals (EDC). The minimum admissible levels set by the EC and USEPA for water intended for human consumption are 0.5 and 0.1 μg L^{-1} for total and individual compounds, respectively and 5 μg L^{-1} for bathing water[16,19,21,22]. The World Health Organization suggest a guide level concentration lower than 200 μg L^{-1} for 2,4,6-trichlorophenol and 9 μg L^{-1} for pentachlorophenol[23].

Separation techniques such as gas chromatography, high performance liquid chromatography (HPLC) and capillary electrophoresis, among others, have been extensively used in analytical chemistry for monitoring, because of their high efficiency and speed[19,24,25]. Gas chromatography (GC) and liquid chromatography (LC), after previous concentration and clean-up, have been used for determining these compounds in water, soil, sediment and leachate samples. Gas chromatography is a popular method for phenol and phenol derivatives

analysis due to its high sensitivity and high resolution power[19,21]. However, high polarity of phenols gives broad and tailed peaks which require derivatization steps when analyzed on gas chromatography[6,21].

Commonly, their preconcentration and clean-up involves liquid-liquid extraction (LLE) with cyclohexane or dichloromethane, solid-phase extraction (SPE) or solid phase microextraction (SPME). After extensive research work, SPE seems to be the most widely used procedure for the isolation, preconcentration and clean-up of endocrine disrupting chemicals in environmental matrices. Solid phase extraction has a number of advantages over the traditional extraction methods to include: simplicity, low cost, shorter time of extraction and low usage of organic toxic solvent. Nevertheless, low per cent recovery, blocking of the pore and discrepancies in breakthrough volume are some of the challenges of this new method[2,26].

TABLE-1
ROUTES OF PHENOLIC COMPOUNDS TO THE ENVIRONMENT

Compounds	Sources	Ref.
Phenol	Car exhaust gases	4
Methylphenols	Wood impregnation	17
Nitrophenols	Combustion processes of motor vehicles Hydrolysis/photolysis of nitrite/nitrate Production of dyes, pigments *etc.*	27 28 17 16 36
Chlorophenols	Wood distillation, disinfection of drinking water, wood pulp bleaching, paper production	29 5 36 37

The validation of an analytical method is mandatory in implementing a quality control system in any analytical laboratory. Validation of an analytical test method is undertaken to ensure that the methodology is selective, accurate, reproducible and robust over the range specified for analysis. Method validation provides an assurance of reliability during normal use and can be referred to as the process of providing documented evidence that the method does what it is intended to do.

The aim of this paper is to develop an analytical method for the specific identification and quantification of 11 priority phenolic pollutants (classified as endocrine disrupting chemicals) in water samples using a newly launched kinetex C_{18} column-solid phase extraction-liquid chromatography. This is to allow for routine monitoring of these compounds in South Africa, as information on their availability is inadequate. The experimental conditions for SPE were optimized and the method was validated under the best conditions using different water samples from Cape Town, South Africa. The method is simple, reducing the potential for analyte loss during the extraction, avoiding derivatization steps, minimizing solvent use and consequently reducing environmental contamination.

EXPERIMENTAL

Phenols were obtained from the following sources: phenol (99 %), 2-nitrophenol (99 %), 2-chlorophenol (98 %), 2,4-dinitrophenol (99 %), 2,4-dimethylphenol (99 %), 4-chloro-3-methylphenol (98 %), 2-methyl,4,6-dinitrophenol (99 %), 2,4-dichlorphenol (99 %), 2,4,6-trichlorophenol (99 %), pentachlorophenol from Sigma Aldrich (South Africa); 4-nitrophenol (99 %), 2,4,6-tribromophenol (99 %) from separations (South Africa), phosphoric acid 85 % Sigma Aldrich, 2,4,6-tribromophenol (99 %) from Dr. Ehrenstorfer (Germany). Standard solutions of phenols, (1000 mg L^{-1}) were prepared in methanol; aliquots of the standard solution were further diluted with methanol to prepare the working solutions. Methanol and acetonitrile gradient-grade were purchased from Sigma Aldrich and Merck (Germany), respectively. The mobile phase acetonitrile was further purified through distillation and filtered through a 0.22 µm Millipore filter paper from Sigma Aldrich before use.

