

YAKOV I. KORENMAN
VLADIMIR N. FOKIN

Voronezh State Technological
Academy, 394017 Voronezh, pr.
Revolutsii, 19, Russia

SCIENTIFIC PAPER

547.562:66.082.2:66.062:543.544.3

CONCENTRATING OF PHENOLS BY EXTRACTION WITH MIXTURES OF ORGANIC SOLVENTS

A means of phenol, cresol and xylenol determination in natural, drinkable, purified sewage water and natural brines of marine origin is presented in the study. The procedure includes sampling, the introduction of an internal standard, extraction concentrating by applying a binary mixture of extracting agents based on tributyl phosphate and, finally, gas-chromatographic analysis of the concentrate. Some regularities in the application of the internal standard method were investigated for the analysis of aqueous media. The procedure is tested for the determination of phenols in saturated marine natural brine and mineral water from sources in gas-oil-bearing regions of Russia and the Ukraine.

The most widely spread and, at the same time, the most dangerous toxicants of organic genesis and anthropologic pollution are phenol and its volatile derivatives. The maximum allowed concentrations (MAC) of these compounds in water are the order of $1.0 \mu\text{g}/\text{dm}^3$ and even lower. A complex ecological situation is often connected with the influx of phenols into natural water [1].

The solution of analytical problems in the determination of microamounts of phenols in aqueous media is often aggravated due to the absence of procedures characterized by selectivity and low detection limits. In the last ten years specially developed devices for the analysis of environmental samples (for example, portable chromatomass-spectrometers) are often inaccessible even for large scientific laboratories. Nevertheless, in the analysis of drinkable water the lowest limit of the determined concentrations of phenols should not exceed 0.5 MAC. At present, procedures for determining microamounts of volatile phenols are absent. Many requirements for special standard documents are not provided with corresponding systematic elaborations for performing the analysis.

We propose a way of detecting and determining volatile phenols in drinkable and mineral water, natural brine of sea estuaries and other natural brines [2]. The method may be performed in two variants and it includes sampling, extraction concentrating with mixtures of organic solvents based on tributyl phosphate (TBPh) and the subsequent gas-chromatographic determination of phenols in the obtained concentrate [3, 4].

EXPERIMENT

The results of the experiment are strongly affected by the correctness of the sampling. At elevated temperatures in a closed system, phenols are decomposed

by microorganisms and the dissolved oxygen. For the preservation of the aqueous samples, acids and alkalis are applied, as well as the salts of heavy metals (e.g. copper sulphate, tin and mercury chlorides) [5, 6]. The introduction of these components prevents the growth of microflora and the biochemical oxidation of phenols. There is no unition opinion on the advantages of any of the preservatives.

It was found that samples of natural water containing $10\text{--}50 \mu\text{g}/\text{dm}^3$ of phenols should be analyzed within 4 hours of sampling. The introduction of heavy metals is not recommended, since it is accompanied by the deposition of hydroxides and the sorption of phenols on the deposits. Mercury salts are excellent antiseptics, however, they are rather toxic. The most effective and safe preservative is NaOH which is introduced in amounts necessary for neutralizing natural organic acids and the formation of a strongly alkaline medium. At pH 11–12 the vital activity of microorganisms is totally suppressed and phenols are transformed into more stable compounds (phenolates). The aqueous sample can be preserved under these conditions in a dark glass flask at $16\text{--}20^\circ\text{C}$ for more than 5–7 days. The internal standard (o-fluorophenol) was introduced into the analyzed sample just after sampling.

Samples were acidified up to pH = 2–4 and the extraction concentrating of phenols was performed with a mixture of organic solvents based on TBPh. The variant of concentrating was chosen depending on the sample composition and the content of inorganic salts. For example, in the investigations of natural brines or marine brines, we recommend the first variant of concentrating, assuming deposition of the mixture of solvents directly on the surface of the extraction vessel.

If the ratio of the volumes of the organic and aqueous phase is 1:100–1:500, there are many technical problems. They are connected with an increase of the time of equilibrium attainment and a comparatively small extent of phenol extraction even with the most effective

Author address: Y.I. Korenman, Voronezh State Technological Academy, 394017 Voronezh, pr. Revolutsii, 19, Russia
Paper received: March 31, 2000
Paper accepted: June 10, 2000

extracting agents. These problems can be overcome when analyzing aqueous solutions containing salts (introduction of large amounts of desalinators for the analysis of weakly mineralized water is not economically feasible). The proposed method assumes the extraction of phenols with a binary mixture of solvents and the subsequent gas-chromatographic analysis of the concentrate.

