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Evaluation of a novel PVC-based efficient potentiometric sensor containing a tripodal diglycolamide (TREN-DGA) ionophore for europium(III) estimation

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HIGHLIGHTS

- TREN-DGA ligand containing PVC membranes were developed
- The polymeric membranes were characterized using conventional techniques
- The polymeric membranes were used for Eu³⁺ ion sensing from dilute acid feeds
- The stability and interference studies were highly encouraging
- The TREN-DGA based sensor was found to be much superior to the TODGA based sensor

Abstract

Polymeric membrane-based electrodes containing a multiple diglycolamide (DGA), such as a N-pivot diglycolamide (diglycolamide-TREN (DGA-TREN) and a C-pivot diglycolamide (tripodal diglycolamide) (T-DGA) as ionophore, and polyvinyl chloride (PVC) as the base polymer were fabricated. These membranes were tested for the potentiometric determination of europium ions in acidic feed solutions. The membrane with a composition of 81.5% PVC and

18.5% DGA-TREN showed a wide dynamic range (3.2×10^{-7} to 1.0×10^{-2} M) with a slope of 17.2 ± 0.4 mV per decade for europium ion. The presence of sodium tetraphenyl borate (NaTPB) as ionic additive in the DGA-TREN containing membrane marginally improved the dynamic range in the detection of europium ion. On the other hand, the membrane with a composition of 77.3% PVC and 22.7% T-DGA does not show any systematic potential response against variation of the concentration of europium ions in the external solution containing 1 M HNO_3 . The physical characterization of these membranes was carried out using techniques such as thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) in order to understand the effect of the different constituents of the membrane on the potential response for europium ions. AFM measurements revealed that the morphology of the membrane remained intact even in prolonged use of the membrane. The interference effect of Ca^{2+} , Mg^{2+} , Cu^{2+} , Fe^{3+} , Bi^{3+} , Zn^{2+} , Cd^{2+} and UO_2^{2+} on the potential response was investigated. The response time of the proposed sensor was found to be less than five s. The lifetime of the sensor electrode was found to be three months under proper storing conditions. The membrane sensor was employed in the determination of Eu^{3+} in synthetic water samples.

Keywords: *polymeric membrane, ion selective electrode, europium, DGA-TREN*

1. Introduction

Europium is a rare earth element widely used as a doping agent in phosphor to produce a bright red colour in colour television, computer monitors, in street light to produce more natural type of light in combination with a mercury vapour lamp, and also used in compact fluorescent bulbs [1,2]. Europium compounds are also used in different glass types, ceramics, metallurgy,

electronics, agriculture, and natural sciences [3]. Europium can form stable compounds in its +2 and +3 oxidation states, unlike most of the other rare earth metal ions, which form stable compounds in the +3 oxidation state [4]. Due to the high thermal neutron absorption cross section of Eu, it is used in thermal reactors to control the excess reactivity [5]. The presence of europium in nuclear fuel is undesirable for thermal reactor fuel [6]. Therefore, the development of an efficient analytical method, which will be able to determine europium in trace level with a short analysis time and a minimum sample preparation step, is a challenging task for an analytical chemist. There are different methods to determine europium at low level, such as spectrophotometry [7], inductively couple plasma optical emission spectrometry (ICP-OES) [8], inductively couple plasma mass spectrometry (ICP-MS) [9,10], isotope dilution mass spectrometry (IDMS) [11], X-ray fluorescence spectrometry (XRF) [12], fast fourier transform continuous cyclic voltammetry (FFT-CCV) [13], and potentiometric methods [14-17]. These methods generally involve expensive instruments, a complicated sample preparation step and are time consuming. On the other hand, a potentiometric method is simple to operate, involves a low cost instrument, has a fast response, and offers the required reproducibility. There are numerous examples of potentiometric sensors based on neutral ionophores [3, 16-19]. Neutral ionophore-based membranes are generally composed of a polymer, plasticizer, and an ionic additive along with an ionophore [20-21]. Polyvinyl chloride (PVC) is a popular choice as polymer in the construction of membranes for ion selective electrodes (ISEs) [22]. A good polymer for ISEs should fulfill certain requirements such as, it should be mechanically robust, elastic (low glass transition temperature, T_g), stable within a reasonable temperature range (0-50 °C), must be chemically inert, not soluble in water, and can be used in both acidic and basic solutions [22]. The plasticizer provides elasticity to the polymeric membrane (decrease in T_g) and hence provides mobility to the ion and ionophore in the membrane. The plasticizer also acts as a solvent for the ionophore in the membrane. The ionophore binds the metal ion of interest, whereas the lipophilic additives decrease the membrane resistance and suppress the uptake of the counter ion [20, 21]. In this investigation we have used PVC, TREN-DGA or T-DGA and NaTPB as polymer, ionophore, and anionic additive, respectively, in the construction of the polymeric membrane. As reported previously [23], the best membrane composition was found to be without any added plasticizer content, since part of the ionophore acts as plasticizer.

Therefore, in this study we have not added any plasticizer in the construction of the polymeric membrane.

