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Phase-transfer catalytic determination of phenols as methylated derivatives by gas chromatography with flame ionization and mass-selective detection

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Abstract

A convenient method for the GC determination of phenols as methylated derivatives is proposed, taking advantage of the beneficial features of phase-transfer catalysis (PTC). The optimal experimental conditions of pH, temperature, organic solvent, time of extraction–derivatization and amounts of the participating reactants and catalysts, were properly established. Several catalysts in soluble or polymer-bound form were tested. Most of them demonstrated appreciably high-performance characteristics but the polymer-bound catalyst is most favourable due to its facile separation from the rest of the reaction system after the extraction–derivatization. Interferences with the extraction and derivatization yield were not noticed. The chromatographic separation of 11 methylated derivatives of phenols was complete within 23 min. The detection limits of the method, which range from 0.005 to 0.120 μg, are inadequate for drinking water analysis. However, the method was successfully applied to the analysis of fortified composite lake water samples using GC–flame ionization detection and GC–MS in the single ion monitoring mode with the most abundant characteristic ions. Spiked recoveries of phenolics were in the range 94–102%, on the basis of distilled water calibration graph, signifying that PTC determination of phenols is not affected by the composition of such matrices.

Keywords: Phase-transfer catalysis; Phenols; Chlorophenols; Nitrophenols

1. Introduction

Phenols are generated by a number of processes including those in the petroleum industry, the paper industry and the synthesis of plastics and pharmaceuticals [1,2]. Chlorinated phenols have been used as insecticides and are found in drinking waters as a result of chlorination [3]. Because of the toxicity of phenols, the US Environmental Protection Agency has included some of them in the list of high priority pollutants [4]. Their determination in waste and drinking waters is therefore of importance and many analytical methods have been developed to meet this requirement. Spectrophotometric methods are employed for the determination of the sum of phenolic compounds [5–10] while chromatographic methods are suitable for the selective determination of individual phenolic compounds. Acetylation [11–13], benzylation [14–16], benzoylation [17,18], alkylation [19–21], silylation [22,23] are methods, which

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have gained ground in the literature for gas chromatographic analysis of phenols at pg levels.

Extraction is a prerequisite to isolate and preconcentrate analytes prior to gas chromatographic analysis. Conventional liquid–liquid extraction has several disadvantages such as unfavourable partitioning of highly polar compounds into the extraction solvent, the extracts require an additional cleanup, which is sometimes elaborate and gives rise to further losses.

Phase-transfer catalysis (PTC) is widely used in industrial processes for reactions involving water-soluble and water-insoluble reactants [24–26]. Particularly, in synthetic organic chemistry numerous phase-transfer catalysts have been utilized, while in analytical chemistry such applications are scant. Quaternary ammonium compounds are the most common catalysts due to their low toxicity and proven effectiveness for a wide range of reactions [27–31]. Conceptually, the quaternary ammonium cation forms in the aqueous phase an ion-pair with a water-soluble reactive anion. The ion-pair is more soluble in the organic phase than in water, so the reactant is ''dragged'' through the interface into the organic phase where the derivatization reaction takes place. The small organic layer into which the derivatives are located can easily be injected into the GC system directly or after further preconcentration. To accomplish the PTC goal, except for two-phase PTC systems, various polymer-bound phase-transfer catalysts have also been reported and Regan was the first to call these systems tri-phase catalysis [32,33]. The reactivity of a liquid–solid–liquid tri-phase reaction (i.e., polymer-supported catalytic reaction) is influenced by the structure of the active sites, particle size, degree of crosslinkage, degree of the ring substitution, swollen volume, and spacer chain of a catalyst [34].

PTC has been implemented as a tool for the simultaneous extraction, preconcentration and derivatization in the analysis of certain phenolic compounds after pentafluorobenzylation [35]. However, a systematic study for the assessment of the experimental parameters in the analysis of phenols in multi-phase systems is lacking. In this paper, a convenient method for the GC determination of phenols, as methylated derivatives, is detailed, taking advantage of the beneficial features of PTC. In addition to the abovementioned, the diverse possibilities of using PTC in different formats (i.e., soluble and polymer-bound) are explored. The phenols selected to be studied span a wide range of pK_a values, from the slightly acidic thymol to the highly acidic pentachlorophenol and from the highly water-soluble and polar resorcinol, to the sparingly water-soluble pentachlorophenol.

