

## Liquid-Liquid Microextraction of Tetrahedral Oxoanions by Nano-baskets

B. Mokhtari\*, K. Pourabdollah†

Razi Chemistry Research Center (RCRC), Shahreza Branch, Islamic Azad University, Shahreza, Iran

(Received 18 May 2012; revised manuscript received 01 June; published online 17 August 2012)

This paper introduces a nano-based microextraction and examines its ability in preconcentration of di-negative tetrahedral oxoanions in the produced water. Nano-baskets of diacid *p-tert*-butylcalix[4]arene in the cone conformation were synthesized and used. The related parameters including ligand concentration, volume of water disperser, salt effect, and extraction time were optimized. The linear range, detection limit ( $S/N = 3$ ) and precision (RSD,  $n = 6$ ) were determined to be in the range of 1.0–280, 2.0–42.0  $\mu\text{gL}^{-1}$  and 2.6–11.0 %, respectively.

**Keywords:** Nano-baskets, Supramolecular Platform, Microextraction, Oxoanion, Calixarene

PACS number: 82.45.Cc

### 1. INTRODUCTION

Produced water is a by-product of the production of oil and gas hydrocarbons from underground reservoirs. In the first stages of processing of the production platforms, the water component is decanted from the oil, and has generally been discharged to the sea. The chemical composition of produced water varies over a wide range and depends mainly on attributes of the reservoir's geology. Hence, the produced water's composition may change slightly through the production lifetime of the reservoir. This would displace the water's composition away from equilibrium and change the dissolution of dissolved ions.

Liquid-phase microextraction (LPME) achieved extensive attention as a novel sample pretreatment technique owing to its advantages such as simple operation, low cost, rapidity, miniaturization, low consumption of sample volume and extraction solvent. Recently, dispersive liquid-phase microextraction (DLLME) [1] has been developed as a novel and successful mode of LPME, avoids the volatilization and loss of extractants, and provides possibility for the enhancement of sensitivity and simplification of the extraction procedure. Other examples of sample preparation by DLLME have been presented for trace determination of pesticides in soils [2], organophosphorus pesticides in water [3], nickel [4] and Cu(II) [5] in water, and chlorobenzenes in water [6].

Calixarenes have been subjected to extensive researches [7] and reviews [8] in development of extractants, transporters, stationary phases, electrode ionophores, optical sensors and medical researches over the past decades. The acid moieties participate in cooperative complexation of oxoanions and enhance transferring the anions from the aqueous phase into the organic phase by acting in a anion-exchange mode.

In this paper, a novel approach, entitled inclusion dispersive liquid phase microextraction, is introduced and is used for preconcentration and determination of oxoanions in the produced water. The quantitative merits of new method reveal the selective and sensitive

preconcentration and determination of di-negative tetrahedral oxoanions in the produced water.

### 2. EXPERIMENTAL

#### 2.1 Materials

All compounds were obtained in the highest-grade purity available and were stored at standard conditions to prevent decomposition or damage. Potassium chromate and potassium permanganate were supplied by Fluka (Buchs, Switzerland). Potassium vanadate and potassium arsenate were supplied by Aldrich (Steinheim, Germany). Doubly distilled water was used. Spiked water samples of above-mentioned oxoanions in 1-300  $\mu\text{g/L}$  were prepared. The samples of produced water were collected from the drainage stream in the Salman Platform located in Persian (Arabian) Gulf. The experiments carried out using derivative 4.

#### 2.2 Apparatus

The extractions and injections were performed by microsyringe (Agilent, CA, USA) bearing an angled cut needle tip (needle id: 0.11 mm and glass barrel id: 0.6 mm). Atomic absorption spectrometer of Shimadzu (model AA-670G) with deuterium lamp background correction and a graphite furnace atomizer (GFA-4B) was used. A reversed phase (RP)  $C_{18}$  column (4.6mm diameter, 100 mm length, 2  $\mu\text{m}$  macropore size, and 13 nm mesopore size) was obtained from Merck (Darmstadt, Germany). A RP- $C_{18}$  guard column was fitted upstream of the analytical column. The mobile phase was optimized to be 45:55, v/v methanol–water and was delivered by an HPLC pump (Waters LC-600). The UV detection wavelength was set at 254 nm and the flow rate of the mobile phase was adjusted to be 3 ml/min.