Generally, three to four N,N,N',N'-tetraoctyl diglycolamide (TODGA) molecules are involved to form a reverse micelle in dilute nitric acid solutions, in the core of which trivalent lanthanide / actinide ions are extracted preferentially in a size selective manner [24,25]. Therefore, it would be expected that preorganization of 3 to 4 TODGA molecules on a molecular platform would enhance the extraction of lanthanide or/and actinide ions from nitric acid solution. We found that preorganized structured molecules, such as calix[4]arene DGA derivatives and tripodal DGA (T-DGA) [26,27] (Fig. 1), showed promising extraction of actinide and lanthanide ions from acidic feed solutions. Recently, a new tripodal N-pivot DGA, TREN-DGA (Fig. 2), exhibited promising extraction and selectivity of Eu^{3+} over UO_2^{2+} , Cs^+ and Sr^{2+} in acidic feed solution [28]. In our earlier investigation [23] we have reported the preparation and analytical application of a PVC-based potentiometric sensor for Eu^{3+} containing TODGA as ionophore. It showed that an optimum composition of the membrane corresponding to 30.3% TODGA, 9.1% NaTPB, and 60.6% PVC gives a wide dynamic range (1.5×10^{-6} M to 1.2×10^{-2} M) with a slope of 17.3 ± 0.1 mV per decade, and 1.2×10^{-6} M as the detection limit for Eu^{3+} . The sensor was found to work even in dilute nitric acid solution (1 M HNO_3) with 1 M HNO_3 as inner filling solution, and with a marginally narrower dynamic range when compared with 0.1 M $\text{Eu}(\text{NO}_3)_3$ kept as inner filling solution. In view of the excellent extraction and selectivity for Eu^{3+} with TREN-DGA (vide infra), it was decided to study the applicability of this ligand as an ionophore in the construction of a potentiometric sensor for Eu^{3+} from acidic feed solutions. In this work, we have investigated the performance of a PVC-based potentiometric sensor containing TREN-DGA as ionophore by determining its dynamic range, detection limit, response time and analytical lifetime. An extensive study was also carried out for the physical characterization of the pristine membrane and used membrane by using techniques such as thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and atomic force microscopy (AFM). The possibility of another tripodal ligand (T-DGA) as ionophore in sensing Eu^{3+} potentiometrically was also investigated in dilute nitric acid solution along with a similar characterization of the membrane as mentioned. There are several reports of using TODGA as ionophore for the potentiometric determination of rare earth ions in a multi sensor approach [29,30]. However, to the best of our knowledge, this is the first report in which a

multiple-DGA-based ligand is explored as an ionophore in the construction of a potentiometric sensor for Eu^{3+} .

2. Experimental

2.1. Reagents

TREN-DGA and T-DGA were synthesized and characterized as reported previously [28, 31]. Polyvinyl chloride (PVC) (Sigma-Aldrich), sodium tetraphenyl borate (NaTPB) (Sigma-Aldrich), and tetrahydrofuran (Sigma-Aldrich) were used as received. Dilute solutions of nitric acid were prepared using suprapur nitric acid (Merck). Europium oxide was procured from Sigma-Aldrich and the required quantity of the reagent was dissolved in concentrated suprapur nitric acid. Subsequently, it was brought to 1 M nitric acid to prepare a stock solution of 100 mg L^{-1} . All the other reagents were of analytical reagent grade. The different kinds of membranes that were prepared are listed in Table 1.

2.2 Membrane preparation

Polymeric membranes were prepared following a previously reported method [32]. 2% (w/v) solutions of PVC in THF and 1.0% (w/v) solutions of NaTPB in THF were prepared. The membrane was prepared by mixing the required quantity solutions of PVC, TREN-DGA / T-DGA, and NaTPB in THF in a 25 mL beaker and homogenized by ultrasonication (for about 5 minutes). The resulting solution was poured into a flat bottom Petri dish (50 mm diameter) and covered loosely with a watch glass to allow the solvent to evaporate slowly at room temperature. After 2 days of evaporation, the membrane was carefully peeled off using a tweezer after adding a few drops of water on top of the film to help loosen it from the glass surface of the Petri dish. The membrane looks to be transparent and mechanically strong. The thickness of the membrane was measured using a Mututoya digital micrometer and it was found to be uniform (0.0084 ± 0.0009 cm). The membrane composition was fixed in correspondence with our earlier investigation with a TODGA-based membrane sensor [23] and keeping in mind that one TREN-

DGA / T-DGA molecule contains three DGA units.

2.3 Assembling of the sensor and instrumentation

The potentiometric sensor electrode was fabricated using the membranes as listed in Table 1. A small piece of the membrane was cut and attached at the base of a glass tube. The tube after attaching the sensor membrane was filled with 1 M HNO_3 as the inner filling solution up to $3/4^{\text{th}}$ of the capacity of the tube. A silver/silver chloride electrode was used as an internal reference electrode. A saturated calomel electrode was used as external reference electrode in conjunction with the sensor electrode to measure the potential. The test solution was composed of 1 M HNO_3 with a varying concentration of europium ions. The EMF generated from the sensor out of the test solution has the following cell assembly:

$\text{Ag-AgCl (3 M KCl) / 1 M HNO}_3\text{/Membrane/Test solution/Hg-Hg}_2\text{Cl}_2, \text{KCl (sat.)}$

A potentiostat (model CHI 1120) was used for measuring the potential at 25 °C. A thermal analyzer from Setaram Setsys Evolution was used to study the weight loss of the membrane as a function of temperature. FT-IR of the pristine and the used membrane was carried out using the Tensor II FTIR system from Bruker. AFM measurements were carried out using a flex AFM instrument from Nanosurf.

The potentiometric measurements were carried out by taking 20 mL of 1 M HNO_3 as the test solution in a glass electrochemical cell, in which the potentiometric sensor and the reference electrode were dipped and connected to the respective terminal of the instruments. The solution was stirred at a fixed speed of 100 rpm using a precisely controlled magnetic stirrer. The electrode potential response was recorded with subsequent addition of Eu^{3+} in the solution.

3. Results and discussion

3.1 Characterisation of the membrane

3.1.1 FTIR measurements

The characteristic peaks of the FTIR measurements are marked in the spectra as shown in Fig. 3. The band in the range of $600\text{-}650\text{ cm}^{-1}$ corresponds to the C-Cl gauche bond in PVC, which is present in all the membranes. A broad band at $3400\text{-}3500\text{ cm}^{-1}$ is due to the O-H

hydroxyl bond and can be attributed to water adsorbed by PVC. The peak at 1645 cm^{-1} corresponds to C=O stretching in TREN-DGA for both the membranes S. No. 1 and 2 (Table 1). The peak at 1648 cm^{-1} corresponds to C=O stretching in T-DGA in the membrane S. No. 3 (Table 1), whereas the peak at 1653 cm^{-1} is the C=O stretching frequency of TODGA in the membrane S. No. 4 (Table 1). The C=O stretching frequency of the TODGA-containing membrane is comparatively at higher frequency than that of the TREN-DGA-containing membranes, which indicates that the C=O moiety remained relatively free in the TREN-DGA-containing membranes. The C=O stretching frequency does not modify upon the addition of NaTPB in the TREN-DGA-containing membrane.

