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Separation and preconcentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in blood samples by inclusion emulsion membranes and its determination by gas chromatography

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ABSTRACT

The nano-mediated preconcentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin from blood samples was reported by inclusion-facilitated emulsion liquid membrane process. The novelty of this study was application of nano-baskets of calixarene and emulsion liquid membranes in selective and efficient preconcentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. For this aim, four derivatives of *p-tert*-calix[4]arene bearing different sulfonamide moieties were synthesized and their inclusion–extraction parameters were optimized including calixarenes' scaffold and concentration (**3**, 4 wt%), diluent type in membrane, phase and treat ratios (0.8 and 0.3), mixing speed (300 rpm), and initial solute concentrations (0.1–10 pg g^{-1}). The extraction efficiency was determined by dioxin's concentration using gas chromatography equipped with electron capture detector and the results revealed that in optimized operating conditions, the preconcentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was improved and the limit of detection decreased.

1. Introduction

Before industrial revolution, dioxins in low concentrations were formed in nature owing to geological processes and natural combustion. Today, concentrations of dioxins are found in all humans, with higher levels commonly found in persons living in more industrialized areas. The most toxic dioxin, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), became well known as a contaminant of agent orange, a herbicide used in the Vietnam War [1].

The United States environmental protection agency (US EPA) has reported the sources and releases of dioxins. Base upon the reports, Fig. 1 shows the concentration profile of polychlorinated dibenzo-dioxins (PCDD) in a dated sediment core. Dioxins are produced in small concentrations when organic material is burned in the presence of chlorine, whether the chlorine is present as chloride ions or as organochlorine compounds, so they are widely produced in many contexts. According to the most recent US EPA data, the main sources of dioxins are: combustion sources, metal smelting, process sources and refining, chemical manufacturing, natural sources and environmental reservoirs [2–4]. Fig. 2 depicts the total exposure to dioxins by food ingestion and other environmental exposure [5]. Dioxins enter the general population almost exclusively from ingestion of food, specifically through the consumption of fish, meat, and dairy products since dioxins are fat-soluble and readily climb the food chain [5,6]. Dioxins are also in typical cigarette smoke [7]. Owing to the halogen atoms in the structure of dioxins, the best method for determination of dioxins by gas chromatography is using electron capture detector (ECD) [8].

Dioxins are absorbed primarily through dietary intake of fat and accumulate in animals and humans. In humans, the highly chlorinated dioxins are stored in fatty tissues and are neither readily metabolized nor excreted. The estimated half-life for elimination of highly chlorinated dioxins (4–8 chlorine atoms) in humans is in the range of 5–13 years [9]. The accredited methods for sample collection, clean up and analysis of dioxins are presented in Table 1.

Emulsion liquid membrane (ELM) was invented by Li [10] in 1968 and is known as one of the most promising separation methods for trace extraction of metal contaminants [11–13] and hydrocarbons [14,15] owing to the high mass transfer rate, high selectively, low solvent inventory and low equipment cost. Frankenfeld et al. [16] reported that the ELM could be up to 40% cheaper than that of other solvent extraction methods. This process combines both extraction and stripping stage to perform a simultaneous purification and concentration. Fig. 3 represents the ELM setup, schematically.

In the ELM process, three steps are followed including an emulsification, extraction, and demulsification. In the first step, the emulsions are prepared by mixing the membrane and the internal phases as water-in-oil (W/O) droplets. In this step, water

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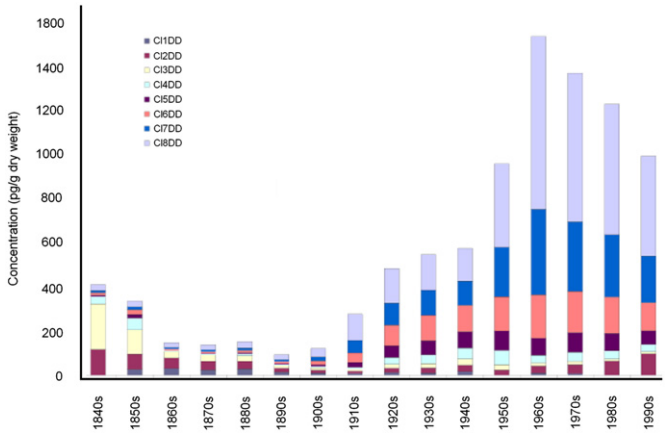

Fig. 1. The concentration profile of PCDD in a dated sediment core.