2. Experimental

2.1. Reagents and solutions

The phenolic compounds used throughout the study were obtained from Aldrich (Sigma–Aldrich Hellas). Their pK_a values and water solubilities are collected in Table 1. Standard stock solutions at

Table 1
Physicochemical data on the studied phenolic compounds along with the amounts in the reaction mixture

Phenolic compound	pK_a	Solubility in water at 20 °C (g/l)	Amount in reaction mixture (μg)
Phenol	10.0	83	4.8
3-Chlorophenol	9.02	26	2.5
4-Chlorophenol	9.37	24	4.8
3,5-Dimethylphenol	10.1	4.8	2.8
Resorcinol	9.32	717	3.3
Thymol	10.6	0.9	2.3
2,4-Dichlorophenol	7.85	4.5	7.6
3-Nitrophenol	8.40	13.5	4.4
2-Nitrophenol	7.23	2.5	3.5
2,3,5-Trichlorophenol	6.00	0.09	2.9
Pentachlorophenol	4.70	0.01	4.5

concentrations of 1 mg/ml were prepared in acetone and appropriate dilutions were made to obtain lower concentrations. The organic solvents used were of GC grade and were supplied by Riedel-de Haën. Methyl iodide was of 99% purity (GC grade) and was purchased from Aldrich along with the humic acid, sodium salt. Tetrabutylammonium bromide (TBAB), tetrahexylammonium bromide (THAB) and cetyltrimethylammonium bromide (CTAB) were obtained from Aldrich and their respective stock solutions were made in dichloromethane. The critical micellar concentration (CMC) of CTAB is 1 m*M*. The polymer-bound tri-*n*-butylmethylphosphonium chloride (1.4 mmol Cl^-/g resin) and the sodium dodecylbenzene sulfonate (LAS) were obtained from Fluka. Stock solution of *n*-pentadecane, used as internal standard (I.S.), was prepared at a concentration of 1 mg/ml in dichloromethane.

2.2. Instrumentation

The gas chromatograph was a Shimadzu GC-17A (Shimadzu, Kyoto, Japan) equipped with a split/splitless injection port and a flame ionization detection (FID) system. The mass spectra of phenols, as methylated derivatives, were obtained using a Shimadzu GC-17A gas chromatograph coupled with a QP5000 mass-selective detection system, which was manually tuned using perfluorotributylamine with the masses m/z 69, 219, 502. Standard electron impact (EI) conditions (70 eV) were used with a source temperature of 280 °C.

The separation of phenolic derivatives was performed on a Supelco SPBM-5 capillary column (Bellefonte, PA, USA) (30 m×0.32 mm I.D., 0.25 μm film thickness) with helium of 99.999% purity as carrier gas.

2.3. Analytical procedure

In a typical procedure, the sample pH is adjusted to 10.6, with concentrated NaOH. An aliquot of 10 ml of standard solution containing the amounts of phenols reported in Table 1 is transferred to a vial with PTFE-lined screw-caps. To this solution are added the appropriate amount of phase-transfer catalyst in the soluble or polymer-bound form, 1 ml of dichloromethane, the internal standard and 230 mg (1.62 mmol) methyl iodide. The reaction vial is sealed and vigorously shaken for 45 min, at 65±0.5 °C with a magnetic stirrer, so that a vortex is formed throughout the liquid volume. After phase separation, the organic phase is dried with anhydrous sodium sulfate and evaporated to 200 μl under a stream of nitrogen. An aliquot of the organic layer is subjected to GC analysis.

The aqueous real samples, taken from Pamvotis lake (Epirus, Greece) to check the matrix effects are treated in the same manner, as previously described.

2.4. Gas chromatographic conditions

A 2-μl portion of the organic layer is injected into the GC system in the splitless mode (purge delay time, 0.5 min). The injector and detector temperatures are set at 250 and 300 °C, respectively. The oven temperature is programmed from 50 °C (5 min) to 150 °C at 6 °C/min and finally from 150 to 210 °C (1 min) at 20 °C/min. The total analysis time is 25.7 min. Signal acquisition and processing are carried out with a Chrompack integrator (Shimadzu) and a CLASS-5000 Version 1.24 Chromatography Software (Shimadzu).