3.1.2 Thermal analysis results

Results of the thermal analysis of the PVC/TREN-DGA and PVC/TREN-DGA-NaTPB membranes are shown in Fig. 4. The PVC/TREN-DGA- showed the starting of weight loss at around $200\text{ }^{\circ}\text{C}$, whereas the PVC/TREN-DGA-NaTPB-containing membrane exhibited a pre decomposition of the membrane starting at $130\text{ }^{\circ}\text{C}$, while at $200\text{ }^{\circ}\text{C}$ it resembles the weight loss pattern of the PVC/TREN-DGA membrane. The early decomposition in the case of the PVC/TREN-DGA-NaTPB membrane is due to the incorporation of a phenyl group into the matrix, which decomposes prior to the other hydrocarbons present in the film. The presence of TREN-DGA decreases the decomposition temperature of the PVC membrane, which was also observed in our earlier investigation with a TODGA-based membrane sensor [23]. This suggests that part of the TREN-DGA may act as plasticizer as like TODGA in the PVC-based membrane [23]. A similar observation with other plasticizers has been reported in the literature [33,34]. The general weight loss pattern is similar to the thermal decomposition of the PVC membrane, however, the temperature range in the present case is narrower in the ranges of 200 to $300\text{ }^{\circ}\text{C}$ and 340 to $520\text{ }^{\circ}\text{C}$ compared to the reported ranges of 200 to $350\text{ }^{\circ}\text{C}$ and 450 to $600\text{ }^{\circ}\text{C}$. Other than the pre-decomposition step at lower temperature, addition of NaTPB does not alter the thermal decomposition pattern of the film significantly. Overall, it can be stated that the thermal stability of the membranes is quite reasonable to study them at higher temperatures.

3.1.3 AFM investigation of the membrane

AFM investigations of all the membranes were carried out using the freshly prepared membrane and after its use as ion selective electrode. The micrograph of the PVC/TREN-DGA

membrane is shown in Fig. 5. Before use, the membrane is characterized with spherical shaped particles agglomerated with each other to form spherical shaped assemblies with a diameter of 1.2 μm . No significant change in the overall shape and dimension of the assembly was observed when the membrane was used as ion selective electrode. The absence of any swelling in the membrane indicates that there was no degradation upon its use as a sensor and consequently the membrane can be used repetitively. The morphology of the PVC/T-DGA membrane was different from that of the PVC/TREN-DGA where elongated grains were observed for the unused membrane. The AFM micrograph of the PVC/T-DGA membrane showed a spherical agglomeration of the nanoparticles and the increase in the number of such agglomerations might be related to the uptake of europium ions. AFM experiments were also carried out using the TREN-DGA-NaTPB membrane and the results at different resolutions and before and after use are shown in Fig. 6A, B, C and D. The observed particles are spherical in shape with an average particle size of 40 nm for the dry membrane. The shape of the particles remained the same after the membrane was used as sensor, however, their size was modified to 50 nm. Interestingly, no agglomeration of the particles was observed like in the case of the membrane without NaTPB.

3.2 Potentiometric investigation and response of the sensor

It is well known that the performance of an ion selective sensor is largely influenced by the properties and the concentration of the components in the membrane. In our earlier report on the TODGA-based sensor [23], we have investigated in detail the effect of varying compositions of the membrane on the performance characteristics of the sensor and the best membrane contained 30.3% TODGA, 9.1% NaTPB, and 60.6% PVC. The presence of 30.3% TODGA in the membrane indicates that it is present at its critical micelle concentration (CMC), which is 0.1 M TODGA. The present membrane was made assuming that one TREN-DGA unit is equivalent to three units of TODGA and accordingly the concentration of TREN-DGA/T-DGA was taken in the preparation of the membranes (Table 1).

The sensor was prepared as described in the experimental section using the optimized membrane composition. The sensor was used for the determination of Eu^{3+} in Eu^{3+} -containing solutions of varying concentration. A calibration plot was constructed, which is shown in Fig. 7A. The measured potential was shifting towards more negative direction upon the addition of more and more Eu^{3+} in the test solution in the case of the PVC/TREN-DGA membrane. The calibration plot was found to be linear in the concentration range from 3.2×10^{-7} M to 1.0×10^{-2}

M Eu^{3+} . Fig. 7B clearly shows that the presence of borate as electrophilic additive improved the linear dynamic range of the calibration plot.

The PVC/T-DGA membrane was tested with varying Eu^{3+} concentrations and the results are shown in Fig. 7C. In this case no linear correlation was observed. The PVC/T-DGA membrane is reported to have very good transport properties for Eu^{3+} ions compared to the PVC/TREN-DGA membrane [28]. However, this is not reflected in the calibration plot of the potentiometric sensor PVC/T-DGA membrane. Nghiem et al. [35] suggested that a polymeric membrane can become a suitable potentiometric sensor for a given metal ion, provided it should show a very fast interfacial reaction at the membrane-aqueous interface and very slow transport of a metal ion through the polymeric membrane at a reasonable time scale as required for an ion selective electrode. Thus, the T-DGA containing membrane is an inferior membrane for the potentiometric sensing of Eu^{3+} ions from acidic feed solutions, but a rather superior membrane for the extraction of Eu^{3+} ions [27]. The chemical structures of the two ligands, T-DGA (Fig. 1) and TREN-DGA (Fig. 2), slightly differ, the former one having extra oxygen atoms, while the latter one has an additional nitrogen atom. The molecular arrangement of the TREN-DGA and the additional interaction of the central nitrogen atom with Eu^{3+} may be responsible for the favorable interaction between the membrane and Eu^{3+} ions for its use as potentiometric sensor. The detection limit using the NaTPB incorporated PVC/TREN-DGA membrane was calculated to be 100 nM. Three membrane sensors were fabricated and the analytical response of all the sensors were investigated, the slope of the calibration plot was obtained as 17.2, 16.8 and 17.5 mV per decade of europium ion. The mean and sample standard deviation of three measurements were obtained as 17.2 and 0.4 mV per decade of europium ion.

For the sake of comparison, the analytical performance of the TODGA-containing membrane as published by us was compared with the present membrane; the calibration plot of the TODGA-containing membrane has been placed as Fig. 7D [23]. Comparison shows that the presently developed membrane based on PVC/TREN-DGA is superior to the TODGA-containing membrane.