Columns and cartridges: C_{18}-E cartridges (strata) containing 500 mg/6 mL of adsorbent (Separations, South Africa) and a newly launched kinetex C_{18}-100A column (150 mm × 4.6 mm i.d., 5 µm particle size) from Phenomenex (Torrance, CA, USA) were used.

Instrumentation and software analyses were performed using a Agilent high-performance liquid chromatograph (1100) equipped with a quaternary pump, a vacuum membrane degasser, an automatic autosampler, an automatic injector and connected "on-line" to a Agilent photodiode array detector (DAD). A gradient mobile phase of 0.1 % phosphoric acid in acetonitrile/water was used for the chromatographic separation flow-rate of 1.0 mL min^{-1}. The gradient programme is shown in Table-2. A Supelco Visiprep SPE vacuum manifold (South Africa) was used for the elution of SPE columns. Detection was conducted at 280 nm for all the target analytes.

TABLE-2
CHROMATOGRAPHIC PARAMETERS USED FOR THE ANALYSIS OF PHENOLS

Chromatograph	Agilent Technologies 1100 series		
Detector	DAD		
Column (length × internal diameter × particles)	Kinetex 100 C_{18} 100A (150 mm × 4.6 mm × 2.6 µm)		
Injection volume	20 µL		
Mobile phase	A: Water with 0.1 % H_3PO_4 B: Acetonitrile with 0.1 % H_3PO_4		
Flow rate	1 mL/min		
Gradient elution	Time (min)	A (%)	B (%)
	0	70	30
	5	60	40
	10	30	70
	15	0	100
Temperature	Ambient (25 ºC)		
Data collection	Chemstation D-7000 HPLC System Manager (HSM) Software (Version 3.0)		

Water samples: MiliQwater was used as the matrix for all the recovery experiments. Blank experiments showed that phenols were undetectable in this water. The water pH was adjusted to 2 using sulphuric acid. All solvents and solutions prepared for LC were filtered through 0.22 µm cellulose acetate disk filters (Millipore) before use. Water samples were collected from our laboratory, student residences and ponds, swimming pools and informal settlements in the city of Cape Town. All water samples were collected in glass bottles and stored in a refrigerator at 4 ºC prior to extraction. Water samples were filtered using vacuum system through 0.45 and 0.22 µm to

remove particulate matter. The phenolic compounds were concentrated on SPE as described below.

Chromatographic conditions: Mobile phases were water (0.1 % phosphoric acid) and acetonitrile (0.1 % phosphoric acid). All solvent and mobile phases were first filtered under vacuum through 0.45 μm nylon filters and degassed using a vacuum degasser. The chromatographic system was conditioned by passing the solvents through until a stable baseline signal was obtained. Once the chromatographic system was conditioned with mobile phases, the chromatograms were obtained by injecting 20 μL of appropriate mixture of phenols. For optimization purposes, mobile phase methanol/water (1 % acetic acid) and acetonitrile/water (0.1 % phosphoric acid) was used. The flow rate was in the range of 0.6-1.2 mL min^{-1} while the temperature was maintained at 25 ºC. The eluent condition varied from 70 % water (5 min isocratic) to 100 % of organic modifier (gradient) in 15 min at 1 mL min^{-1}. The UV was set at 280 nm. After use, the column was washed by 50:50 (v/v) water-acetonitrile mixtures (0.75 mL min^{-1}) for 0.5 h.

Extraction procedures

Strata C_{18} SPE cartridge: Prior to extraction, cartridges were washed with 2 mL of acetonitrile to remove impurities. They were then conditioned with two 5 mL portions of methanol and left to soak for 1 min before methanol was drawn off; excess of methanol was subsequently displaced with 2 mL of MilliQ water at pH 2. Air contact with the column was avoided until sample extraction had been completed. The water sample was pumped through the column by a vacuum pump, connected by PTFE tubing, with the vacuum adjusted to give a flow-rate of 7-8 mL min^{-1}. After passage of the water sample, the cartridge was dried by vacuum suction for 1 min. The analytes were eluted from the cartridge with 1.5 mL of acetonitrile and concentrated to 0.5 mL under gentle flow of dry nitrogen and 20 μL was injected for LC analysis.

