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Solid-phase extraction of fluorinated benzoic acids for the chromatographic analysis of oil tracer agents

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The extraction of fluorinated benzoic acids from aqueous solutions and water–oil emulsions with preconcentration on a sorbent with a surface layer of Zn, Cu, Co and Ni phthalocyanines is proposed.

Fluorobenzoic acids (FBAs) have become a major substance for oil tracer monitoring. They are characterized by poor biodegradability; conventional treatment techniques such as flocculation, chemical oxidation and membrane separation are not suitable. Nevertheless, adsorption is potentially powerful due to its imaginable opportunity to design the chemical composition of adsorbent surfaces.[1–3] During oil field monitoring, it is necessary to control fluorobenzene acid contents at a level of 5×10^{-3} mg dm^{-3}.[4] In many analytical procedures for determining low analyte concentrations, preconcentration should be carried out by solid-phase or liquid extraction.[5–7] Solid-phase extraction is widely used owing to its relative simplicity and convenience.[8,9]

We tested chelate-containing sorbents based on metal phthalocyanines for the solid-phase extraction of fluorinated benzoic acids from aqueous solutions to improve sample preparation procedures.

The chelate-containing sorbents were synthesized from phthalic anhydride, urea, silica gel (Silipor 075) with bonded metal chloride[10] and ammonium molybdate after heating to 180 °C at a rate of 2 K min^{-1} in a reactor with stirring and holding under isothermal conditions for 6 h (Table 1). IR spectroscopy (Spekord-75JR) and thermal analysis (Q-1500D derivatograph) were used to examine the synthesis products.

Preconcentration was carried out on a steel column (70 mm in length and 4 mm in diameter) packed with 0.7 g of a Silipor 075 sorbent with a chelate complex adsorption layer or an equivalent amount of 0.8 g of an Oasis HLB sorbent.

Based on the results of the polarographic analysis of washing solutions, we calculated the amounts of bonded metal atoms. We found that $(2.6–3.0)\times10^{21}$ metal atoms were supported as a result of chemical bonding; this value is consistent with published data[11] on four hydroxyl groups per square nanometer of the Silipor surface. The amounts of metal phthalocyanines formed after chemical bonding were also determined by thermal analysis. The high thermal stability of the immobilized complexes was noted; that is, destruction came into play at temperatures higher than 330 °C.

Table 1 Properties of Silipor 075 silica gel surfaces modified with metal chelates.

Metal chelate	Specific area/m^2 g^{-1}	Average pore volume/cm^3 g^{-1}	Average pore diameter/nm	Metal ion content (wt%)
ZnPhC	71.6±0.8	1.2±0.1	16.0±2.0	1.6±0.1
CuPhC	74.2±0.7	0.8±0.1	9.0±1.0	2.0±0.2
NiPhC	76.2±0.8	0.9±0.1	11.0±2.0	1.8±0.1
CoPhC	68.0±0.8	0.8±0.1	10.0±2.0	1.7±0.1

Sorption in the dynamic mode was performed by pumping 10^{-3} M aqueous solutions of fluorinated benzoic acids through a concentrating cartridge at a flow rate of 1 ml min^{-1} using a Gilson Minipuls-2 micropump. After the preconcentration, the cartridge was purged with a flow of air for 5 min to remove an excess of water. Desorption was performed with 3 ml of methanol, and the resulting solution was evaporated to dryness and dissolved in 50 µl of THF.

The liquid extraction of FBAs was carried out three times in a separatory funnel using 10 ml portions of ethyl acetate. The ethyl acetate extract was evaporated to dryness, and the residue was dissolved in 50 µl of THF.

Chromatographic analysis was performed on an YL9100 HPLC instrument with a Tracer Excel 120 ODSA 5 µm 25×0.46 column at a detection wavelength of 230 nm. The sample volume was 10 µl; the column temperature was 40 °C, and a 70:30 mixture of (water and 0.1% formic acid)–acetonitrile was used as an eluent.

The use of various metal phthalocyanines as modifying components changes the acid–base properties of the initial sorbent. To study the effect of a modifying additive on the acid–base properties of the sorbents, we plotted the kinetic curves of metal phthalocyanines (Figure 1). For example, NiPhC and ZnPhC exhibited basic and weakly acidic properties, respectively.

The acid–base nature of modified surfaces has the greatest effect on the sorption of fluorinated benzoic acids. An analysis of the values of $\Delta pH_{10} = pH_{10} - pH_0$ showed that Lewis acid sites were present on sorbent surfaces. The pH values for the samples of CuPhC varied from 7.8 to 8.2, which differ only slightly from the pH of the initial sorbent. At the same time, the supporting of Ni^{II} and Co^{II} phthalocyanines changed pH by more than 1.5 units.