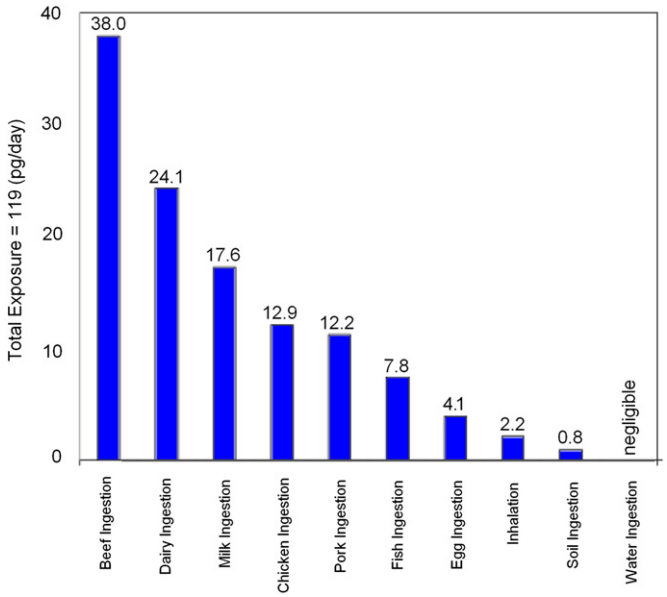

Fig. 2. Total exposure to dioxins by food ingestion and other environmental exposure.

is dispersed into the oil phase as fine globules. The second step followed by permeation of solutes from the feed phase, through the liquid membrane, to the receiving phase. In the third step, the emulsions are settled and demulsified to release the internal phase containing the concentrated solutes. This step is associated with the recovery of the membrane phase.

In this study, nano-baskets of calixarene [17–49] were used as bi-functional surfactant/carrier and the method of "one-at-a-time" was used to study and optimize the influences of different factors on ELM performance. In this approach, the experiments are designed to study the effect of a tuned variable at a time while keeping all other independent factors constant. By the method of one-at-a-time, the ELM process for selective extraction of dioxins was investigated. The process factors such as calixarene type and concentration (as surfactant and carrier), phase and treat ratios, mixing speed, and solute concentration in feed were investigated and optimized.

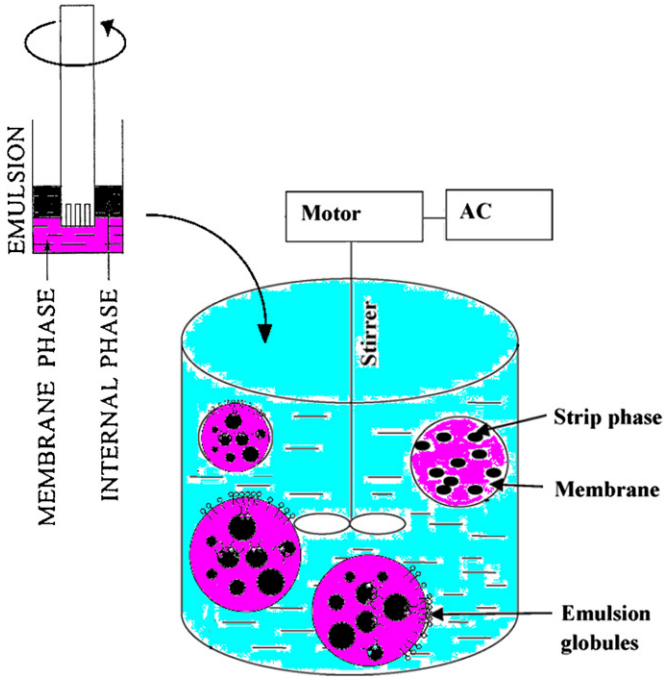

Fig. 3. Schematic illustration of ELM setup.

Table 1
Accredited methods for sample collection, clean up and analysis of dioxins.