The peak area ratios relative to the I.S. are used for all the quantitative calculations of recovery tests.

3. Results and discussion

3.1. Confirmation of the derivatives

Upon the simultaneous PTC methylation reaction, all hydroxyl groups of phenols are converted to their corresponding methyl ethers, via an S_N2 substitution reaction, yielding a single derivative for each phenolic compound studied. The EI-MS data, which are gathered in Table 2, give assurance as to whether the derivatives have been formed. In the majority of the derivative spectra, molecular ions coincide with the base peaks. Other prominent ion fragments emanate, mostly, from the cleavage of bonds between phenolic oxygen and carbon of the methyl group. In thymol (isopropyl cresol), the elimination of the isopropyl group from the molecule gives a less abundant characteristic mass fragment at m/z 137. The structure of resorcinol (1,3-dihydroxybenzene) is readily

Table 2
Characteristic ions and relative abundances for the derivatized phenols

Phenolic compound	M^+	M^+-15	$M^+-29(-28)$	M^+-30	Other ions
Phenol	108 (100)	93 (20)		78 (80)	78 (80), 65 (30)
3-Chlorophenol	142 (100)	127 (10)		112 (75)	99 (55), 77 (50)
4-Chlorophenol	142 (100)	127 (60)		112 (5)	99 (70), 77 (10)
3,5-Dimethylphenol	136 (100)	121 (45)		106 (15)	91 (85), 77 (40)
Resorcinol	138 (100)		109 (45)		95 (25), 78 (40)
Thymol	180 (10)		152 (2)		110 (100), 95 (85)
2,4-Dichlorophenol	176 (100)	161 (95)			133 (65), 97 (10)
3-Nitrophenol	153 (85)	137 (10)		123 (10)	77 (100), 63 (35)
2-Nitrophenol	153 (40)	137 (2)		123 (35)	77 (100), 63 (30)
2,3,5-Trichlorophenol	212 (100)	197 (15)			169 (70), 109 (20)
Pentachlorophenol	280 (100)	265 (100)			130 (25), 95 (30)

confirmed by the presence of an intense ion at m/z 109 arising from the loss of two methyl groups.

3.2. Optimization of derivatization conditions

The concept of the simultaneous PTC extraction and derivatzation in the studied system is portrayed in Fig. 1 and rationalized as follows: the phenolic compounds present in the aqueous phase are deprotonated and the anionic phenolates are transferred into the organic phase as ion pairs. The ''naked'' analyte anions, in the organic phase, react with methyl iodide towards the formation of methylated derivatives, which remain in the organic phase.

In order to optimize the conditions for PTC-based phenol analysis the following sets of experiments were conducted: (i) kind of PTC and concentration of catalyst, (ii) pH of extraction and derivatization, (iii) selection of organic solvent, (iv) temperature and time needed for PTC, (v) stirring and static conditions versus ultrasonication, (vi) concentration of methyl iodide, (vii) sample volume-to-organic solvent ratio and (viii) interference study.

3.2.1. Selection of catalyst

Cationic surfactants or surfactant-like compounds are best suited for the purpose of PTC extraction of phenols. In order to explore the nature and fix the quantity of PTC, in the methylation of phenols, the procedure was carried out in aqueous alkaline standard solution of phenolics using increasing quantities of different PTC, under stirring. The concentration of TBAB and THAB used as catalysts was varied from 10^{-4} to 10^{-2} *M*. It was found that the catalysts exhibit almost identical behaviour with regard to the extraction and derivatization capability. In both cases, the extent of methylation is increased with the