The solution of this problem is possible if one applies mixtures of extracting agents providing practically the total extraction of phenols at a high multiplicity of concentrating. The mixture is reliably fixed on the surface of the extraction vessel and it is then separated by a special method. In the experiments it was found that an extracting agent containing TBPh (61%) and cetyl alcohol (39%) is optimal.

The mixture was prepared at 50–60°C and at 20°C it is a viscous wax-like substance. The introduction of small amounts of cetyl acetate or some phosphorus-organic compounds (not more than 5–8 % of the mass of the obtained mixture) considerably reduces the time of attaining interphase equilibrium due to the improvement of the kinetics of mass transfer at the liquid-liquid boundary.

The prepared mixture (100–500 µl) heated up to 60–70°C was held on the internal surface of the extraction vessel heated to the same temperature. Under rotation of the vessel in different planes the mixture is uniformly distributed over its surface and is reliably fixed under cooling to room temperature. TBPh provides effective extraction of the phenols, while cetyl alcohol, due to its high hydrophobicity, maintains the extracting agent mixture on the surface of the glass. The surface of the vessel was previously treated with a chromic mixture, carefully washed with distilled water and the traces of moisture completely removed (blowing with dry nitrogen). Treatment of the internal surface of the vessel with vapours of hydrofluoric acid is rather effective.

To extract phenols from marine brine or natural brine, a mixture of extracting agents was placed into the extraction vessel together with acidified sample (100–250 cm³). The vessel was shaken in a vibromixer for 40–50 min (with a frequency of 70–80 vibrations per minute). After attaining interphase equilibrium, the aqueous phase was separated from the other part of the mixture and the vessel was then rinsed with bidistillate (pH 3–4) and heated with care. During heating the viscosity of the extracting agent mixture is considerably reduced and it is collected in the form of concentrate in a hollow on the internal surface of the vessel. 1–10 µl of the concentrate was extracted with a microinjector and introduced into the evaporator of a gas chromatograph or deposited onto silufole film (thin layer chromatography).

Conditions for performing of gas chromatography were chosen based on the composition of the sample and the assumed level of concentrations of the determined components. Fluorophenols satisfy the requirements for an internal standard as they are easily separated from phenol and its derivatives.

The second variant of concentrating was applied to the analysis of natural water containing comparatively high amounts of organic substances of different classes. It included extraction with a mixture of diethyl ether (95 %) and TBPh (5 %) in the presence of a desalinator and the obtaining of a concentrate by evaporation in vacuum produced by a water-jet pump.

For the determination of phenols water samples (50–100 cm³) were collected. If the content of phenols was at the MAC level the volume of the sample was increased to 200–300 cm³. The internal standard was then introduced and the sample acidified to pH 2 – 4 and distilled in a unit consisting of a Wurtz flask and Liebig condenser. The distillate was saturated with NaCl containing 1% KHCO₃ and then extracted with mixture of diethyl ether and TBPh (ratio of organic to aqueous phase to 1:20). The extracting agent was dried with anhydrous Na₂SO₄ and then placed into an evaporator supplied with a water-jet pump. Before evaporation the extract was treated with a solution of sodium ethylate in ethanol (5%). The final volume of the obtained concentrate was of 0.05 – 0.10 cm³. Before GC analysis the phenolates were destroyed with formic acid or wet CO₂.

RESULTS

When the phenols were concentrated according to the first variant, we analysed aqueous samples which did not contain suspensions of solid particles and hydrosols (they both contaminate the concentrate). Table 1 presents the results of phenol determination in natural marine brine (Black Sea region, health resort of Kuyal'nik). o-Fluorophenol was used as the internal standard. It was well separated from all the components of the concentrate and was not observed in the analyzed

Table 1. Results of phenol determination in marine brine (µg/dm³); n = 5, P = 0.95

Phenols	Obtained	Introduced	Obtained after the introduction of impurity
	µg/dm ³		
Phenol	8 ± 1	10.0	16 ± 3
o-Cresol	6 ± 1	10.0	15 ± 3
m- and p- Cresols	10 ± 2	10.0	19 ± 4
o-Ethylphenol	15 ± 3	10.0	25 ± 5
3,5- Xylenol	7 ± 1	10.0	16 ± 3