Source	Method number	Method description
	EPA Method 1613b	Tetra- through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS
	EPA Method 1668	Chlorinated Biphenyl congeners in water, soil, sediment, and tissue by HRGC/HRMS
	EPA Method 8290A	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometry (HRGC/HRMS)
	EN 1948-1	Stationary source emissions. Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs. Sampling of PCDDs and PCDFs
	EN 1948-2	Stationary source emissions. Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs. Extraction and clean-up
	EN 1948-3	Stationary source emissions. Determination of the mass concentration of PCDDs/ PCDFs and dioxin-like PCBs. Identify cation and quantitation, sample collection and clean up general information
	JSA JIS K 0311	Method for determination of tetra- through octachlorodibenzo-p-dioxins, tetra- through octachlorodibenzofurans and dioxin-like polychlorinated biphenyls in stationary source emissions
	JSA JIS K 0312	Method for determination of tetra-through octachlorodibenzo-p-dioxins, tetra- through octachlorodibenzofurans and dioxin-like polychlorinated biphenyls in industrial water and waste water limits

2. Experimental

2.1. Chemicals and reagents

The liquid membrane consists of a diluent and a calixarene (as surfactant and extractant). The calixarenes were synthesized as described below. Carbon tetrachloride (CCl_4) for HPLC was gifted from Biosolve B.V. (Valkenswaard, The Netherlands). Doubly distilled water (DDW) with a specific resistivity of 18 MΩ cm, from a Milli-Q water purification system (Millipore, Bedford, MA) was used. Chlorobenzene (C_6H_5Cl), tetrachloroethylene (C_2Cl_4) and n-decane ($C_{10}H_{22}$) were purchased from Fluka and Sigma-Aldrich, respectively. Anhydrous sodium sulfate, $(NH_4)_2CO_3$, acetone and hexane were purchased from Merck (Darmstadt, Germany). TCDD was supplied by Analabs (New Haven, CT, USA) via Iran-hormone (Tehran, Iran).

The experiments carried out using four derivatives of *p-tert*-calix[4]arene di-[*N*-(phenyl)sulfonyl carboxamide], *p-tert*-calix[4] arene di-[*N*-(*para*-hydroxy phenyl)sulfonyl carboxamide], *p-tert*-calix[4]arene di-[*N*-(*para*-nitro phenyl)sulfonyl carboxamide], and *p-tert*-calix[4]arene di-[*N*-(*para*-methyl phenyl)sulfonyl carboxamide]. The synthesis procedures were given in the previously work [17]. The chemical structure of calixarene scaffolds **01–04** used in the experiments is presented in Fig. 4.

2.2. Preparation and characterization of ELMs

The specific amounts of calixarenes were solved in the specific amount of each diluent and thus membrane solutions were prepared. The selected membranes were carbon tetrachloride, chlorobenzene, tetrachloroethylene, and n-decane. $(NH_4)_2CO_3$ solution (25 mL, 0.5 mol L^{-1}) was used as a stripping solution. In 100-mL beaker, stripping solution (10, 15, 20, 25, 30 mL; variable) was added dropwise to the stirred membrane solution (25 mL; constant) and the two-phase system was stirred continuously for 30 min at a mixing speed of 1500 rpm by a variable speed mixer equipped with a turbine-type Teflon impeller. The mixture of the membrane and the stripping solution was emulsified.

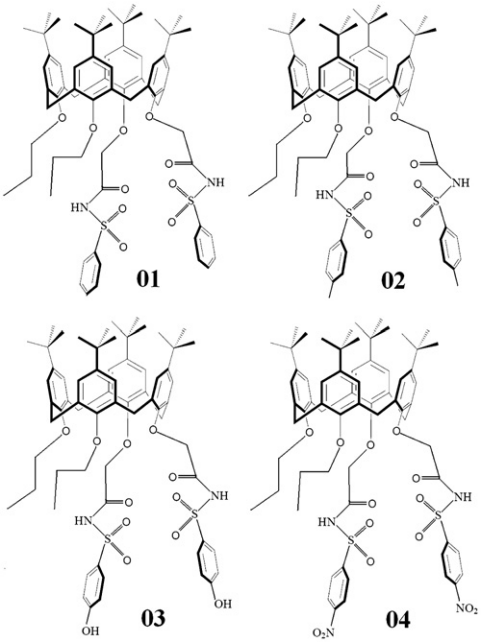

Fig. 4. Chemical structure of derivatives **01–04**.

The size, size distribution and stability of emulsions were characterized to examine the method. Size and size distribution of (w/o) droplets were obtained by optic microscopy (Mettler FP). The digital format of the captured micrographs was analyzed by means of an image analyzer software (Digital Micrograph TM, Gatan Inc.). Using a Neubauer camera, the volume of the analyzed samples was controlled. By size distribution changes at constant times, the stability of w/o droplets was monitored and evaluated by image analyses from photographs obtained during the diafiltration experiments.