Real water sampling: Water samples were either purchased or collected from the following sources: grocery shops (Brand 1, Brand 2 and Brand 3), student residences, laboratory, lake, pond, swimming pool and informal settlements (Khayelitsha, Guguletu and Langa) in Cape Town for analysis. Water samples were stored on ice from point of purchase or collection and kept at 4 ºC in the fridge until analysis. The samples were extracted, treated and analyzed as reported as above.

Quality assurance and quality control (QA/QC): Pocedural blanks spiked with the surrogate standards, solvent blanks and control samples were included in each batch of analyses. Blanks and controls were treated in the same manner as the samples were always analyzed after every sample injection. A calibration standard solution of 2.5 ng μL^{-1} was injected in duplicate to monitor the instrumental sensitivity and reproducibility every time before sample analyses.

RESULTS AND DISCUSSION

An in-house validation of the proposed analytical method was performed in order to establish essential parameters, linearity range, detection limits, precision and accuracy. Because no certified reference material was available, the reliability of the analytical method was assessed through the recovery of a standard mixture target analyte. Fourteen point calibration curves were constructed using triplicate injections of extracts of laboratory prepared standard.

Chromatographic separation: Fig. 1 shows a SPE-HPLC-DAD chromatogram of a standard mixture of all the eleven priority phenols and surrogate standard (2,4,6-tribromophenol) under the chromatographic conditions described in the experimental section. As can be seen in Figs. 1 and 2, the chromatographic conditions used yielded an adequate resolution of the target compounds in less than 14 min (acetonitrile/water) and 25 min (methanol/water). Methanol/water (Fig. 2) take longer time thus not in conformity with the aim of reducing organic solvent used for analysis.

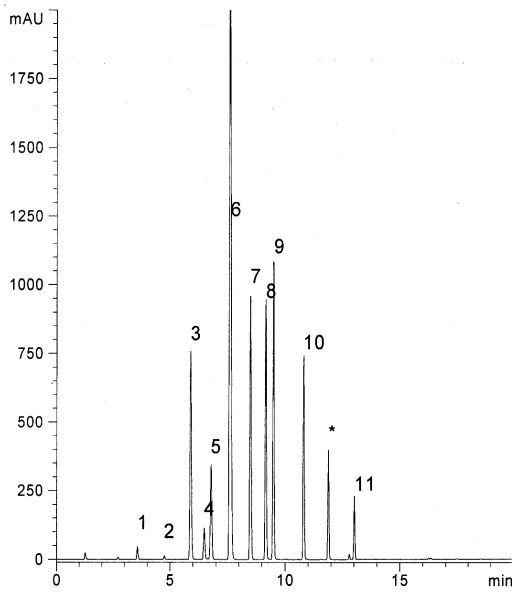

Fig. 1. Acetonitrile/water separation of phenol (1) phenol (2) 4-nitrophenol (3) 2-chlorophenol (4) 2,4-dinitrophenol, (5) 2-nitrophenol (6) 2,4-dimethyl phenol (7) 4-chloro, 3-methyl phenol (8) 2,4-dichlorophenol (9) 2-methyl, 4,6-dinitrophenol (10) 2,4,6-trichlorophenol, (11) 2,4,6-tribromophenol (12) pentachlorophenol