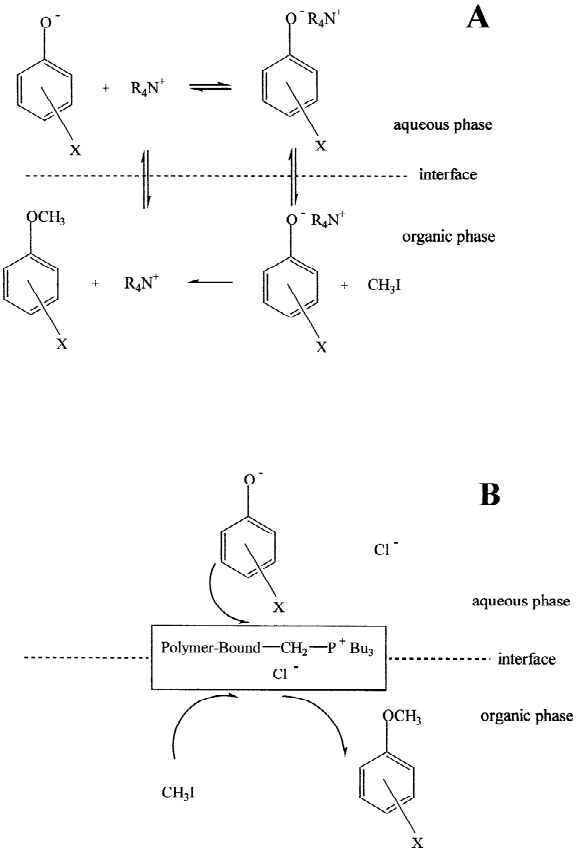

Fig. 1. Methylation scheme of phenols via (A) two-phase and (B) tri-phase catalysis systems.

increasing amount of PTC. Compounds such as TBAB and THAB employed in this study may exhibit some surface-active behaviour but they do not form micelles and are not surfactants in the classical sense. Hence, along with them the effect of the cationic surfactant CTAB on the alkylation of phenols through PTC, was investigated. The CTAB was proved to be better suited than the reported TBAB and THAB in terms of reaction product yields. It is noteworthy that amelioration of yield was significant at CTAB concentrations higher than CMC. However, despite improved performance of CTAB as a catalyst, foaming may form at high concentrations, which hampers the phase separation in the reaction vial. Relevant methylation experiments conducted with sodium dodecyl sulfate (SDS) (anionic surfactant) and Triton X-100 (non-ionic surfactant) showed that they did not exhibit PTC properties at any concentrations even above their CMC. This can be ascribed to the complete absence of transfer of products into the organic layer. Also, this finding supports the presumed action of the cationic surfactant as phase transfer catalyst and rules out its role as a carrier of the organic compounds at surfactant concentrations higher than its CMC [36], under the predominant experimental conditions.

The disadvantages of using a quaternary salt in soluble form include the formation of emulsion as well as its presumable introduction into the GC system. Polymer-bound catalysts, which behave as ion-exchange resins and can bind to anionic analytes have been proposed, as reported previously, capturing all the catalytic advantages of the respective catalysts in the soluble form. The interface plays, again, a paramount role in the reaction mechanism. Relying on previous research findings, it is assumed that the derivatization proceeds inside or on the surface of the resin, which is ''drenched'' with the organic solvent containing methyl iodide [29,37]. In this vein, polymer-bound tri-*n*-butylmethylphosphonium chloride was employed in PTC for the extraction and methylation of phenols. An amount of 10 mg of the aforementioned catalyst was enough to attain results comparable with those of the catalyst in soluble form, as we can infer from the reaction yields for total phenols (data not shown). The amount of 15 mg was finally selected for subsequent experiments to compensate for higher concentrations of phenols and possible interferences, which may interact with the resin. In view of the high reaction yields observed by the tri-phase system, no mass-transfer limitations of the reactants and ion-exchange rate in the aqueous phase were foreseen [38,39].

3.2.2. Influence of sample pH

It is anticipated that being in charge-neutralized form, phenolic molecules are phase-transferred incompletely and inadequately, thus resulting in poor derivatization. Based on the assumption that ionized phenolates are the reactive species for methylation, the optimum pH value is closely related to the pK_a of phenolics. Although for individual phenolic compounds (e.g., 2-nitrophenol, 2,3,5-trichlorophenol and pentachlorophenol) the increase in pH brings about some peak deterioration, for most of them betterment occurs at a pH value of 10.6. This value was found to account for the simultaneous extraction and methylation of the phenols concerned. It is worth mentioning that the employment of so high pH, in the present work, is in contrast with examples in the literature reporting that the catalysts involved are unstable at such an ambience [40]. However, the methylation was satisfactorily performed with both soluble and polymer-bound catalyst, under the pH conditions chosen. Going further, the high conversion with the increase in medium pH, underscores the absence of competition effects of excess hydroxide anion with phenols, which are present in the anionic form [35]. That is, the interactions in the ion-pair phenolate–catalyst should prevail in the organic phase. To establish the necessity of PTC in the tri-phase system, the methylation of phenols was studied without catalyst. At pH values 2 and 3 where phenolic compounds are in the undissociated form, no derivatization products at all were noticed, even by saturating the phenolic aqueous solution with sodium chloride to promote extraction.