2.3. Sample preparation

Plasma samples were accurately weighed to 5.0 g and mixed with 4.0 g Isolute (International Sorbent Technology Ltd., Hengoed, Mid Glamorgan, UK). Then, it was extracted by 10 mL acetone:hexane (1:4, v/v) under temperature (50 °C) for 10 min. The extract was concentrated to dryness after treatment with anhydrous sodium sulfate, and the lipid contents were determined gravimetrically. The lipid was emulsified in DDW and used as the feed solution. The analysis results for the determination of TCDD in the blood samples were determined and presented in Table 2.

2.4. Batch ELM experiment

In 500-mL beaker, the ELM prepared (35, 40, 45, 50, 55 mL) was added to feed solutions (4.5, 9.0, 13.5, and 18 mL) and were stirred by a variable speed mixer equipped with a turbine-type impeller at speed of 500 rpm for extraction time of 30 min. The speed of the mixer was regulated by a voltage regulator. To determine the important variables governing the permeation and separation of TCDD, calixarene type and concentration, the phase and the treat ratios, membrane's diluent type, mixing speed, and initial solute concentration in the feed phase were varied to observe their effects on the separation. The samples were taken from the stirred cell periodically during the course of the run. The feed phase of the samples was separated from the emulsions by filtration using a filter paper. The emulsion was demulsified by freezing. The concentration of TCDD was analyzed using gas chromatography.

2.5. Analytical instruments

Chromatographic analyses were performed on an Agilent 6890 series gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with an electron capture detector (ECD). In each chromatographic run, the samples (20 μL) were injected onto the GC equipped with a split/spiltless injector. The temperatures of injection port and detector were maintained at 280 °C. Nitrogen gas (purity 99.99%) at a flow rate of 35 mL min^{-1} was used as the make-up gas. Additionally, N_2 at a flow rate of 1.0 mL min^{-1} was used as the carrier gas. Chromatographic separation was conducted on a DB-17 (50% phenyl, 50% methylpolysiloxane),

Table 2
The experimental and optimum conditions for the extraction of TCDD.

1	Calixarene type	01	02	**03**[a]	04	–
2	Calixarene concentration (wt%)	1	3	**4**	5	10
3	Phase ratio	0.4	0.6	**0.8**	1.0	1.2
4	Treat ratio	0.1	0.2	**0.3**	0.4	–
5	Membrane type	**$C_{10}H_{22}$**	C_6H_5Cl	C_2Cl_4	CCl_4	–
7	Stirring rate (rpm)	100	200	**300**	400	500
8	Solute concentration in feed (pg g^{-1})	0.1	**1.0**	10	–	–

[a] The bold items were obtained and used as the optimum conditions.

capillary column (30 m × 0.32 mm i.d. × 0.25 μm, J & W Scientific Inc., Folsom, CA, USA). In each test, the oven temperature was programmed as follows: the column was maintained at 140 °C for 1.0 min, raised to 260 °C at 10 °C min^{-1} and maintained at 260 °C for 2.0 min. A 10 μL Hamilton (Reno, NV, USA) syringe was used to inject 2 μL of the samples to the GC.

The amount of injected sample into the analytical system was calculated based upon the minimum detectable level of lindane as a reference material (< 5.5 fg). According to the limit of detention (LOD = 4.7 pg/mL), the minimum amount of sample was determined to be 1.17 μL (5.5 fg/4.7 pg/mL = 1.17 μL).

3. Results and discussion

In several studies, it was shown that calixarenes are appropriate carriers for extraction of chlorinated aromatics in the organic phase. At the basic internal interface of the membrane phase, TCDD was stripped by the internal agent and transformed into a new species that cannot penetrate the membrane reversibly. The reversible interaction of calixarene and TCDD at both interfaces of membrane phase of ELM system is drawn as Eq. (1).

$$Dioxin + Calix \leftrightarrow Dioxin : Calix \quad (1)$$

where *Calix* shows the calixarene scaffold in the molecular form, and *Dioxin*:*Calix* presents the calixarene complex with TCDD.

Calixarenes and di-ionizable calixarenes in the acidic solutions are formed as molecular state, while are hydrolyzed in the natural or acidic solutions. The ionic form includes the cationic species, while the molecular form cannot capture them. After that, the new uncharged complex state diffuses throughout the organic membrane. In the side of natural or acidic feed phase, the calixarene complex dissociates as an uncharged molecular calixarene and diffuses into the organic membrane again. This transportation is repeated during the extraction until the chemical potentials in both sides be equal. Fig. 5 depicts the mechanism of facilitated transport of TCDD in ELMs process.