#### 2.3 Sample Preparation

5.0 mL standard solutions or real samples of produced water were placed into a 10-mL screw-cap glass centrifuge tube with conic bottom. Calixarene deriva-

\* [mokhtari@iaush.ac.ir](mailto:mokhtari@iaush.ac.ir)

† [pourabdollah@iaush.ac.ir](mailto:pourabdollah@iaush.ac.ir)

tive (0.1 g), dispersive solvents (0.8 mL) containing extraction solvents (10.0  $\mu$ L) were rapidly transferred into the above-mentioned centrifuge tube and was gently shaken. The selected dispersive solvents were include methanol, acetonitrile, acetone, while the selected extraction solvents were carbon tetrachloride, chlorobenzene, tetrachloroethylene and chloroform.

The volume of the settled phase was determined using a 20.0  $\mu$ L microsyringe, and was completely transferred to another tube. After evaporation of the water under a gentle nitrogen flow, the residue was used in the next step of instrumental analysis by atomic absorption spectrometer or reversed phase HPLC.

### 3. RESULTS AND DISCUSSION

The optimum conditions for dispersive liquid-liquid microextraction, chromatographic separation, identification and quantification of di-negative tetrahedral oxoanions ( $\text{CrO}_4^{2-}$ ,  $\text{MnO}_4^{2-}$ ,  $\text{VO}_4^{2-}$  and  $\text{AsO}_4^{2-}$ ) were assessed. The effects of other parameters (that influence the performance of microextraction) were investigated including the concentration and the volume of the extraction solvents as well as the dispersive solvents, the extraction and centrifugation times, pH, temperature, and ionic strength. They were investigated and optimized in order to achieve the higher enrichment factor and recovery of di-negative tetrahedral oxoanions from the samples of produced water.

#### 3.1 Type of dispersive solvent

Selection of dispersive solvent is limited to miscible solvents with both aqueous (sample solution) and organic (extraction solvent) phases. Therefore, acetonitrile, acetone and methanol were used for this purpose. A series of sample solutions was assessed by using 0.8 mL of each dispersive solvents containing carbon tetrachloride (10.0  $\mu$ L) as extraction solvent in the predefined optimum volume. Based upon the results, the extraction efficiencies increased as methanol > acetonitrile > acetone. However, owing to the better chromatographic behavior of acetonitrile with respect to methanol, acetonitrile was selected as the dispersive solvent.

#### 3.2 Volume of dispersive solvent

The volume of acetonitrile (as dispersive solvent) controls the settled volume of extraction solvent. To achieve a constant volume of the settled phase, the volume of extraction and dispersive solvents were changed simultaneously. Therefore, different volumes of acetonitrile in the range of 0.20 – 1.2 mL, containing the proper volumes of carbon tetra chloride, were assessed. The extractions were improved with the increase of dispersive solvent volume up to 0.8 mL. At low volumes of acetonitrile, the cloudy state was not formed well; hence, the recovery was low. At higher volumes of acetonitrile, the extraction efficiency was reduced since the solubility of amines in water increased. Therefore, 0.8 mL volume of acetonitrile was selected as the optimum value for further experiments.

#### 3.3 Type of extraction solvent

Selection of proper extraction solvents is the most important parameter in the optimization of the dispersive liquid-liquid microextraction. The extraction solvent should meet the below-mentioned requirements including: to be separated from analyte peaks in the chromatogram, to extract analytes well, to have larger density than sample solution (to be settled at the bottom of tube), and to form a cloudy solution of tiny droplets in the presence of dispersive solvents.

Owing to high density of halogenated hydrocarbons, they were selected as extraction phases and compared for extraction of di-negative tetrahedral oxoanions from water solution. The selected extraction phases were including carbon tetrachloride (1.59 g/mL), chloroform (1.48 g/mL), chlorobenzene (density 1.11 g/mL), and tetrachloroethylene (1.62 g/mL).