Finally, in the range of pH 7–11, the chromatographic signals attributed to the catalysts are remarkably constant.

3.2.3. Selection of organic solvent

The distribution of PTC reagents between water and an organic medium depends, to a large extent, on the nature of the latter. Several organic solvents

immiscible with water such as hexane, toluene, dichloromethane, *tert*-butyl methyl ether and ethyl acetate were tested. Dichloromethane and ethyl acetate showed, by far, the most favourable behaviour with respect to extraction and derivatization yield. But dichloromethane was preferred to ethyl acetate due to its capability to exclude extraneous interfering peaks from the chromatograms.

3.2.4. Extraction and derivatization experimental conditions

The extractive methylation reactions in aqueous solutions were further examined using dichloromethane as the organic phase containing methyl iodide as derivatizing agent in basic pH for the different PTC systems, under stirring. When the tri-phase PTC is carried out, the methylation progresses rapidly in the first 30 min and reaches completeness after almost 40 min, as represented graphically in Fig. 2. As for the catalysts in soluble form, in general, slightly faster kinetics were observed with the more water-soluble TBAB, since it is reasoned that the highly lipophilic catalyst cations do not exist in the aqueous phase in appreciable concentration.

Temperature is expected to be a rate-determining parameter on the reaction kinetics and product yield. Fig. 3 illustrates an improvement in chromatographic responses with an increase in temperature. Increasing temperature can accelerate the product formation, which is the case for both types of catalysts. This is especially striking for resorcinol, a highly water-soluble dihydroxybenzene. However, high temperatures can be the cause of degradation of the quaternary ammonium salts due to their low thermal stability at elevated temperatures albeit phosphonium salts are somewhat more stable [29]. For all the above reasons, the temperature of 65 °C was selected as the optimum.

One of the important factors accelerating an L–L heterogeneous reaction is the thorough dispersion of the minor-organic phase into the major-aqueous phase. To bring out the importance of stirring in comparison with static conditions as well as with sonication, pertinent experiments were carried out. A close dependence of reaction yield and stirring speed indicates that the anticipated interfacial phenomena are consequential. The reaction kinetics are significantly faster when the surface of the reaction interface is increased by vigorous stirring and pronouncedly lower under no-stirring conditions. In addition to above, the effect of stirring and heating at 65 °C was compared with that of mere sonication and sonication with stirring. It is demonstrated that sonication along with stirring is quite advantageous to the PTC-methylation of phenolics, unequivocally better than sonication and slightly better than stirring alone. Heating is indispensable to obtain the highest derivative yields. In our experiments, stirring under heating was judged to be sufficient to drive the reaction yield to its highest, within 45 min.

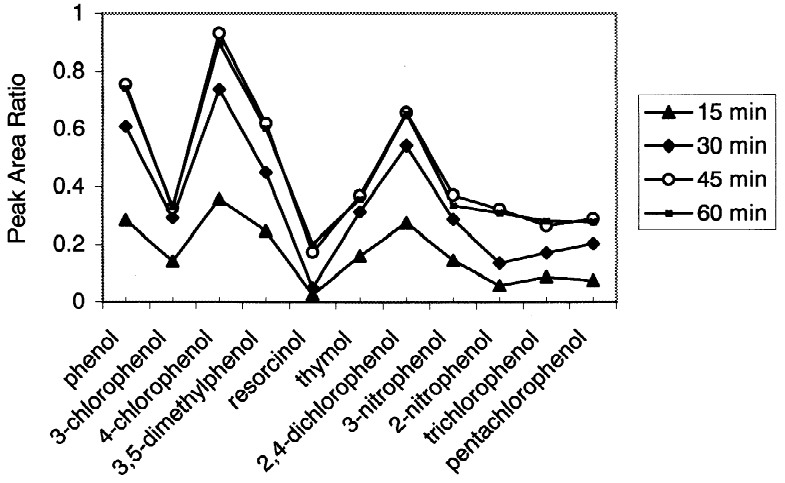

Fig. 2. Time course of the tri-phase extractive methylation of phenols. Medium pH: 10.6, reaction temperature: 65 °C.

