

Separation of Phenolic Compounds and Organic Anions Using ODS Column Coated with *Meso*-octamethylcalix[4]pyrrole and Water as Eluent

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Abstract: Octadecylsilanized silica (ODS) was coated with *meso*-octamethylcalix[4]pyrrole to obtain a novel calix[4]pyrrole containing stationary phase for HPLC. Compared to ODS, the new stationary phase showed a relatively large retention and an improved separation for phenolic compounds and organic anions, using pure water as mobile phase. The results can be ascribed to the interaction between analytes and calix[4]pyrrole.

Keywords: *Meso*-octamethylcalix[4]pyrrole, coated-column, phenolic compounds, anions, HPLC.

Molecular recognition chemistry associated with the calixpyrroles, an easy-to-make class of neutral macrocycles, has attracted intensive interest in recent years. Sessler and coworkers pioneerly reported that calixpyrroles are effective and selective receptors for anions and neutral substrates, and have been used for anions binding, chemical sensing^{1,2}, and new anions separation technologies^{3,4}. In the previous study⁵, we reported calix[4]pyrrole, as additives in capillary zone electrophoresis, can affect the separation of haloid anions. In this paper, we investigated ODS column coated with *meso*-octamethylcalix[4]pyrrole⁶ for separation of phenolic compounds and organic anions using pure water as mobile phase in HPLC.

Comparing to the retentions of the phenolic compounds (phloroglucinol **A**, hydroquinone **B**, *m*-aminophenol **C**, catechol **D**, resorcinol **E** and phenol **F**) on the unmodified column eluted only by water, longer retentions and better separation were obtained with the same eluent (**Table 1**). The increase of retentions of all analytes resulted from the intermolecular interactions between calix[4]pyrrole and phenolic compounds. Meanwhile, competitive interaction of calix[4]pyrrole coated on the column and mobile phase to analytes, involving the hydrophilic interaction with mobile phase and hydrogen bond interaction with calix[4]pyrrole, resulted in a different extent increase in retentions of analytes and an enhanced resolution. As illustrated in **Table 1**, the increase in retention (Δt_R) of phenol is maximum because of its weakest hydrophilicity and strongest interaction with calix[4]pyrrole among analytes studied. In especially for *m*-aminophenol and catechol, phloroglucinol and hydroquinone.

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Table 1 Chromatographic data of phenolic compounds on the modified columns

analytes	A		B		C		D		E		F	
	t _R /min	*Rs	t _R /min	Rs	t _R /min	Rs	t _R /min	Rs	t _R /min	Rs	t _R /min	Rs
column 1 (t _{R1})	3.85		4.21	0.82	5.90	1.57	5.90	0	7.63	1.24	16.82	6.6 2
column 2 (t _{R2})	5.69		6.63	1.56	9.66	3.83	10.75	1.2 2	14.02	3.12	30.91	9.8 9
*Δt _R /min	1.84		2.42		3.76		4.85		6.39		14.09	

Chromatographic conditions: column 1: C₁₈ (10 μm, 150 mm×4.6 mm i.d.), column 2: C₁₈ coated with *meso*-octamethylcalix[4]pyrrole (10 μm, 150 mm×4.6 mm i.d.); mobile phase: deionized water, flow rate: 0.5 mL/min; detector: set at 252 nm.

column 1 (unmodified), column 2 (modified)

* Δt_R=t_{R2}-t_{R1}, Rs: the resolution of adjacent peak.

In addition, organic anions (benzoate, salicylate, phthalate), which were almost co-eluted in void time on the unmodified column using water as eluent, could be separated successfully on the column modified with calix[4]pyrrole under the same condition. The order of retention of analytes was benzoate > salicylate > phthalate, which could be interpreted that the interaction between the analytes and calix[4]pyrrole resulted in the increase in retentions of all compounds, however, benzoate interacted with calix[4]pyrrole more strongly than the others did, owing to their ability of forming intramolecular hydrogen bond.

Furthermore, there is no significant change in the retentions of analytes after elution with 6000 mL of the eluent, which shows the coated-stationary phase is stable under this chromatographic condition.

The novel coated-stationary phase with calix[4]pyrrole showed certain potential for separation of phenolic compounds and organic anions in HPLC using only water as eluent, and the selective recognition ability of calix[4]pyrrole is promising to be exploited to manipulate the separation of an assortment of analytes like the other macrocyclic compounds such as crown ether, cyclodextrin and calixarene.

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