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Boron isotopes enrichment via continuous annular chromatography

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ABSTRACT

Boron has two stable isotopes namely ^{10}B and ^{11}B isotopes. The large cross section of ^{10}B isotope for thermal neutrons is used for reactor control in nuclear fission reactors. The thermal neutrons absorption cross sections of pure ^{10}B and ^{11}B are 3837 and 0.005 barns respectively. In the literature, amongst others, batch elution chromatography techniques are reported for ^{10}B isotope enrichment. This work focuses on continuous chromatographic ^{10}B isotope separation system via continuous annular chromatography (CAC) where isotope enrichment from boric acid solution is studied. CAC is slurry packed with commercially available n-methyl glucamine functionalized boron-specific anion exchange resin (Diaion CRB03 - Mitsubishi). The nominal height of AISI 316 stainless steel pipe outer and inner cylinders of CAC is 200 cm. The outside diameter of column is 20 cm and inside diameter of inner column is 14 cm. The liquid level above the top of the resin is monitored with an ultrasonic sensor. Its level is kept between the set values by air injection from the top of the column. For this purpose, the liquid level signals received from the ultrasonic sensor is fed to a proportional controller unit so as to adjust the column head pressure by regulating air injection pressure and its flow rate. Dilute aqueous nitric acid solutions were used as the eluent. Eluent ^{10}B and ^{11}B isotope ratios are measured by ICP-MS spectrometer (Perkin Elmer, ELAN 9000). It is determined that depending on the operation parameters ^{10}B isotope ratio can be increased over 27% in a single pass mode operation of the present CAC apparatus.

1. Introduction

Chromatography is a widely used and highly selective process of separation, employed in the separation of complex mixtures of which the overall product yield of petrochemicals, sugars, proteins, pharmaceuticals, fine chemicals, flavorings, foods, enantiomers and isomers is governed by the individual yields of discrete operations. It is admitted by several researchers that no other separation method is as powerful and generally applicable as is chromatography [1-4].

Chromatographic separation techniques are also employed in isotope enrichment studies. Atoms of the same element can have different numbers of neutrons and the different possible versions of each element are called isotopes. Helium, Lithium, Boron, Nitrogen, Sulfur, Chlorine are the some elements that have stable isotopes found in different abundancy ratios in nature. Common stable isotopes of Boron are; ^{10}B and ^{11}B. The naturel abundance of Boron stable isotopes, namely ^{10}B and ^{11}B are given as 19.92% and 80.12% respectively [5]. That makes the isotope ratio of 19.92/80.12 = 0.2486.

In a nuclear reactor, fission reaction rate is the function of the thermal neutron number found in the reaction medium. Thus, one of the most important parameter in nuclear reactor design is to prevent the increase in thermal neutron number in reaction medium that can cause uncontrollable fission rate. In other words, regulating thermal neutron number continuously and thus

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avoiding the chain reaction to melt the reactor core. The neutron capture cross section of an isotope of a chemical element is a measure of the probability of neutron capture. It is the effective cross sectional area that an atom of that isotope presents to absorption, and usually measured in barns (b) where 1 barn is defined as 10^{-28} m^2.

Isotope of boron, ^{10}B isotope is unique between other thermal neutron capture cross section materials used in nuclear reactors and ^{10}B isotope has the longest continuous service history of any neutron absorbing material, performing its intended function in high gamma and neutron radiation fields. The neutron capture mechanism of ^{10}B isotope is shown in Figure 1.