3.3 Response time and lifetime of the sensor

The practical response time of the sensor was investigated by keeping the sensor inside the test solution and 7.4×10^{-6} M Eu^{3+} solution was added to it under stirring conditions. It was

observed that with <5 s the sensor reached its characteristic potential, which remained stable for a measuring time of about 1800 s. This fast response time and the stability of the potential is ideal for its application for online sensing of Eu^{3+} even under stirring conditions and for batch sensing processes. The results of the stability are shown in Fig. S1 of the supporting information, as seen from the calibration plot recorded on storing the membrane electrode in 1 M HNO_3 solution, the calibration plot remained unaltered after 30 days. The slope of the calibration plot was decreased by 7% when it was kept in air for 30 days. Based on the single point measurements it was observed that the sensor remained stable for 3 months when stored in a blank supporting electrolyte medium of a 1 M HNO_3 solution.

3.4. Interference study

The possibility of interference of some of the commonly occurring metal ions in the determination of Eu^{3+} with the developed PVC/TREN-DGA sensor was investigated. The results due to the interference of Ca^{2+} , Mg^{2+} , and Cu^{2+} are shown in Fig. 8. The concentration of the interfering ions was varied by keeping the Eu^{3+} concentration fixed at 0.2 mM. In case of Ca^{2+} the measured potential remained constant up to the addition of 1.5 mM Ca^{2+} in the test solution, however, upon further addition of Ca^{2+} the potential changed significantly [Fig. 8A]. Similarly, the present sensor tolerated the presence of Mg^{2+} ions in the test solution up to a concentration of 3.3 mM, after which the potential decreased drastically upon the further addition of Mg^{2+} ions [Fig. 8B]. As seen in Fig. 8C the potential corresponding to Eu^{3+} tolerated up to a Cu^{2+} concentration of 1 mM. The selectivity coefficient of the present measurements we determined using the matched potential method (MPM) as recommended by IUPAC in 1995 [36] and this method has been adopted in our previous publication [23], the results of the selectivity coefficient measured for some of the commonly occurring interfering ions are placed in Table 2. As can be seen from Table 2, the selectivity coefficients of the sensor due to the commonly occurring metal like, Ca^{2+} , Mg^{2+} , Cu^{2+} , Ba^{2+} and Fe^{2+} , Pb^{2+} , Cd^{2+} are very high, and these metal ions do not interfere in Eu^{3+} determination even at 250 times higher concentration to the Eu^{3+} . The sensor is tolerant up to 20 times higher concentration of trivalent and tetravalent metal ions like Ce^{3+} and Zr^{4+} investigated. The selectivity coefficient of the presently developed membrane has been improved compared to the TODGA containing membrane reported in our previous publication. Therefore, the tolerance study indicated that the tolerance of the commonly

occurring metal ions on Eu^{3+} determination using this membrane-based sensor is reasonably good.

3.6 Analytical performance of the membrane sensor

The analytical performance of the fabricated PVC/TREN-DGA sensor was tested through the spike recovery method. A recovery sample was prepared by adding a known concentration of Eu^{3+} in deionized water, whereupon the concentration of Eu^{3+} ions in the solution was determined by dipping the membrane sensor inside the sample solution. The analysis results for the spike recovery test are shown in Table 3. ICP-OES was also used to determine Eu^{3+} ions in the spike recovery samples. The blank solution was having a Eu^{3+} concentration below the detection limit of the present membrane sensor. The percentage recovery of the samples was within 5% variation relative to the concentration of a standard added to the recovery sample and similar results were obtained using the fabricated PVC/TREN-DGA sensor and ICP-OES techniques.

4. Conclusions

An electrochemical sensor for Eu^{3+} ions with a membrane composition of 81.5% PVC and 18.5% DGA-TREN was fabricated, which showed a wide dynamic range (3.2×10^{-7} to 1.0×10^{-2} M) with a calibration sensitivity of 17.2 ± 0.1 mV per decade. The membrane sensor operates in 1 M HNO_3 medium with a very fast response time (<5 s) under stirring conditions. Another membrane with a composition of 77.3% PVC and 22.7% T-DGA failed to show any systematic change in the potential upon addition of Eu^{3+} under similar conditions. A TGA study indicated that part of the DGA-TREN also acts as plasticizer, overall the thermal stability of the membranes being reasonably good. An FT-IR study showed the presence of C=O groups in all the membranes. An AFM study indicated a significant change in the morphology of the T-DGA-containing membrane upon contact with Eu^{3+} ions in 1 M HNO_3 medium, whereas no such drastic change in morphology was observed in case of the TREN-DGA-containing membrane under similar conditions. This could be the reason why the former failed to show any electrochemical potential response. The detection limit using the NaTPB incorporated PVC/TREN-DGA membrane was calculated to be 100 nM. This study shows the advantage of a

multi-DGA-containing membrane sensor having a wider dynamic range than the TODGA-based one, which may be of use for different applications.

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Author biography



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Mr. Andrea Leoncini was born in Poggibonsi, Italy, in 1988. He studied Chemistry at the University of Pisa, Italy, where he received his MSc in 2013. Subsequently, he did his PhD at the University of Twente, the Netherlands, under the supervision of Dr. Willem Verboom and Prof. Jurriaan Huskens. His PhD thesis was entitled 'Alkylation and pre-organisation of diglycolamide ligands on flexible platforms for nuclear waste treatment'.



Prof. Jurriaan Huskens was born in Sittard, The Netherlands, in 1968. He studied chemical engineering at the Eindhoven University of Technology. He obtained his PhD from the Delft University of Technology in 1994. Following postdoctoral stays at the University of Texas at Dallas and at the Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, he began his academic career at the University of Twente, Enschede in 1998, where he is now full professor “Molecular Nanofabrication”. The research in his group is focused at fundamental and applied studies of self-assembly, surface chemistry and nanotechnology.



Dr. Willem Verboom was born in Goes, The Netherlands, in 1954. He studied chemistry at Utrecht University, where he also obtained his PhD (1980). Subsequently, he went to the University of Twente, where he now is an associate professor of organic chemistry. He is the (co-)author of about 410 scientific publications. His current research interests involve the design of specific ligands for different applications and the use of microreactors.