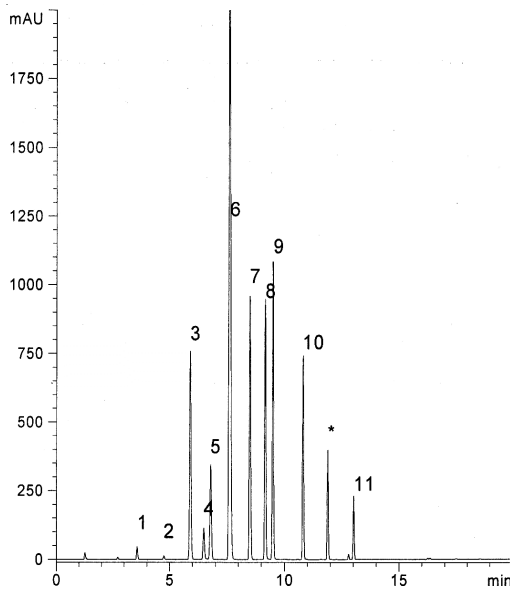

Fig. 2. Methanol/water separation of phenol (1) phenol (2) 2,4-nitrophenol (3) 4-nitrophenol (4) 2-dinitrophenol (5) 2-chlorophenol (6) 2,4-dimethyl phenol (7) 2-methyl, 4,6-dinitrophenol (8) 4-chloro, 3-methyl phenol (9) 2,4-dichlorophenol (10) 2,4,6-trichlorophenol, (11) 2,4,6-tribromophenol (12) pentachlorophenol

Linearity and precision: For the analytes investigated, calibration plots were built reporting the peak area (relative units as given by the integrator) *versus* standard concentration in a concentration range between 0.1 and 30 ng μL^{-1} for all the analytes except for 4-nitrophenol (2.5-30 ng μL^{-1}). Straight lines were obtained for the regression parameters reported in Table-3 together with the correlation coefficient (r^2). The highest coefficient of determination was 0.99991 (2,4,6-trichlorophenol and 2,4-dichlorophenol) and the lowest was 0.99919 (4-nitrophenol).

The slope and the intercept of the analytes studied varied from 0.8574-204.50267 and -0.45357-0.16901, respectively. The precision of the method, based on measurement of repeatability, was obtained from the repeatable standard deviation expressed as the co-efficient of variation (CV %) by replicates injections (n = 7) of standard mixture (prepared in the laboratory) components and the internal standard (IS), by taking into consideration the concentration and the retention time of each compound (Table-5). This was further confirmed by the prepared standard of the analytes supplied by Sigma Aldrich, South Africa at known concentration.

Limit of detection (LOD) and limit of quantification (LOQ): Different procedures for the determination of limits of detections (LODs) and limit of quantifications (LOQs) are reported in the literature. These limits can be experimentally estimated from the injection of serially diluted standard solutions[30,31] or extracts of fortified water samples until the signal-to-noise ratio (s/n) ratio reaches a value of three. LOD could also be estimated as three times the noise level of the baseline in the chromatogram, while the limit of quantification (LOQ) is set at three times the LOD[32]. LOD and LOQ can be calculated further using the equation: LOD = 3.3 × Sb/a and LOQ = 10 × Sb/a where a is the slope and Sb is the standard deviation of the y-intercept[33].

The detection limit ranged from 4 to 166 μg L^{-1} while the limit of quantification ranged from 15 to 502 μg L^{-1} as shown in Table-4. The detection limit was calculated by comparing the signal-to-noise (S/N) ratio of the lowest detectable concentration. In this study, LOD and LOQ were calculated by multiplying the standard deviation of the lowest detectable concentration by 3.3 and 10, respectively[34,35]. The obtained values for both LOD and LOQ for the analytes were low, indicating that the method is capable of not only quantifying all of the used standards, but also of detecting traces of these phenolic compounds in different water samples. The result proved to be 10 times better than result obtained on HPLC Waters 2210 in our laboratory.

Accuracy: Some experiments of recovery yield were performed by analyzing, under the same chromatographic conditions, MilliQ water samples was spiked to obtained 1000 mg L^{-1} of each analyte. No significant matrix interference was observed. The obtained recoveries were within the same order of magnitude as reported by other researchers[2,3,23,26]. The standard concentrations used were the same as for precision studies. The result reported in Tables 3 and 5 provide evidences

TABLE-3
CALIBRATION PLOT EQUATIONS: PEAK AREA (y, RELATIVE UNITS) *VERSUS* STANDARD CONCENTRATION (x, ng μL^{-1}), CORRELATION COEFFICIENTS, RETENTION TIMES AND LINEARITY