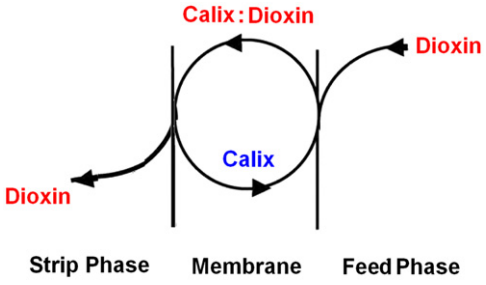

Fig. 5. Facilitated transport mechanism of TCDD in ELM.

The optimum conditions for the extraction of TCDD were determined by the method of one-at-a-time. Table 3 presented all conditions that were tested as well as the optimum conditions in bold. The methodology of optimizations is discussed in the following sections.

3.1. Effect of calixarene type

Type of calixarene is the most important factor that influences the selectivity of an inclusion–ELM system, and can often be used in related liquid–liquid extractions. The effect of calixarene type on the extraction efficiency of TCDD was studied in the ELM process and the results obtained are shown in Fig. 6. According to the results, although calixarene **03** gives higher rate of extraction in the first 10 min compared to calixarenes **01, 02, 04**, it gradually deteriorates with time. Examination of these results indicates that **03** was more favorable than **01, 02, 04** as emulsifier/carrier. Therefore, derivative **03** was selected among other scaffolds. The volume of emulsion (stripping solution and membrane) and feed phases were 45 (20 and 5) and 13.5 mL, respectively.

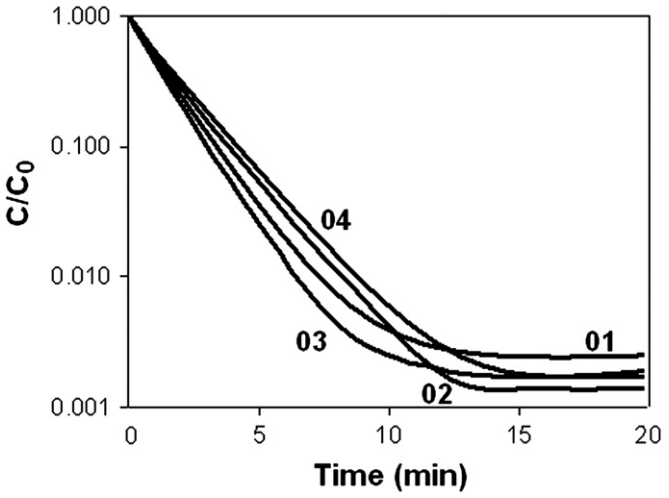

Fig. 6. Effect of calixarene type on the extraction efficiency of TCDD in the ELM process.

Table 3
Recovery information of extractions in each step of experiments.

Category	Conditions	Recovery (%)	RSD (n=5) (%)	Category	Conditions	Recovery (%)	RSD (n=5) (%)
Calixarene type	01	96	± 1.8	Treat ratio	0.1	80	± 7.5
	02	89	± 1.0		0.2	92	± 5.0
	03	99	± 0.7		**0.3**	98	± 4.5
	04	85	± 0.9		0.4	94	± 12.4
Calixarene concentration (wt%)	1	92	± 3.3	Stirring rate (r/min)	100	73	± 8.5
	3	95	± 4.6		200	92	± 2.2
	4	98	± 4.3		**300**	98	± 1.5
	5	94	± 7.5		400	93	± 4.9
	10	72	± 11.0		500	85	± 2.8
Phase ratio	0.4	60	± 8.7	Membrane type	**$C_{10}H_{22}$**	99	± 3.5
	0.6	90	± 4.4		C_6H_5Cl	35	± 7.3
	0.8	99	± 2.5		C_2Cl_4	35	± 10.5
	1.0	92	± 2.5		CCl_4	90	± 6.1

The bold items were obtained and used as the optimum conditions.

3.2. Effect of calixarene concentration

Extraction of TCDD was enhanced by increasing the calixarene concentration from 1% to 5%, while more increasing from 5% to 10% hardly affected the extraction performance. As depicted in Fig. 7, further increase of calixarene's concentration decreased the efficiency of extraction, owing to the access of molecular calixarene in membrane phase. Increasing of calixarene concentration up to 5% increased the stability of ELMs, which led to the decrease in the break-up rate. Hence, the extraction of solutes was increased. Further increase in the concentration of calixarene leads to the decrease in the rate of capturing and stripping reaction; and hence, decreasing the final recovery of ELM process. The reason is accumulation of TCDD in the complex form in the membrane media and decreasing the content of stripped calixarene and TCDD.