Dr. P. K. Mohapatra (b. 1964) joined Radiochemistry Division, Bhabha Atomic Research Centre in 1987 and has been one of the most recognized scientists in the area of Separation Science and Technology involving actinides, lanthanides and fission product elements. An honorary Fellow of National Academy of Sciences, Allahabad, India, he is an honorary professor at the Homi Bhabha National Institute (Deemed University), Mumbai. Currently, he is heading actinide chemistry section and has over 320 publications in peer reviewed international journals.

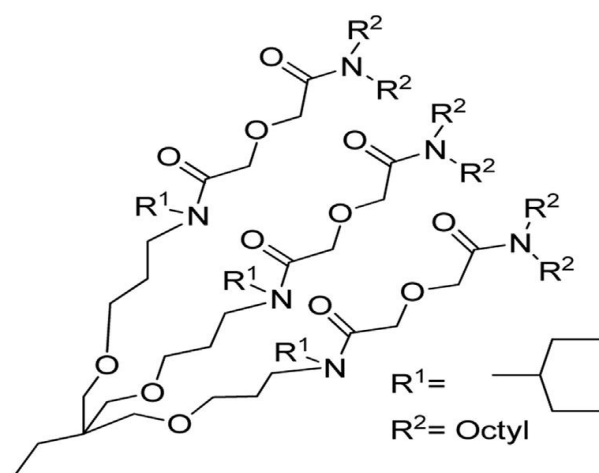


Fig. 1: T-DGA



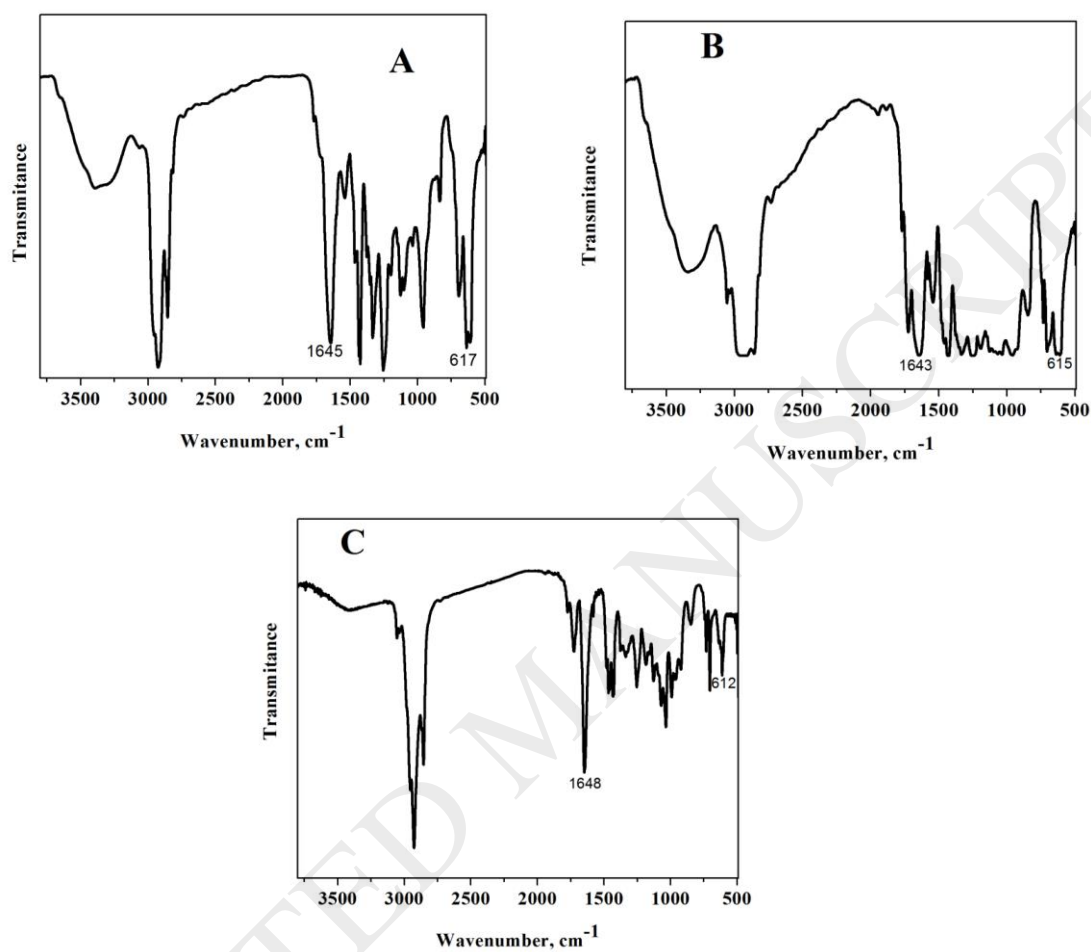


Fig. 3. FTIR analysis of (A) PVC/TREN-DGA, (B) PVC/TREN-DGA-NaTPB, and (C) PVC/T-DGA.

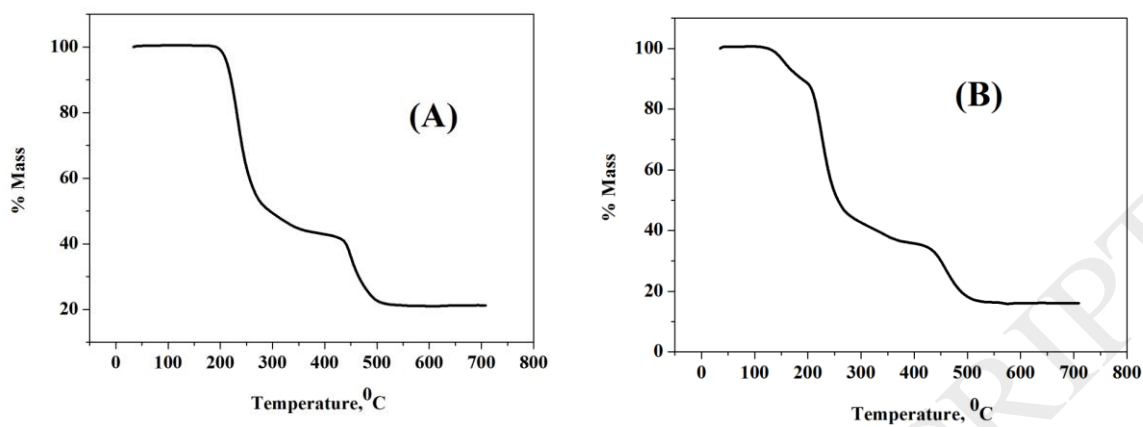


Fig. 4. Thermogravimetric analysis of (A) PVC/TREN-DGA and (B) PVC/TREN-DGA-NATPB; carrier gas: high purity Ar, heating rate: 10 °C/min.