Analyte	Retention time	Calibration plot	r^2	Linearity dynamic range (ng μL^{-1})
Phenol	3.543	y = 10.28493x + 0.38296	0.99972	0.30-30
4-Nitrophenol	4.706	y = 0.85740x + 0.00285	0.99919	2.50-30
2-Chlorophenol	5.865	y = 204.65811x – 9.7233	0.99986	0.20-30
2,4-Dinitrophenol	6.452	y = 38.36583x – 4.4209	0.99976	0.20-30
2-Nitrophenol	6.746	y = 27.76183x – 4.22382	0.99979	0.20-30
2,4-Dimethylphenol	7.550	y = 185.29596x – 9.6088	0.99989	0.20-30
4-Chloro-3-methylphenol	8.464	y = 11.28097x – 0.51992	0.99990	0.30-30
2,4-Dichlorophenol	9.127	y = 11.77682x – 0.53496	0.99991	0.30-30
2-Methyl, 4,6-Dinitrophenol	9.450	y = 49.8612x – 3.12107	0.99990	0.20-30
2,4,6-Trichlorophenol	10.738	y = 9.19452x – 0.61745	0.99991	0.20-30
2,4,6-Tribromophenol	11.778	y = 5.16817x + 0.16299	0.99990	0.20-30
Pentachlorophenol	12.911	y = 3.124950x + 0.26393	0.99985	0.30-30

TABLE-4
DETECTION LIMIT, LIMIT OF QUANTIFICATION AND PERCENT RECOVERY

Analyte	LOD (ng μL^{-1})	LOQ (ng μL^{-1})	Recovery (%)		
			Average ± SD	Min	Max
Phenol	0.052	0.158	81.52 ± 0.43	81.05	81.90
4-Nitrophenol	0.166	0.502	71.73 ± 1.07	70.50	72.30
2-Chlorophenol	0.005	0.015	81.43 ± 0.65	80.80	82.10
2,4-Dinitrophenol	0.018	0.158	72.97 ± 0.47	72.60	73.50
2-Nitrophenol	0.025	0.076	72.40 ± 1.11	71.40	73.60
2,4-Dimethylphenol	0.004	0.015	89.35 ± 0.31	89.10	89.70
4-Chloro-3-methylphenol	0.044	0.133	76.53 ± 1.00	76.90	77.30
2,4-Dichlorophenol	0.056	0.169	69.43 ± 1.76	67.80	71.30
2-Methyl, 4,6-Dinitrophenol	0.021	0.062	78.00 ± 0.61	78.00	79.21
2,4,6-Trichlorophenol	0.009	0.027	101.87 ± 0.45	101.40	102.30
2,4,6-Tribromophenol*	0.019	0.064	101.57 ± 0.91	100.60	102.40
Pentachlorophenol	0.028	0.085	92.03 ± 2.19	90.30	94.50

LOD = 3.3 × δ; LOQ = 10 × δ; δ = Standard deviation of the signal to noise ratio.

TABLE-5
PRECISION (n = 7) FOR ALL THE ANALYTES

Analyte	Concentration (ng μL^{-1})	Precision (CV %)
Phenol	0.2	7.425
4-Nitrophenol	2.4	2.084
2-Chlorophenol	0.1	1.492
2,4-Dinitrophenol	0.2	1.992
2-Nitrophenol	0.3	2.348
2,4-Dimethylphenol	0.1	1.186
4-Chloro-3-methylphenol	0.3	4.614
2,4-Dichlorophenol	0.2	6.299
2-Methyl, 4,6-Dinitrophenol	0.1	5.511
2,4,6-Trichlorophenol	0.2	0.966
2,4,6-Tribromophenol	0.3	1.563
Pentachlorophenol	0.3	10.498

that the optimized method for all the analytes have acceptable repeatability (RSD = 11 %).

Water analysis: The developed analytical method was applied to analyze phenol from real water samples. Figs. 3 and 4 shows the chromatograms of tap water and flavor water from a grocery shop in the city of Cape Town. Figs. 5-8 shows the graphical representation of concentration of analytes in water samples.