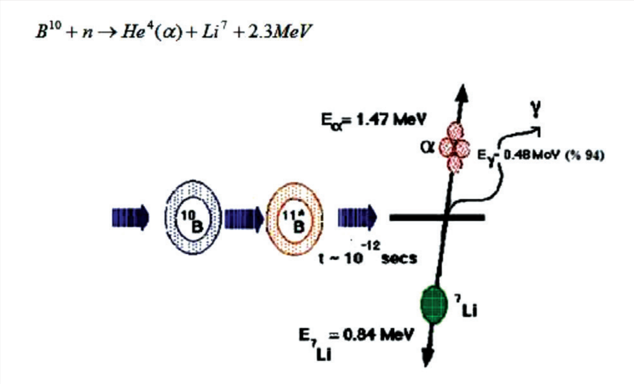

Figure 1. Boron neutron capture (BNC) mechanism

Thermal neutrons capture cross sections of pure ^{10}B and ^{11}B isotopes are 3837 and 0.005 barns [6] respectively. This makes the thermal neutrons capture cross section of ^{10}B isotope is 767,400 times more than that of ^{11}B isotope [7, 8]. Therefore, ^{10}B isotope is an extremely effective neutron absorber playing a crucial role in controlling the reactivity of nuclear fuel rods in nuclear reactors. Furthermore it is an indispensable material for neutron shielding purposes such as anti-activation covering for nuclear waste containment. Besides the importance in nuclear power plant as neutron radiation control, ^{10}B isotope is also used for boron neutron capture therapy of brain tumors and melanotic cancers because the formed α-particles and ^7Li nuclei destroy cancer cells when irradiating a tumor by neutrons and it can be injected into a human organism more easily and safely than other neutron absorbents [9]. While ^{11}B isotope is an excellent neutron reflector, it is used as an additive to semiconductor grade silicon as a doping agent. Although it does not absorb neutrons, it is used as an additive to steels that are used in the construction of reactors to enhance their heat and radiation resistance.

The main isotope separation processes of boron are: distillation, ion exchange chromatography, gaseous diffusion, gas centrifuge and laser isotope separations. For separation of isotopes of lighter elements, such as boron isotopes, distillation [9] and ion exchange chromatography techniques are generally considered as industrially viable.

The first experiment on ion exchange separation of boron isotopes was done by Yoneda et al. [10] and they used strong base anion exchange resin in hydroxide form as column packing material. They conclude that the lighter isotope, ^{10}B isotope was enriched in resin phase and the single stage separation factors which is the ratio of the relative concentration of the desired isotope after processing to its relative concentration before processing, increased from 1.010 to 1.016 for concentrated solutions of boric acid.

Isotopic plateau displacement chromatography is one of the most preferred techniques for isotope enrichment found in literature. Sakuma et al. [11] showed that by using weak base anion exchange resin ^{10}B isotope can be enriched up to %91 from isotope mixture solution. Fujii et al. [12] improved an explicit expression for isotope profile in migration bands. The applicability of this expression was proved by experimental results obtained from boron isotope separation chromatography with ion exchange. Oi et al. [13] performed experiments in liquid chromatography by using column packing material of which boron specific resins with n-methyl glucamine as the functional group and observed that column performance change with temperature and resin form. Based on the specific affinity of glucamine type resins to boron ions, Sonoda et al. [14] made experiments in ion exchange chromatography with three different glucamine resins. In these experiments they used columns having 1cm inside diameter and 1 m packing height and conclude that ^{10}B isotope can be enriched with fractional operation. The results in boron isotope enrichment chromatography using kaolin clay as packing material showed that system can be efficient under 12.0 MPa pressure [15]. Resin regeneration with electrochemical techniques was studied in ion exchange chromatography of boron separation and besides that band movement was investigated both in batch and column operations [16].

In literature, the studies performed with column chromatography, isotope exchange separation factor for boron changes between 1.009 and 1.014 however some researchers conclude that this value can increase to 1.020 [13, 16] The point that should be taken into consideration is that the column height with other operating conditions is the most important parameter that affects isotope exchange separation factor.

All of these studies are batch processes that isotope enrichment is governed by the individual yields of discrete operations. As it is concluded in several studies it is possible to separate boron isotopes at higher ratios in cascade operations. Nevertheless the disadvantage with these batch preparative operations is the low productivity of enriched boron isotopes due to the low feed quantity as well as the dilution effect as an outcome of high quantity of eluent. While theoretically it is possible to increase the boron enrichment productivity with the employment of exceptionally large scale systems in a single pass operation, their operation costs would be extremely high. Thus large scale isotope enrichment is not feasible with conventional preparative chromatographic techniques that small amount of the product is separated per unit volume of stationary phase. For large scale separation and purification applications, continuous chromatographic separation processes, have gained greater interest in the last decades due to its advantages in terms of productivity and efficiency. The continuous annular chromatography (CAC) is a potential and promising downstream process that allows large-scale continuous preparative chromatographic separation and purification of multi-component mixtures. CAC is a process intensified technology that replaces the conventional chromatography columns with a smaller unit for the same separation task and eliminates the drawbacks of conventional chromatographic processes, operating in a batch mode by operating in a continuous mode, increasing the productivity and separation factor.