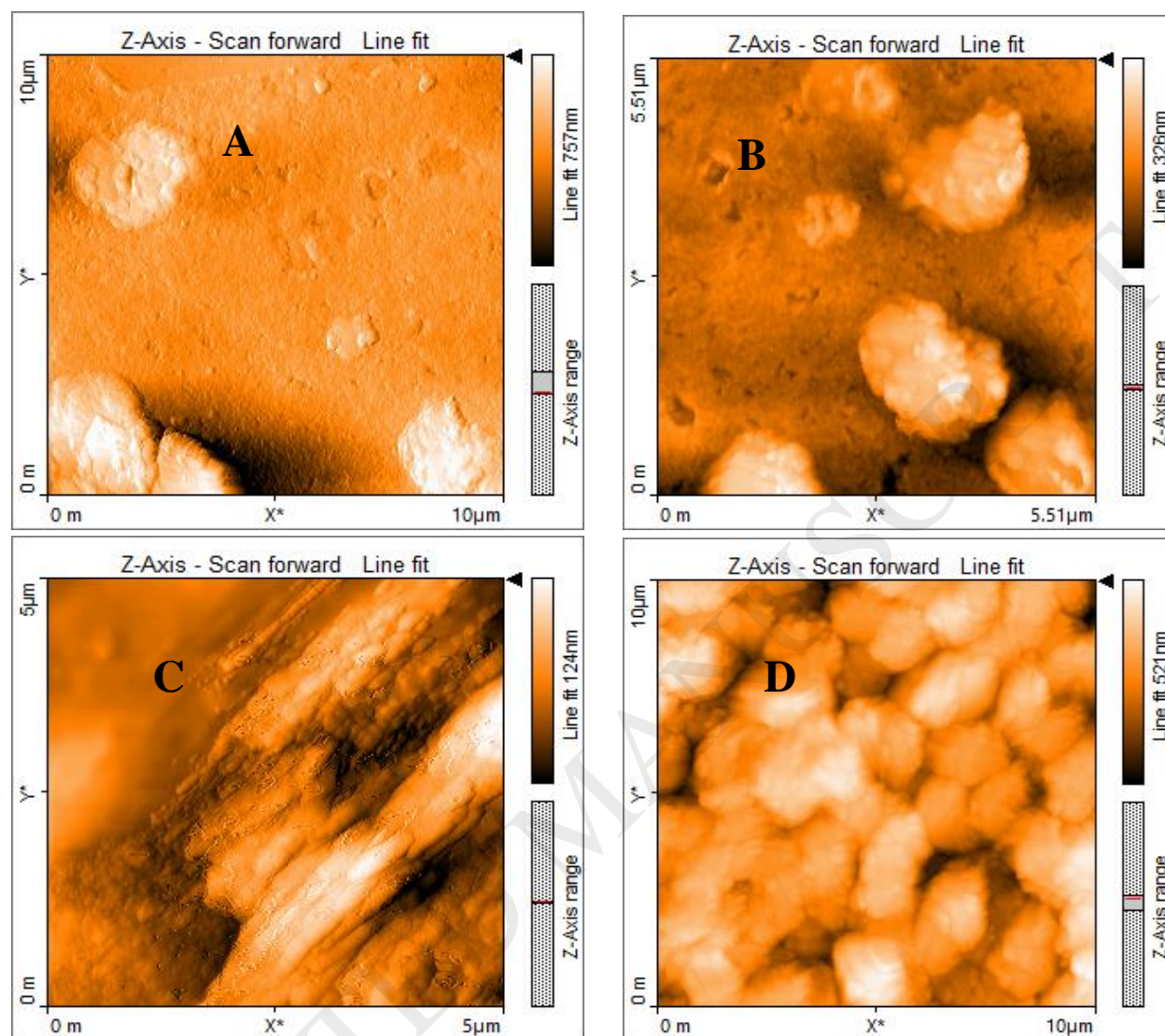


Fig. 5. AFM images of (A) PVC/DGA-TREN before use (B), PVC/DGA-TREN after use, (C) PVC/T-DGA before use, and (D) PVC/T-DGA after use.