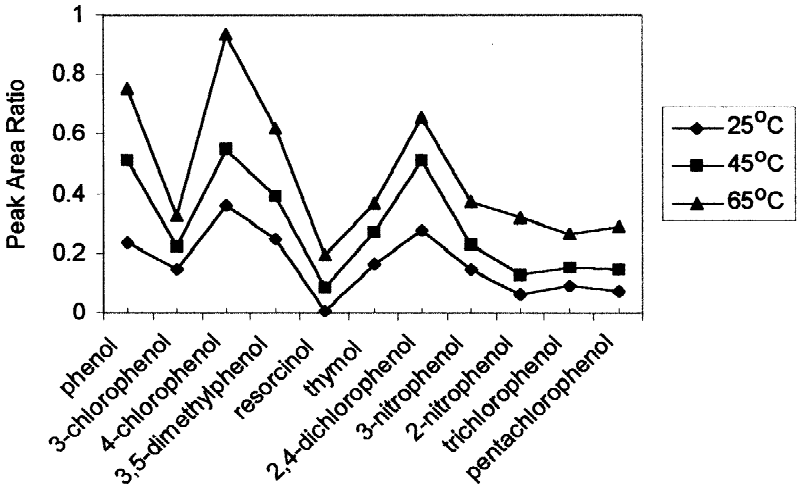

Fig. 3. Influence of temperature on the tri-phase methylation of phenols. Medium pH: 10.6, reaction time: 45 min.

Methyl iodide is a very efficient methylating agent leading to high derivatization yields in a rather short reaction time. It was used in the overwhelming excess of 230 mg/reaction vial to ensure complete derivatization.

3.2.5. Influence of sample volume:organic solvent ratio

For complete mixing of the two phases, their ratio should be the optimum. In the present study, experiments were carried out with different volumes of water samples (5, 10 and 25 ml) spiked with known amounts of the 11 phenols keeping constant the volume of the organic phase (1 ml). The samples were subjected to the established PTC process in screw-capped vials of proper volume capacity. When TBAB is used in PTC, a decrease in methylation yield for all the phenols studied was noted with an increase in sample volume. In contrast, the tri-phase polymer-bound catalyst led to unchanged area ratios in the domain of the studied volume of sample for most of the phenols concerned. Additional experiments were carried out with regard to the sample volume keeping constant the aqueous-to-organic phase ratio at 5:1. The organic phase was collected and invariably concentrated to 1 ml by blowing nitrogen. It was seen that phenolic compounds can efficiently be concentrated into the organic layer in the form of their alkylated derivatives. The overall response for each phenol when using PTC, slightly declined with increasing sample volume. Again, it is proved that the format of PTC has the same significant bearing on the reaction, as in previous experiments, with the polymer-bound catalyst performing better than the soluble TBAB.

3.2.6. Study of the effect of possible interferences

It is conceivable that co-existing inorganic anions might depress the extraction with concomitant effects on the derivatization of the analytes because of their competitive sorption on and consumption of the phase-transfer catalyst. Interference with the derivatization rate and conversion yield of an anionic analyte arising from co-existing anions depends on the differences in their nucleophilicities, lipophilicities and affinities for the catalyst. On the other hand, the occurrence of salts in high concentrations can cause higher extraction yield because of the salting-out effects. The derivatization efficiencies for a mixture of 11 phenols were examined in individual solutions containing sodium salts of chloride, sulfate, nitrate and phosphate, at concentrations 15 mg/l as well as in a mixture of them. In addition, the methylation reaction was conducted in a saturated solution of sodium chloride. It is interesting that anions neither exhibit any interference effect nor give rise to higher responses.

Humic substances are also candidate interferents because of the competitive binding of their carboxylic and phenolic moieties on the active catalysts.

The GC traces obtained for the whole group of the studied phenolics were similar in terms of peak composition and peak height regardless of the presence or the increasing content of humic acids in the range 1–10 mg/l, thus signifying a remarkable tolerance of PTC to samples containing varying amounts of humic acids.