Table 2. Results of phenol determination in purified sewage water of coke-chemical plant ($\mu\text{g}/\text{dm}^3$); $n = 6$, $P = 0.95$

Phenols	Content of phenols in the analyzed water	Obtained	Introduced (total content)	s
	$\mu\text{g}/\text{dm}^3$			
Phenol	20 ± 3	10.0	31 ± 5	0.08
o- Cresol	17 ± 3	10.0	25 ± 4	0.09
p- Cresol	34 ± 5	10.0	52 ± 6	0,13
2,5- Xylenol	10 ± 3	10.0	23 ± 3	0.22
3,5- Xylenol	16 ± 3	10.0	20 ± 5	0.25

samples. The formation of this compound during biochemical processes in natural samples is practically excluded. Similar results were obtained when m-ethyl phenol was used as the internal standard.

For testing the second method of concentrating, sewage water from a coke-chemical plant after sorption purification was taken as a sample. The results of the phenol determination are presented in Table 2. The excess of aromatic and aliphatic hydrocarbons was removed by hexane extraction. The results of the test demonstrated that the developed method of analysis allows accurate and reliable determination of phenol and cresols in the analyzed water. This method is also applicable for the determination of xylenols. However, the error of determination in this case is higher. When the evaporator temperature is increased by 30–40°C one may observe more symmetrical peaks in the chromatogram. The column is cleaned of non-volatile compounds at least once a week. The identification of phenol and its homologs was performed using a chromatograph supplied with a capillary column with known retention parameters for the determined compounds and the main impurities.

DISCUSSION

The first variant of extraction concentrating is characterized by relative simplicity and reproducibility of results. The duration of extraction does not exceed 1 hour when concentration of phenols is less than 10 $\mu\text{g}/\text{dm}^3$. One should note some specific technical difficulties connected with the removal of the carrier of the concentrate (cetyl alcohol, organic and inorganic non-volatile compounds) from the evaporator chamber. The relative error of phenol determination in natural marine brine does not exceed 25 %. Taking into account the reproducibility of the results, five independent determinations are sufficient to obtain reliable data.

Second variant of concentrating is more selective than the first one. The most effective way of removing

substances which prevent the determination of phenols is distillation of the water sample. Volatile phenols, unlike other organic compounds with a boiling point higher than 200°C, are distilled with water vapour practically in quantitative amounts. It is of major importance that phenols adsorbed on suspensions and sediment (investigations of aqueous heterogeneous samples) are desorbed in hot water and then transferred to the distillate.

The introducing of sodium ethylate into the concentrate before evaporation reduces the detection limits and increases the selectivity of the phenol determination. This can be explained by the fact that the acidic properties of phenols are considerably more expressed than those ones of alcohols, therefore the formation of phenolates in anhydrous medium proceeds more rapidly and may be quantitatively determined. The volatility of phenolates in the presence of excess sodium ethylate is insignificant compared to phenols, which allows evaporation of the concentrate practically to the dry state. Organic bases and neutral compounds completely volatilize. Thus, an extract containing petroleum oil hydrocarbons after evaporation does not reveal any signals in the chromatogram characteristic for these compounds. Organic acids remain in the concentrate and prevent the further GC determination of phenols and thus they should be removed during the extraction. In the experiments it was found that the maximum selectivity of phenol extraction is observed for weakly alkaline solutions. The required value of the pH of the aqueous medium was obtained by the addition of KHCO_3 . Humine, naphthene and other organic acids presented in natural water remain in the aqueous phase. That is why organic compounds are usually present in dry sediment after evaporation. They demonstrate a considerably higher retention time compared to volatile phenols and they do not result in the appearance of false peaks.

CONCLUSIONS

The gas-chromatographic method of determining volatile phenols in aqueous media with preliminary extraction concentrating is proposed in the study. A mixture of tributyl phosphate and cetyl alcohol deposited onto the surface of the extraction vessel rather effectively extracts phenols from natural brines. The introduction of sodium ethylate into the concentrate before evaporation of the volatile extracting agent reduces the detection limits and increases the selectivity of phenol determination. The internal standard method (o-fluorophenol) reduces the relative error of determination up to 25 %. This method is recommended for the analysis of natural, drinkable, purified sewage waters, as well as mineral waters of petroleum oil- and gas-bearing regions.