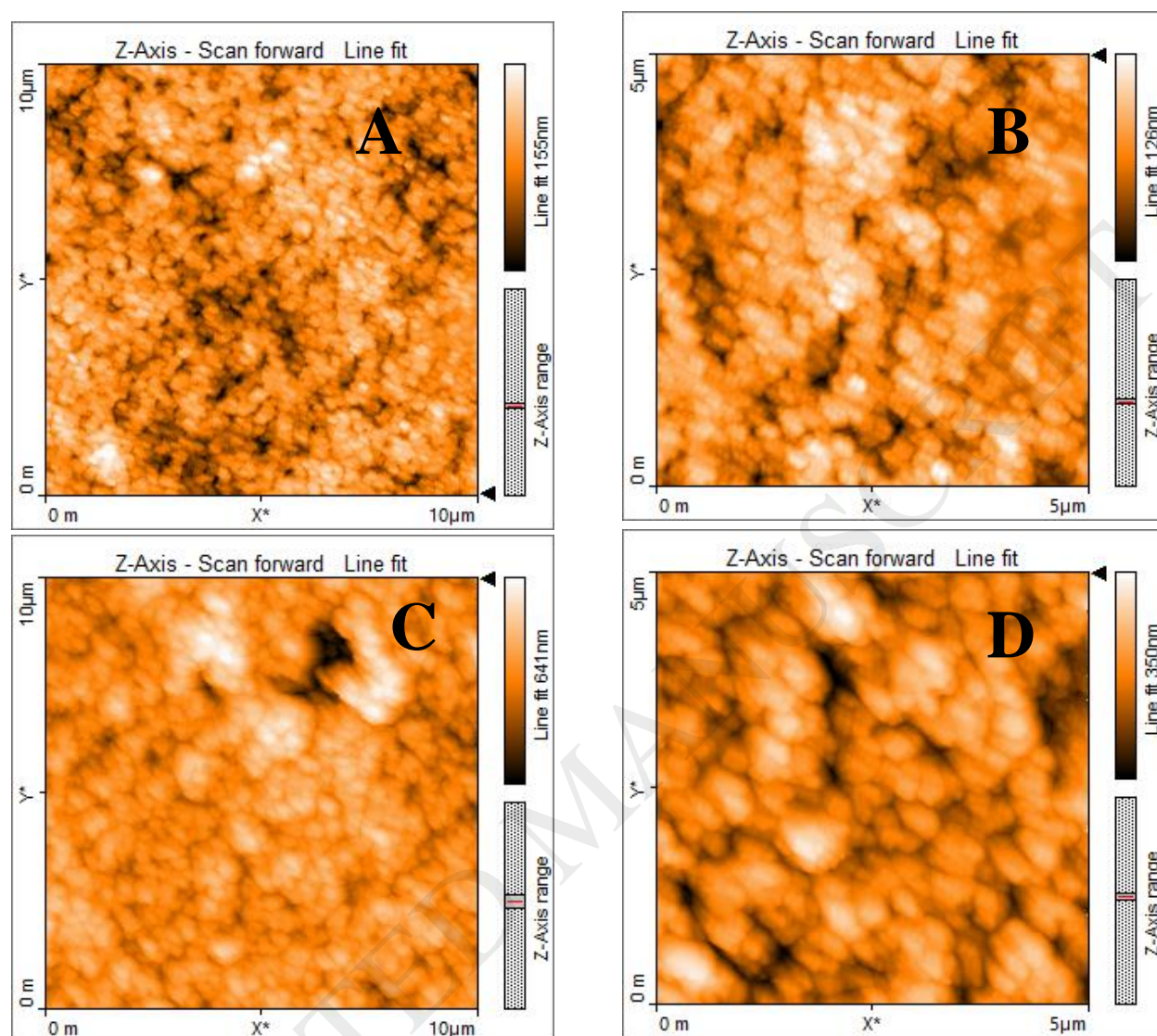


Fig. 6. AFM images of (A) PVC/TREN-DGA-NaTPB before use, (B) PVC/TREN-DGA-NaTPB before use, (C) PVC/TREN-DGA-NaTPB after use, and (D) PVC/TREN-DGA-NaTPB after use.

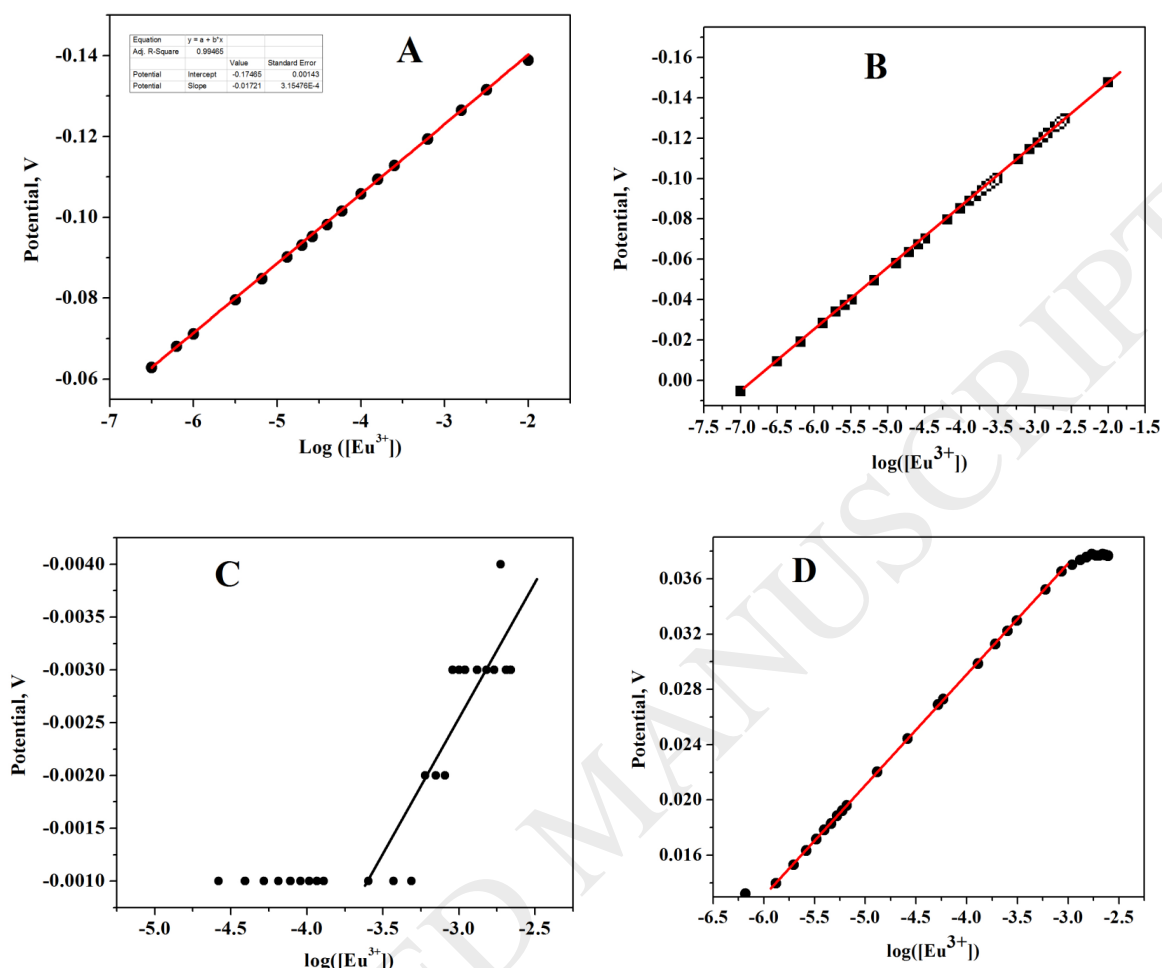


Fig. 7. Calibration curve of (A) TREN-DGA, (B) borated TREN-DGA, (C) T-DGA containing PVC membrane, and (D) TODGA membrane.