A series of sample solutions were studied by using 0.8 mL of acetonitrile (in the optimized value) containing 10  $\mu$ L volume of extraction solvents to achieve about 10  $\mu$ L volume of settled phase. To obtain the required volume of settled phase (considering the solubility of extracting solvent in aqueous phase in the presence of dispersive solvent), 20, 15, 40, and 10  $\mu$ L of carbon tetrachloride, chlorobenzene, chloroform and tetrachloroethylene were used, respectively.

The results showed that the extraction recoveries increased with the order of carbon tetrachloride > chlorobenzene > tetrachloroethylene > chloroform. Therefore, carbon tetrachloride was selected as the extraction solvent for the experiments.

#### 3.4 Volume of extraction solvent

By maximizing the extraction efficiency and minimizing the phase ratio, the method is improved and the preconcentration factor increased. It is obvious that by increasing the volume of the extraction solvent, the volume of settled phase increases. In this regard, volumes (1.0 mL) of acetonitrile containing different volumes of carbon tetra chloride, in the range of 10–20  $\mu$ L, were used. The results revealed that the peak area of the analytes was maximum using 10  $\mu$ L of carbon tetra chloride. Increasing the volume of extraction solvent led to a decrease in the magnitude of the peak area of the analytes. This is owing to increasing the settled volume and the consequent further decrease in the preconcentration factor. Therefore, 10  $\mu$ L of carbon tetra chloride was selected as the optimum value for the volume of extraction solvent in order to achieve the highest possible extraction efficiency and hence the highest preconcentration factor.

#### 3.5 Time of extraction

The extraction time means the time from the moment that the solution containing completely dispersed phase forms to the set interval. The longer the extraction time, the easier to reach the extraction balance. Hence, the best extraction performance was obtained. Therefore, extraction time puts an important role in the process of microextraction. In the rest of studies, a series of experiments were conducted to assess the best extraction time.

Base upon the results, the extraction time of 2 min was the best interval to make calixarene:oxoanions well extracted. In the initial 2 min, the peak areas gradually increased with the time change because the amount of settled phase increased with the time and only a very few phase were not separated from water phase due to the solubility. However, the peak areas would decrease when the extraction time exceeded more. It was maybe owing to the volatile lost of the analytes. Actually, 2 min was selected for use.

### 3.6 Selection of centrifugation time

Centrifugation is known as an important step to achieve the best separations in dispersive liquid-liquid microextraction. The interval of centrifugation seriously affected the separation extent of the mixture and hence, sequentially affected the extraction efficiency. Commonly, a higher rate of centrifugation leads to a shorter centrifugation time.

Hence, the maximum rate of 3000 rpm was used in the experiments. In order to reach the best enrichment, centrifugation time was considered in the range of 1–5 min. The results revealed that the peak areas gradually increased along with the prolongation of centrifugation time. When the centrifugation time was over 2 min, the peak areas almost had no further increase. Because of saving time, the interval of 2 min was selected as the optimal centrifugation time.

### 3.7 Effect of sample pH

Di-negative tetrahedral oxoanions are present as different states in the different pH environment. Hence, the sample enrichment is related directly to the present state of di-negative tetrahedral oxoanions in most cases. In this method, it is obvious that the pH of sample solutions has an important impact on the pre-concentration. Therefore, the effect of sample pH was optimized over the range of 3–9. It was found that the extraction performance all reached a better level at pH 4.5–5.5. When the sample pH was higher or lower than this interval, the peak areas decreased rapidly. In the low and high pH solutions, di-negative tetrahedral oxoanions form in other states and their extraction from water to organic phase was limited. Based on thorough consideration, pH = 5 was used for further tests.

### 3.8 Effect of temperature

The temperature is one of the key parameters to carry out the dispersed phases into the sample solution completely and the analytes have the best chance and more contact area to migrate into the organic phase and realize the constructed microextraction. Therefore, it was studied in detail in the range of 40–70°C. It was found that 70°C was reasonable for obtaining the best extraction. The lower recoveries at lower temperatures were owing to the poor performance of dispersing agent as well as the low diffused rate of the analytes at low temperatures. Those resulted in relatively few amount of analytes migrating into dispersed phase and led to the results of low recoveries. Furthermore, the slight

decrease of recoveries of di-negative tetrahedral oxoanions over 70°C may be owing to weakening of relevant complexes toward calixarene at high temperatures. Therefore, 70°C was finally adopted for further experiments.