The concept of CAC was first suggested in 1949 by Professor A.J.P. Martin [17] who shared the 1952 Nobel Prize in Chemistry for the invention of partition chromatography. The state-of-the-art of the CAC was developed at Oak Ridge National Laboratory, USA [18, 19] and first continuous annular chromatograph was constructed by Fox et al. [20]. The CAC apparatus consist of two slowly rotating concentric cylinders forming an annulus into which the stationary phase is packed. The inlets of the mobile phase are uniformly distributed along the annular bed entrance, while the feed stream is stationary and confined to one sector. The rotation of stationary phase packed into annulus, in its vertical axis, the selectively adsorbed species take different helical paths through the bed and can be continuously collected at fixed locations [21, 22]. The retention time of each component and thus the angular displacement from the fixed feed entry will remain constant as long as operating conditions remain constant. Hence the separation process in CAC is truly continuous. One of the world's leading supplier of nuclear technology, namely Westinghouse Electric Company (USA) has a US patent [23] about isotope enrichment with Pressurized Continuous Annular Chromatography (P-CAC). P-CAC is also applicable technology for the separation of compounds other than isotopes such as hormones, proteins, pharmaceuticals and fine chemicals.

The focus of this work, is to enrich ^{10}B isotope which has a high neutron capture property when compared to ^{11}B isotope, thus having a wide and significant use in nuclear energy technology, from boric acid solution with a single pass mode operation of continuous annular chromatography packed with commercially available n-methyl glucamine functionalized boron-specific anion exchange resin.

2. Material and methods

Feed Solution

Aqueous solution of low-sulphated (130 ppm max.) boric acid (Eti Mine Works General Directorate, Turkey) at the minimum purity of 99.9%, is used as the feed solution. The sulphate ions or other potential impurities in the boric acid feed solution do not effect the boron isotope separation process since the chelating type resin is specific for only the adsorption of borate ions in the feed mixture. It is reported that the concentration of boric acid feed solution is an important factor in isotope enrichment. It was reported that isotope separation factor increases with decreasing feed solution concentration [10]. For this reason, dilute solutions of boric acid are used as feed solutions in the experiments.

Eluent

Aqueous solution of HNO_3 (Merck, Germany) is used as eluent solution in the experiments in order to overcome interference problems with ICP-MS instrument. It is reported in the literature that isotope enrichment is possible by use of aqueous solutions of HNO_3 with concentrations lower than 0.1 M. With higher concentrations of HNO_3 solutions, no isotope separation is seen despite the quick desorption of boron in conventional packed beds [14].

Resin Properties

Diaion CRB 03 resin (Mitsubishi Chemical Corporation, Japan) having average particle diameter of 556 µm is chosen as boron specific resin for P-CAC experiments. Diaion CRB 03 is a borate selective anion exchange resin. N-methylglucamine group bonded onto a highly porous cross-linked polystyrene matrix as a functional group, the borate ion makes a very stable complex with the glucamine group, whilst other anions do not react. The boron adsorption mechanism of chelating resin is given in figure 2.

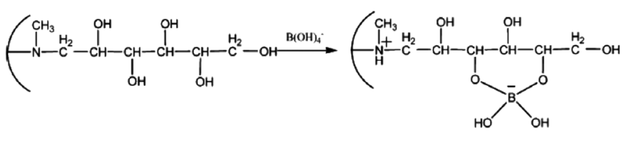

Figure 2. Chelating mechanism for boron adsorption in n-methyl glucamine functionalized adsorbents

2.1. *CAC Apparatus*

Figure 3 illustrates the schematic diagram of continuous annular chromatograph (Sinerji Ltd, Turkey) that consists of two cylinders. The outer and inner cylinder is made of AISI 316 stainless steel and the outer and inside diameters of column are 20 cm and 14 cm respectively. During the experiments P-CAC rotating speed can be regulated between 0.15 – 1.80 rotation/hour. The special step motor is used with computer programming and its sensivity is ± 0.01 rotation/hour. The working pressure is in the range of 0 to 3.0 Bar with 0.01 bar sensitivity which is auto-adjustable. Feed is sent to the column with HPLC pump (Chrom Tech Inc., U.S.A.) of 0-40 mL/min range. Eluent and cleaning solution are fed to the system by use of preparative chromatography pumps (Fluid Metering Inc., U.S.A.) with 0-1240 mL/min flow rate ranges, respectively. The packing height of the column is 168 cm with 72 outlet nozzles.

The head of annular chromatograph is air proof. During the operation, a special pressurization technique is employed for keeping the feed and elution flow rates constant at their setting values regardless of the fluctuations of actual pressure drop in the column during operation that might stem from the small change in bed height i.e. shrinking. This technique is based on monitoring the liquid level at the top of the resin with an ultrasonic sensor. In order to keep the liquid level at its setting value, regulated air is injected from the top of the column. The liquid level signal received from the ultrasonic sensor is fed to a controller unit that adjusts the column head pressure by regulating air injection pressure and its flow rate via proportional control air pressure regulating valve. Proprietary software commands the proportional control valve for regulating head space air pressure so as to maintain the liquid level at the set value within the range of ± 1 mm.