The excessive calixarenes tend to increase the interface's resistance and increase the viscosity of membrane. This increasing from 5% enhances the emulsion stability but the mass transfer is adversely decreased. Hence, there is an optimum in the concentration of calixarenes around 4%. The excess of calixarene's concentration leads to osmotic swelling and membrane breakdown. Hence, the concentration of 4% was accepted as the optimum concentration. The volume of emulsion (stripping solution and membrane) and feed phases were 45 mL (20 and 5) and 13.5 mL, respectively.

Another criterion is the financial aspects, in which the calixarenes are the most expensive agents among the other components of ELM process, and the lower concentrations are preferred.

3.3. Effect of phase ratio (strip phase volume/membrane volume)

The phase ratio is defined as the volume of stripping solution (10, 15, 20, 25, 30 mL; variable) to volume of membrane (25 mL; constant). Fig. 8 shows the effect of phase ratio on the extraction of TCDD, in which it increases with the raise of phase ratio up to 4:5. At this level, the maximum extractions were observed. By increasing the volume of the strip phase, the thickness of film in the emulsion was reduced owing to dispersion of strip phase in the membrane by mixing. This was favorable in extractions and results in an increase in the extraction of TCDD. Beyond 4:5, the further increase in the volume of strip phase caused the instability of globules.

3.4. Effect of treat ratio (feed volume/emulsion volume)

The treatment ratio, defined as the volume ratio of the emulsion phase to the feed phase, plays an important role in determining the efficiency of ELMs process. By increasing the amount of emulsion in the feed phase, the number of available droplets and interfacial surface area per unit volume of the feed solution increases. This leads to increasing the mass transfer of solutes from the feed to the membrane. Increasing of treat ratio slightly increased the size of emulsion droplets and caused inversely a reduction in interfacial surface area. The increment in the size of droplets was suppressed by the increment in the number of droplets. The emulsion volume was optimized before to be 45 mL (20 mL stripping solution plus 25 mL membrane phase). Optimization of treat-ratio was performed by fix volumes of emulsions and tuning the volume of feed-phase from 450 to 118 mL (450, 225, 150, 118 mL). The results are depicted in Fig. 9, in which the extraction efficiency was improved by increasing the treat ratio from 0.1 to 0.3. Beyond 0.3, the further increase in the ratio caused the instability of globules and less extraction efficiency.

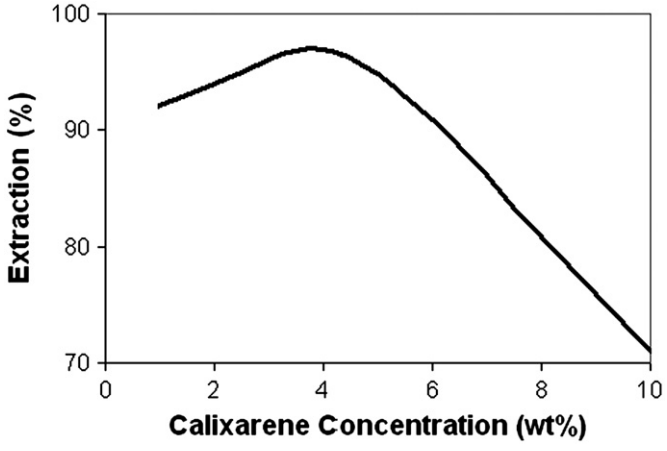

Fig. 7. Effect of calixarene concentration on the extraction efficiency of TCDD in the ELM process.

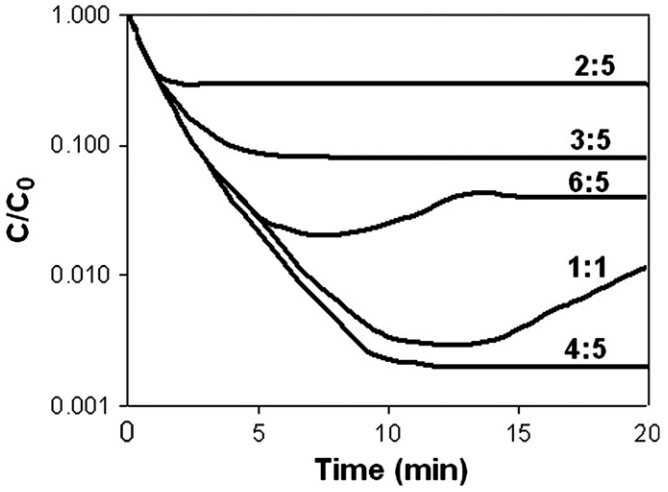

Fig. 8. Effect of phase ratio on the extraction efficiency of TCDD in the ELM process.