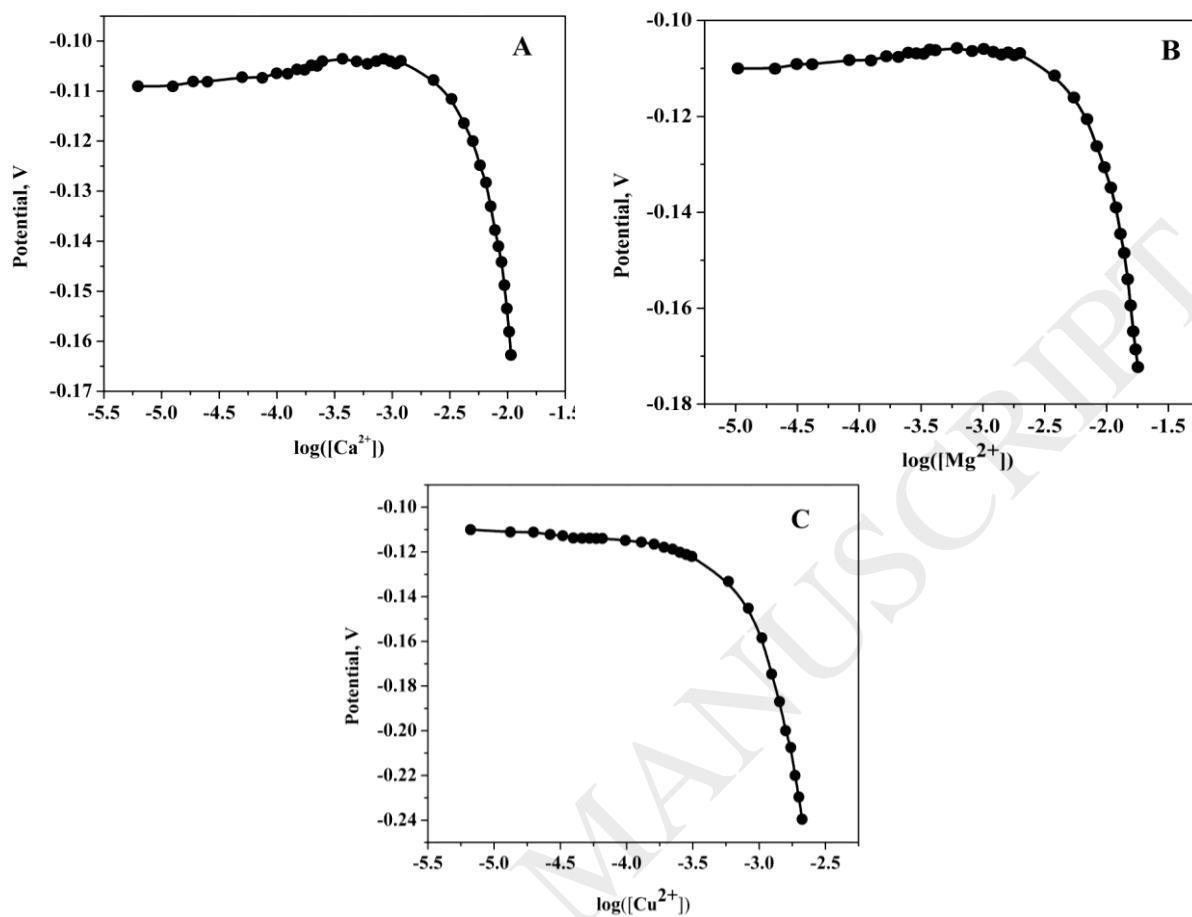


Fig. 8. Interference studies of (A) Ca^{2+} , (B) Mg^{2+} , and (C) Cu^{2+} with 0.2 mM Eu^{3+} , while measuring Eu^{3+} from the membrane.

Table 1 Membrane composition used in the fabrication of the potentiometric sensor.

S. No.	Membrane composition
1	81.5% PVC, 18.5% DGA-TREN
2	77.1% PVC, 17.6% DGA-TREN, 5.3% NaTPB
3	77.3% PVC, 22.7% T-DGA
4	60.6% PVC, 30.3% TODGA, 9.1% NaTPB (Ref. [23])

Table 2: Selectivity coefficient data for different interfering ions measured by matched potential method (MPM)

Interfering ion	Selectivity coefficient	Interfering ion	Selectivity coefficient
Ca ²⁺	1.2x10 ⁻³	UO ₂ ²⁺	1.5 x 10 ⁻²
Mg ²⁺	1.5x10 ⁻³	Ba ²⁺	2.3x10 ⁻²
Cu ²⁺	2.1x10 ⁻³	Ce ³⁺	2.7x10 ⁻²
Fe ²⁺	1.8x10 ⁻³	Pb ²⁺	2.7x10 ⁻³
Zr ⁴⁺	1.2x10 ⁻²	Cd ²⁺	3.1x10 ⁻³

Table 3 Spike recovery test of Eu^{3+} using the direct potentiometric method using the developed membrane in water samples.

Sample	Eu^{3+} added (mg L^{-1})	Eu^{3+} found (using proposed sensor) (mg L^{-1})	Percentage recovery using proposed sensor	Eu^{3+} found (using ICP-OES) (mg L^{-1})	Percentage recovery using ICP-OES
Uranyl nitrate solution	100.0	$(97.8 \pm 4.5)^*$	97.8%	$(98.5 \pm 4)^*$	98.5%
Uranyl nitrate solution	200.0	$(205 \pm 6)^*$	102.5%	$(202 \pm 5)^*$	101%
Deionized water sample	Not added	BDL		BDL	

BDL: Below detection limit; * Based on three repetitive measurements.