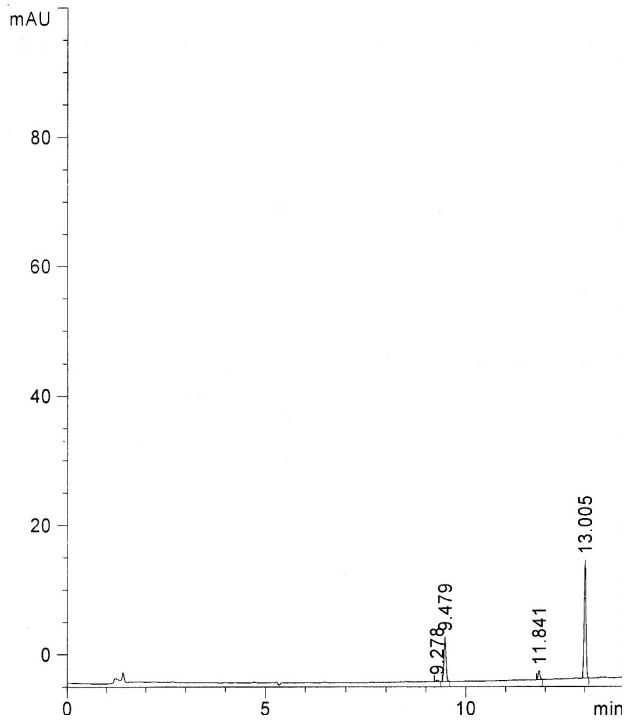

Fig. 3. Tap water analyzed in the laboratory

Pentachlorophenol, 2-methyl, 4,6-dinitrophenol, 4-nitrophenol and 2,4,6-tribromophenol were the most prominent of the analytes. Brand two bottled water shows the present of all the analytes except for 2-chlorophenol, 4-nitrophenol and 2,4-dimethylphenol with 4-nitrophenol having highest concentration of 16.793 ng μL^{-1}. The reported concentration of phenol and phenol derivatives were far higher than the values recommended by EU, USEPA and WHO. The result of this research work collaborates the recent findings as reported that most water supplies in western cape should further be monitored.