### 3.9 Effect of Ionic strength

Salting in/out is often an impact factor in the microextraction and the enrichment performance. Commonly, the effect of ionic strength is surveyed by adding a proper salt. In the rest of experiments, the ionic strength was optimized in the range of 2–10 w/v % NaCl. The results revealed that the peak areas of analytes increased along with the increase of salt concentration. However, when the salt concentration continuously increased, the peak areas began to decrease. Hence, the salt was not added in the followed experiments.

### 3.10 Analytical performance

Using 5 mL of the standard solutions, the calibration curves were obtained and exhibited good linearity in a wide range of concentrations. For this aim, each standard sample was extracted by the recommended DLLME procedure at optimum conditions, and the calibration curves were obtained by plotting the peak area of each oxoanions:calixarene *vs.* its initial concentration in the aqueous phase. A typical chromatogram representing the di-negative tetrahedral oxoanions in the standard solutions is depicted in Figure 1. Table 1 presents the figures of merit of the proposed approach.

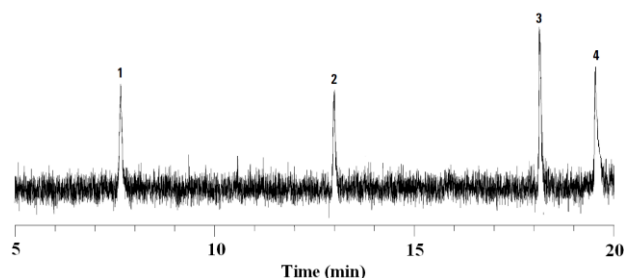


Fig. 1 – Chromatograms of standard solutions containing minimum detectable concentration of di-negative tetrahedral oxoanions. 1:  $\text{CrO}_4^{2-}$ , 2:  $\text{MnO}_4^{2-}$ , 3:  $\text{VO}_4^{2-}$  and 4:  $\text{AsO}_4^{2-}$

The preconcentration factor was calculated as eq. 1.

$$PF = \frac{C_{SET}}{C_0} \quad (1)$$

Where  $PF$ ,  $C_{SET}$  and  $C_0$  are the preconcentration factor, the final concentration of analyte in the settled phase and initial concentration of analyte in the aqueous sample, respectively.  $C_{SET}$  was calculated by direct injection of standard solution of above-mentioned di-negative tetrahedral oxoanions into column. The limits of detection (LODs) were calculated as the concentration equivalent to three times of the blank standard deviation divided by the slope of the calibration curve.

**Table 1** – Figures of merit for DLLME-HPLC determination of di-negative tetrahedral oxoanions.

Analyte	LOD ( $\mu\text{g/L}$ )	Dynamic Linear Range ( $\mu\text{g/L}$ )	Precision (%; n = 6)	Preconcentration Factor	Extraction Recovery (%)
$\text{CrO}_4^{2-}$	2.0	1.0–100.0	6.8	864	88.1
$\text{MnO}_4^{2-}$	42.0	30.0–280.0	11.0	798	92.2
$\text{VO}_4^{2-}$	8.0	4.0–90.0	2.6	830	86.8
$\text{AsO}_4^{2-}$	28.0	15.0–120.0	4.4	813	78.9

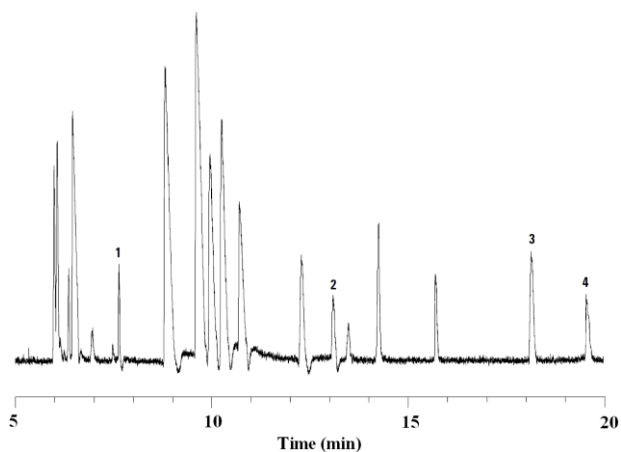
The figures of merits for above-mentioned di-negative tetrahedral oxoanions were determined. The linear ranges and related precisions were determined to be 1.0–100.0  $\mu\text{g/L}$  (n = 6, RSD = 6.8%), 30.0–280.0  $\mu\text{g/L}$  (n = 6, RSD = 11.0%), 4.0–90.0  $\mu\text{g/L}$  (n = 6, RSD = 2.6%) and 15.0–120.0  $\mu\text{g/L}$  (n = 6, RSD = 4.4%), respectively. The LODs were obtained 2.0, 42.0, 8.0 and 28.0  $\mu\text{g/L}$ , respectively. The extraction recovery was obtained by eq. 2.