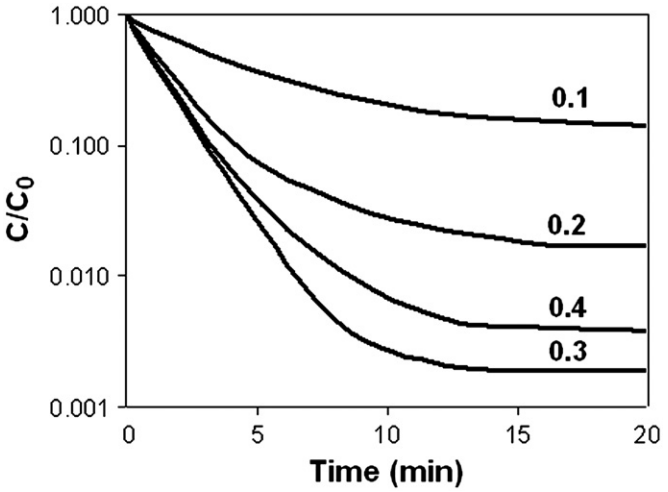

Fig. 9. Effect of treat ratio on the extraction efficiency of TCDD in the ELM process.

3.5. Effect of membrane type

One of the most crucial tasks in all types of ELM processes is the choice of the membrane phase. The interactions of membrane toward the carrier as well as its viscosity are two main

parameters that are controlled by choosing the membrane type. The membrane phase viscosity determines the transport rate of carrier or solutes and the residence or contact time of the emulsion with the feed phase. It is important to note that residence time is system specific and varies for each organic phase under the given conditions. In this work the effect of four organic phases on the extraction performance were investigated. Carbon tetrachloride, chlorobenzene, tetrachloroethylene, and n-decane were the choices of interest. The results are presented in Fig. 10. According to the results, n-decane was selected as the best diluent in the following experiments. The volume of emulsion (stripping solution and membrane) and feed phases were 45 (20 and 5) and 13.5 mL, respectively.

3.6. Effect of stirring rate

The speed of mixing is a key factor in the rate of mass transfer through ELMs. The effect of stirring speed in the basic solution was investigated in the range of 100–500 rpm in order to obtain optimal speed with effective extraction of TCDD in the ELM process. As depicted in Fig. 11, when the mixing speed was increased from 100 to 300 rpm, an increase in extraction rate was observed. Above 300 rpm the extraction rate again reduced. As a result, an increase in the mixing speed would increase the interfacial area, and this was true up to a certain level of mixing speed beyond which an increase in the speed was likely to break the emulsions thereby reducing overall enrichment and the efficiency of extraction. The impact on the wall of a contractor on the emulsion droplets or the shear induced breakage of fragile emulsion droplets near the tip of the impeller imposes upper limit on the speed of agitation. At the same time, swelling was also increased owing to transport of water from feed to strip phase. Some particles are broken owing to shear after reaching larger size. The swollen droplets breakdown on their own or induced by shear. Therefore, the extraction performance is a trade-off between two effects of swelling phenomena and mixing speed. The volume of emulsion (stripping solution and membrane) and feed phases were 45 (20 and 5) and 13.5 mL, respectively.

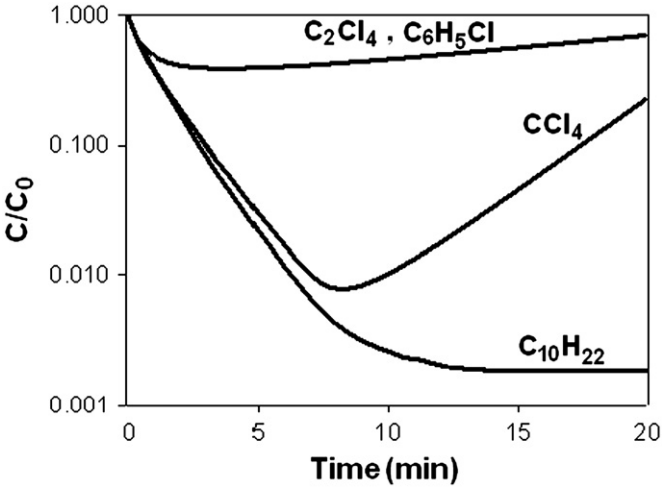

Fig. 10. Effect of diluent (membrane) type on the extraction efficiency of TCDD in the ELM process.