REFERENCES

- [1] G. D. Kharlampovich, Yu. V. Churkin, Phenols, Khimiya, Moscow, 1974.
- [2] Ya. I. Korenman, V. N. Fokin, A. I. Kryukov, K. I. Zhilinskaya, E.M. Nekipelova, Inventions, **43** (1990) 170; Patent No 1608571 USSR, The way of phenols determination in natural brine.
- [3] Ya.I. Korenman, V. N. Fokin, Chem. and Technology of Water (Ukraine), **15** (1993) 530.
- [4] Ya. I. Korenman, V. N. Fokin, Discoveries, Inventions **36** (1988) 167; Patent No 1427296 USSR, A method of determination of phenol.
- [5] V. Leyte, Determination of organic contaminations of drinkable, natural and sewage waters, Khimiya, Moscow, 1974.
- [6] V. G. Berezkin, Chromatographic analysis of the environment, Khimiya, Moscow, 1970.

REZIME

KONCENTRISANJE FENOLA EKSTRAKCIJOM SA SMEŠOM ORGANSKIH RASTVARAČA

(Naučni rad)

Yakov I. Korenman, Vladimir N. Fokin
Tehnološka akademija Voronježa, Voronjež, Rusija

U radu je prezentirana mogućnost i definisana procedura za određivanje fenola, krezola i ksilola u prirodnim, pijaćim i prečišćenim otpadnim vodama kao i u koncentratima morske vode. Procedura uključuje uzorkovanje, definisanje internog standarda, koncentrisanje primenom ekstrakcije sa smešom dva ekstrakciona agensa koji se baziraju na tributil fosfatu i organskom rastvaraču, i konačno, primenu gasno hromatografske analize dobijenih koncentrata. Ispitivana je ispravnost i reproduktivnost primene internog standarda (o-fluorofenol) kod analize vodenih rastvora. Predložena procedura je ispitana za određivanje fenola u zasićenom rastvoru morske vode i mineralne vode iz područja u Rusiji i Ukrajini u kojima su značajni izvori nafte i gasa što sigurno ima uticaja na povećanje koncentracije organskih jedinjenja u podzemnim, pijaćim i prečišćenim vodama kao i u morskoj vodi. U radu su primenjene dve metode ekstrakcije fenola iz vodenih rastvora korišćenjem organskih rastvarača i tributil fosfata. Izbor jedne od dve ispitivane metode ekstrakcije zavisi od sastava uzorka u pogledu fenola i koncentracije neorganskih soli u njemu: obe koriste tributil fosfat ali se po prvoj ekstrakcija fenola ostvaruje u kombinaciji sa cetil alkoholom, a drugoj sa dietil etrom. Po prvoj metodi analiziran je uzorak morskog koncentrata iz Crnog mora gde je koncentracija ispitivanih jedinjenja (fenola, krezola i ksilola) bila od 6 do 15 $\mu\text{g}/\text{dm}^3$, a uz dodatak internog standarda od 10 $\mu\text{g}/\text{dm}^3$ utvrđena njihova koncentracija u granicama od 15 do 25 $\mu\text{g}/\text{dm}^3$. Primenom druge metode analiziran je uzorak prečišćene vode iz koksno-hemijskog kombinata, gde je koncentracija fenola, krezola i ksilola bila od 17 do 34 $\mu\text{g}/\text{dm}^3$, a nakon dodatka iste količine internog standarda kao po prvoj metodi određena u količini od 20 do 52 $\mu\text{g}/\text{dm}^3$. Između ostalog u radu je ispitivana mogućnost poboljšanja osetljivosti detekcije i selektivnosti u pogledu identifikacije odgovarajućih fenolnih jedinjenja. Pokazalo se da uvođenje natrijum etilata u dobijen koncentrat iz ispitivanog uzorka smanjuje granicu detekcije ali povećava selektivnost u pogledu detekcije fenola. Korišćenjem internog standarda smanjuje se relativna greška merenja koncentracije fenola u vodi za 25%.

Key words: Phenole • Cresol • Xylenol • Determination in water • Environment problems • Extraction • Ključne reči: Fenol • Krezol • Ksilol • Određivanje u vodenim rastvorima • Životna sredina i standardi • Ekstrakcija •