$$R_E = \frac{C_{SET}}{C_0} \cdot \frac{V_{SET}}{V_{AQ}} \times 100 \quad (2)$$

Where,  $E_R\%$ ,  $V_{SET}$  and  $V_{AQ}$  are the extraction recovery, volumes of the settled phase and aqueous sample, respectively. In optimum conditions, the preconcentration factors and recovery values were obtained in the range of 798–864%. The relative standard deviations (RSDs%) at minimum detectable concentrations of above-mentioned di-negative tetrahedral oxoanions were found to be less than 6.7%.

### 3.11 Microextraction of Real Samples

The matrix effects on the extraction were also evaluated by studying the applicability of this approach to determine the concentration of di-negative tetrahedral oxoanions in the samples of produced water taken from one of the Iranian offshore fields. The real samples were extracted using DLLME method and analyzed by HPLC. The samples were spiked with standard solutions at different concentration levels to investigate the matrix effects. The chromatogram representing di-negative tetrahedral oxoanions in the real sample of produced water is presented in Figure 2.

**Fig. 2** – Chromatograms of extracted oxoanions:calixarene complexes from the produced water. 1:  $\text{CrO}_4^{2-}$ , 2:  $\text{MnO}_4^{2-}$ , 3:  $\text{VO}_4^{2-}$  and 4:  $\text{AsO}_4^{2-}$ .

## 4. CONCLUSIONS

This study introduced the approach entitled DLLME followed by HPLC for separation, preconcentration and determination of di-negative tetrahedral oxoanions in the produced water of crude oil wells. In comparison with the conventional methods of macro-extraction, in DLLME consumption of toxic organic solvents and sample is reduced. Compared to other microextraction techniques, DLLME is preferred owing to high sensitivity, ease of operation and high preconcentration factor. Low cost, simplicity of operation and high recovery are other advantages of DLLME. In the present study, DLLME showed short extraction time and high sensitivity for preconcentration of di-negative tetrahedral oxoanions in the samples of produced water.

## ACKNOWLEDGEMENTS

This work was supported by Islamic Azad University (Shahreza branch) and Iran Nanotechnology Initiative Council.

## REFERENCES

- H. Shirkhanloo, A. Rouhollahi, H. Zavvar Mousavi, *J. Chin. Chem. Soc.* **57**, 1 (2010)
- L. Fu, X. Liu, J. Hu, X. Zhao, H. Wang, C. Huang, X. Wang, *Chromatographia* **70**, 1697 (2009)
- M.A. Farajzadeh, S.E. Seyedi, M. Safi Shalamzari, M. Bamorowat, *J. Sep. Sci.* **32**, 3191 (2009)
- Q. Zhou, H. Bai, G. Xie, J. Xiao, *J. Chromatogr. A* **1188**, 148 (2008)
- H. Shirkhanloo, A. Rouhollahia, H. Zavvar Mousavi, *J. Chin. Chem. Soc.* **57**, 1 (2010)
- P. Hashemi, S.M. Hosseini, A. Kakanejadifard, G.H. Azimi, S. Zohrehvand, *J. Chin. Chem. Soc.* **57**, 111 (2010)
- B. Mokhtari, K. Pourabdollah, *Bull. Korean Chem. Soc.* **32**, 3855 (2011)
- B. Mokhtari, K. Pourabdollah, N. Dalali, *J. Coord. Chem.* **64**, 743 (2011)