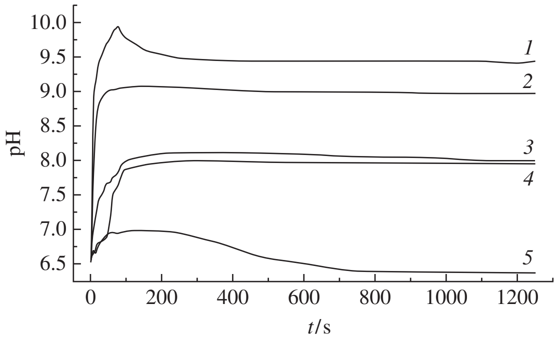

Figure 1 Kinetic curves of pH changes in the suspensions of (*1*) NiPhC, (*2*) CoPhC, (*3*) Silipor 075, (*4*) CuPhC and (*5*) ZnPhC.

Table 2 Results of the HLPC determination of FBAs.

Acid	Added/ μg dm^{-3}	Found/μg dm^{-3}			
		LE	Oasis HLB	ZnPhC	NiPhC
3-Fluorobenzoic	1.5	1.2±0.2	1.5±0.1	1.3±0.2	1.5±0.1
4-Fluorobenzoic	1.5	1.3±0.2	1.5±0.1	1.4±0.2	1.5±0.1
3-Fluorobenzoic	20.0	18.0±2.0	20.0±1.0	18.0±3.0	20.0±1.0
4-Fluorobenzoic	20.0	20.0±2.0	20.0±1.0	18.0±2.0	20.0±1.0
3-Fluorobenzoic	60.0	61.0±5.0	60.0±3.0	56.0±5.0	60.0±2.0
4-Fluorobenzoic	60.0	63.0±5.0	60.0±3.0	55.0±6.0	60.0±2.0

Table 3 FBA extraction ratio (%).

Acid	LPE	Oasis HLB	ZnPhC	NiPhC
3-Fluorobenzoic	74±2	81±3	79±3	84±4
4-Fluorobenzoic	69±2	77±2	76±3	81±4

The predominance of acid properties was observed on the surface modified with ZnPhC.

The sorption preconcentration was carried out with the use of chelate-containing sorbents, which were compared with an Oasis HLB standard polymeric sorbent, and liquid extraction, which is commonly used for sample preparation (Tables 2 and 3).

The chelate-containing sorbents promoted more effective sorption of fluorinated benzoic acids than Oasis HLB owing to the specific intermolecular interactions of electron-donor oxygen atoms in the functional groups of sorbates and metal acceptor ions in chelates. FBAs, which are prone to donor–acceptor interactions as electron pair donors, were more strongly retained on the chelate complexes than on the electron-donor surface of Oasis HLB because they formed associates with the electron-deficient moieties of metal complexes.

The sorbent with copper phthalocyanine is selective for FBAs, which is the result of the sorption of nucleophilic substances due to the selective complexation of electron-deficient chelate moieties in an adsorbed layer. The use of this sorbent for the preconcentration of fluorinated benzoic acids from aqueous solutions followed by HPLC determination is most efficient since it is resistant to the action of water vapor.

Zinc phthalocyanine sorbs FBAs less effectively than nickel phthalocyanine; this is due to the partial destruction of a bond with the complex surface on desorption with methanol. On the elution of a mixture through a sorbent containing zinc phthalocyanine, this sorbent undergoes degradation; the longer this process, the lower the reproducibility of the results of analysis.

The determination limit of FBAs in model solutions with the use of a standard preconcentration procedure is 3×10^{-5} mg dm^{-3}. An HPLC procedure with preconcentration makes it possible to determine fluorinated benzoic acids after solid-phase extraction on a sorbent with a surface layer of copper phthalocyanine with an extraction efficiency of 78%.

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References

1 C. Serres-Piole, H. Preudhomme, N. Moradi-Tehrani, C. Allani, H. Jullia and R. Lobinski, *J. Pet. Sci. Eng*., 2012, **98–99**, 22.
2 K. Müller and A. Seubert, *J. Chromatogr. A*, 2012, **1260**, 9.
3 D. V. Pryazhnikov, I. V. Kubrakova, M. S. Kiseleva, L. Yu. Martynov and I. Ya. Koshcheeva, *Mendeleev Commun*., 2014, **24**, 130.
4 Z. Kresinová, M. Muziká, J. Olsovská and T. Cajthaml, *Talanta*, 2011, **84**, 1141.
5 C. Creaser, L. Freitas dos Santos, D. Lamarca, A. New and J.-C. Wolff, *Anal. Chim. Acta*, 2002, **454**, 137.
6 I. Rykowska and W. Wasiak, *Mendeleev Commun.*, 2013, **23**, 88.
7 U. Sidelmann, S. H. Hansen, C. Gavaghan, A. W. Nicholls, H. A. J. Carless, J. C. Lindon, I. D. Wilson and J. K. Nicholson, *J. Chromatogr. B*, 1996, **685**, 113.
8 M. A. Gavrilenko and Yu. G. Slizhov, *Mendeleev Commun*., 2005, 261.
9 M. A. Gavrilenko and N. A. Gavrilenko, *Mendeleev Commun*., 2006, 117.
10 M. A. Gavrilenko, Zh. V. Malysheva and A. G. Kuzmina, *RF Patent, 2384363, C1*, 2010 (*Byull. Izobret*., no. 8, 20.03.2010).
11 S. M. Staroverov, A. A. Serdan and G. V. Lisichkin, *J. Chromatogr. A*, 1986, **364**, 377.

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