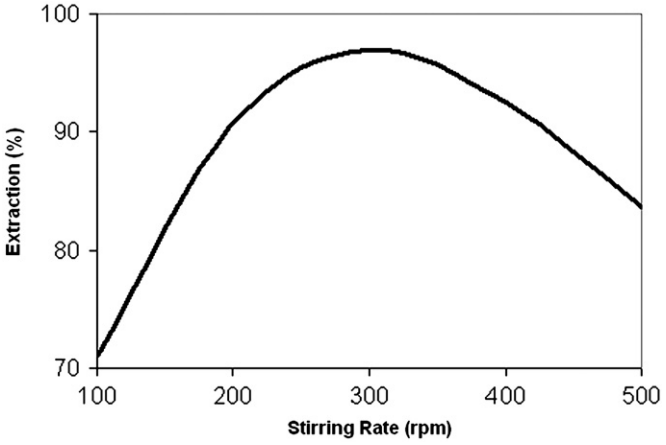

Fig. 11. Effect stirring rate on the extraction efficiency of TCDD in the ELM process.

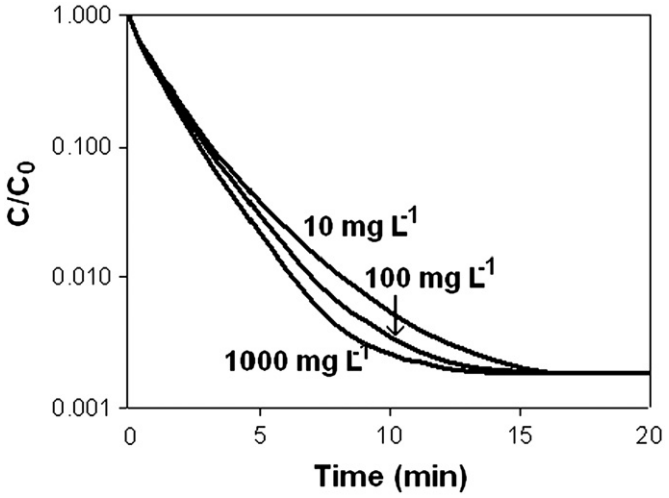

Fig. 12. Effect of solute concentration in the feed phase on the extraction efficiency of TCDD in the ELM process.

Table 4
Analysis results for the determination of TCDD in the blood samples.

Figure of merit	Value/range	Figure of merit	Value/range
Mean value	4.7 pg/mL	Limit of detection	1.0 pg/mL
Linear range	0.6–124.0 pg/mL	Limit of quantitation	3.1 pg/mL
RSD ($n=5$)	± 5.5	Recovery	98–98.5%

3.7. Effect of solute concentration in feed

The effect of initial concentration of solutes on the degree of extraction was studied. The results are presented in Fig. 12. Evidently, the concentration of TCDD in the feed solution was varied from 0.1 to 10 pg g^{-1}. Within 10 min, the concentration of solutes in the feed solution was reduced from 0.1 to 0.01 pg g^{-1}, from 1.0 to 0.06 pg g^{-1}, and from 10 to 0.35 pg g^{-1}, with the extraction efficiencies of 90%, 94%, and 96.5%, respectively. The volume of emulsion (stripping solution and membrane) and feed phases were 45 (20 and 5) and 13.5 mL, respectively. The recovery of TCDD in the blood samples is reported in each stage in Table 4.

4. Conclusion

TCDD in blood plasma was recovered by an ELM process using nano-baskets of calixarene. Hence, an ELM using derivatives of *p-tert*-calix[4]arene bearing different sulfonamide moieties (as both the extractant and the demulsifier) has been investigated to

extract and concentrate TCDD from the feed solutions. From this work the following conclusions can be drawn:

The optimum conditions of inclusion ELM process have been determined experimentally and tabulated in Table 3. The best stirring speed was determined to be 300 rpm and increasing from 300 to 500 rpm resulted in deterioration of emulsion stability and the efficiency of inclusion–extractions. The optimum conditions of both the phase and the treat ratios were determined to be 0.8 and 0.3, respectively. At the optimum conditions, the extraction of TCDD has been achieved with an efficiency of about 98.0–99.0% from the basic solution (ammonium carbonate, 0.4 mol L^{-1}) within almost 10–20 min.

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