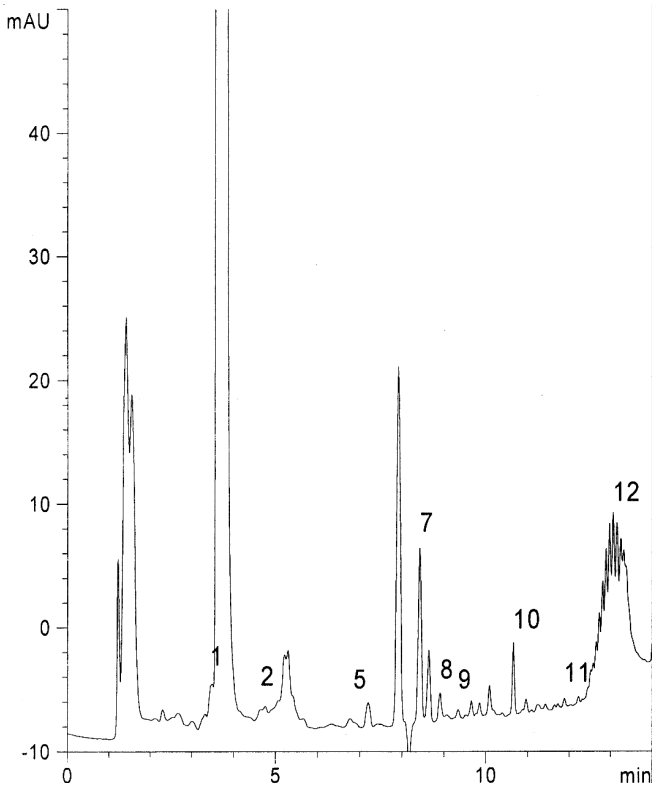

Fig. 4. Brand 2 water from grocery shop

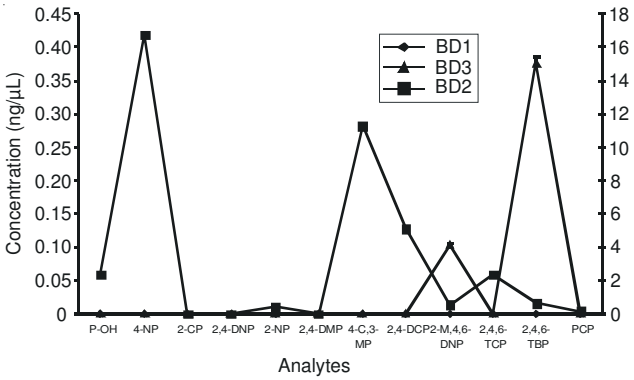

Fig. 5. Phenols concentrations in water samples from a groccery shop

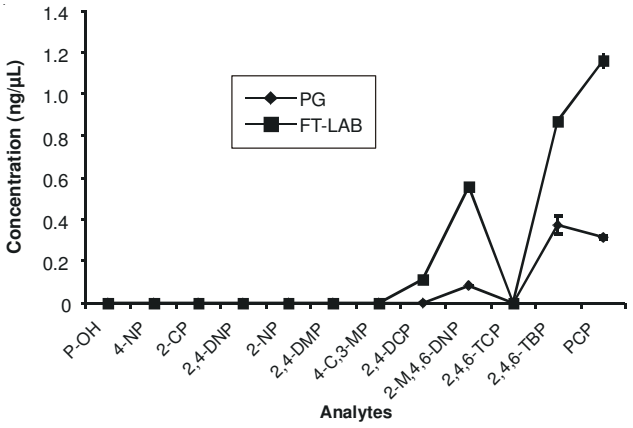

Fig. 6. Phenols concentrations in water samples from student residences and laboratory

The possible effect of phenol in water could be best explained by conducting a health risk assessment on the available phenols. The bottled water sample brand 1 is very safe

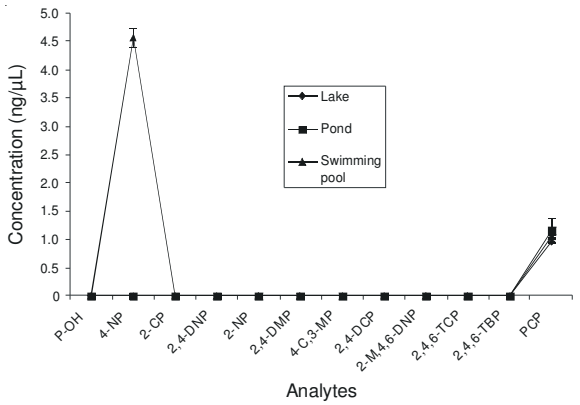

Fig. 7. Phenols concentrations in water samples from water bodies

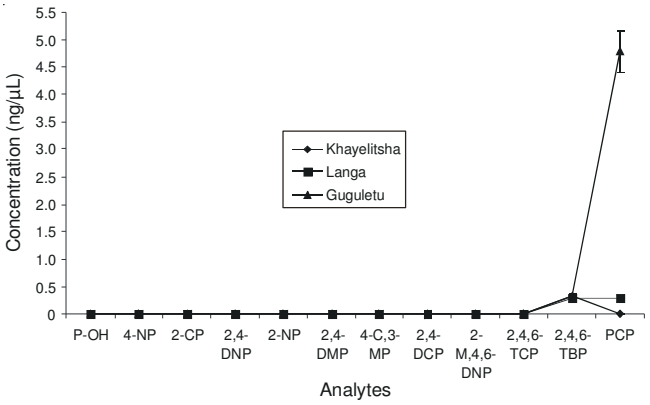

Fig. 8. Phenols concentrations in water from informal settlements

for drinking, while brand 2 which contains phenolic compounds could pose health risk over time. The presence of pentachlorophenol in the pool, lake and pond could be due to chlorination and natural processes that leads to formation of chlorophenol in aquatic environments.

Conclusion

The proposed analytical method (SPE-HPLC-DAD) has been successfully applied to the separation, detection and quantification of the 11 priority phenol pollutants in environmental water samples. The newly launched kinetex column by phonemex proved to be good and fast as all the phenols can be separated in less than 14 min. Overall, the reported work is an important contribution to the field, since phenolic compounds have drawn the attention of many researchers outside South Africa where no or little work is reported. Moreover, a better analytical method for lower detection limits is required for the determination of analytes at lower concentration in more complex samples.

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