As mentioned before, quaternary salts in free form or in the form of bonded solid particles may act as cationic surfactants. The presence of co-existing surfactants as potential components of a real sample might influence the efficiency of phase transfer as well as the derivatization process. To this end, a water sample was spiked with LAS the most widely used anionic surfactant, at a concentration of 100 mg/l. The implementation of the PTC method demonstrated that extraction and derivatization were as quantitative as in the absence of LAS.

3.3. Chromatographic separation—recovery studies

Under the employed chromatographic conditions, the separation of the 11 phenols as methylated derivatives was completed within 23 min, as shown in Fig. 4. Each phenol displayed a single peak with favourable GC properties. The use of the polymer-bound catalyst resulted in the consistent detection of unknown low peaks in the chromatograms, which were corroborated by running sample blanks. These peaks do not disturb the GC separation. Detection limits (signal-to-ratio=3) for a 10-ml sample volume, range from the low 0.005 μg (3-chlorophenol) to the high 0.120 μg (resorcinol) for GC–MS while the respective GC–FID limits are approximately one order of magnitude higher. These method detection limits are inadequate for drinking water routine analysis even increasing the sample volume up to 25 ml, as reported in the study of the influence of sample volume:organic solvent ratio. To check the matrix effects of real-life environmental samples, two lake water samples wherein no recognizable phenols were detected, were spiked and analysed using GC–FID and GC–MS in the single ion monitoring (SIM) mode with the most abundant characteristic ions, as collected in Table 2. The calculated recoveries from these matrices were in the range 94–102%, on the basis of distilled water calibration graph, thus signifying tolerance to relevant matrix compositions. For amounts in the range 0.1–1.5 μg of each of the 11 phenolics, the relative standard deviations were measured in the range of 3.0–5.0%, for five successive replicates.

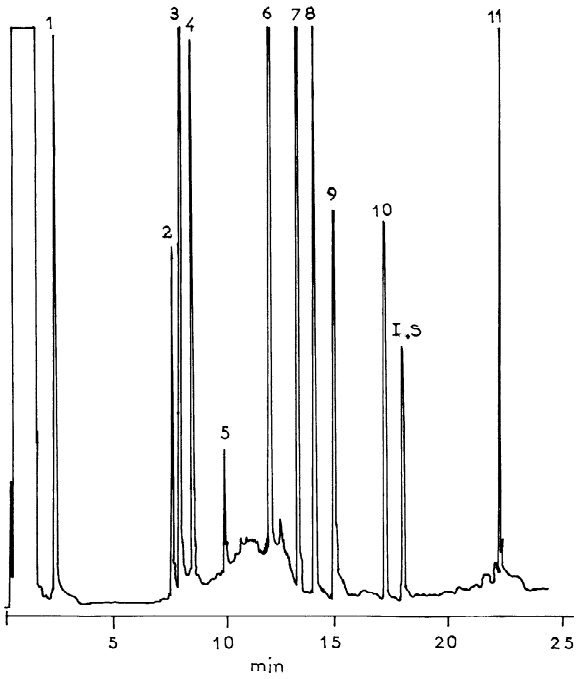

Fig. 4. GC–FID chromatogram of phenols as methylated derivatives separated on a SPBM-5 capillary column. Tri-phase catalysis was the system for the extractive derivatization. Peak assignment: 1=phenol, 2=3-chlorophenol, 3=4-chlorophenol, 4=3,5-dimethylphenol, 5=resorcinol, 6=thymol, 7=2,4-dichlorophenol, 8=3-nitrophenol, 9=2-nitrophenol, 10=2,3,5-trichlorophenol, 11=pentachlorophenol. I.S.=internal standard.

4. Conclusions

In trace chromatographic analysis, the key step to establish a convenient method is the sample pretreatment. In the face of continued need for such methods, PTC can prove a valuable tool for the simultaneous extraction, preconcentration and derivatization in the analysis of phenols in surface waters. Among the various forms of the catalysts tested, ''tri-phase catalysis'' method simplifies the removal of the catalyst after the extraction–derivatization and minimizes or even more precludes undesired peaks in the chromatograms.

At this stage and as the method stands now, the detection limits are inadequate for drinking water monitoring purposes (regulated limits 0.1 μg/l). Preliminary experiments with the aim to ameliorate these limits are producing promising results, which indicate that the applicability of the method will be extended in the future to the analysis of phenols in drinking water.

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