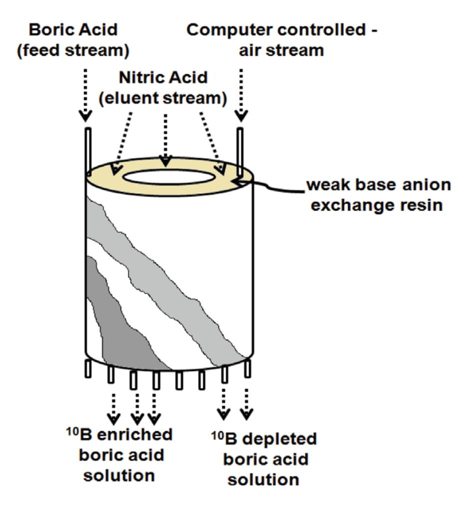

Figure 3. Schematic diagram of the experimental apparatus, P-CAC

2.2. *Packing procedure of anion exchange resin*

Resin in the annulus is a bed formed in between co-centered two cylinders. As for all chromatographic columns, it is very important for the annular chromatograph to be packed with resin without channeling. Channeling and disorder in the bed damage the flow distribution and contribute to band broadening, overlap of zones resulting in decreased product efficiency and quality [24, 25]. Prior to the column packing the top side of the 5 μm stainless steel filter which is placed above the column outlet ports, is covered about 2.5 cm layer of glass spheres (average diameter 750 μm) through the specific port on the head of P-CAC. For packing the annular chromatograph bed, a modified slurry packing method is used. The P-CAC instrument is run under packing mode with a rotating speed of 36 rotations/hour. Thus, combined with the effect of gravitational force, ion exchanger resin particles in the slurry are evenly settled onto the bed surface during the bed formation in the annulus. Slurry solution of 50% water and 50% Mitsubishi Diaion CRB 03 boron specific resin by volume is fed to the annulus until a bed height of 168 cm is obtained. It must be noted that packing mode rotating speed is kept at a much higher rate as compared with rotating speed used in the experiments. The water in the slurry solution is drained from the bottom of the bed. During the packing of bed with resin, it is made sure that there is always a water layer of at least 10 cm length present by controlling the flow rate of slurry solution by use of peristaltic pump. The system's set pressure value changes with feed and eluent flow rates within a range of 0.1 – 3.0 bar. When there is a significant decrease in the liquid level as a result of high set pressure value, the needle valve in the column head is operated manually to decrease pressure and a new set value is defined accordingly via computer. Another operating parameter of the system is the rotating speed of the annulus and the bed inside it. The rotating speed of the bed is held constant at 13.3cm/hour.

The lower surface of the bed in the annulus is open to the atmosphere. The feed and elution solutions are fed to the system through the entrances on the air-blocker head of the column. At the beginning of the each experiment, P-CAC is conditioned as with 0.1 M HNO_3 and washed with large quantities of distilled water.

For boron enrichment from aqueous solutions with N-methylglucamine type resins, it is observed that when pH < 7, adsorption of ^{10}B isotope to the resin phase is greater than that of ^{11}B and for the case of pH values greater than 11, no enrichment in boron isotopes occur [26]. These researchers suggest that the difference between the tetrahedral coordination geometry of boron complex of ^{10}B isotope in the resin and the planar trigonal coordination geometry of boron complex in solution phase result in fractionation. The opposite case occurs for ^{11}B. Kakihana et al. [27] reported a similar case for different studies on conventional packed columns. These results are based on experimental results of breakthrough and reverse-breakthrough type studies in conventional packed columns. Since the feed and eluent are being constantly fed to P-CAC, there are differences on the interaction mechanism of boron isotopes with the resin and liquid phase compared to the studies on batch type conventional column chromatography.

ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) instrument (Perkin Elmer, Model: ELAN 9000, U.S.A.) is used for determination of Boron isotope ratios. ICP-MS instruments are widely used for boron ratio determination because of ease of use and the fact that many samples can be processed quickly [28]. Solutions with 90%, 80% and 70% ^{10}B/^{11}B isotope ratio are prepared by use of primary standard ^{10}B and ^{11}B samples. Primary standards used are solid $H_3{}^{10}BO_3$ (Spectra 2000 Srl, Italy) and $H_3{}^{11}BO_3$ (Cambridge Isotope Laboratories, U.S.A.). It is seen that there is a very good correlation between these prepared solutions of known ^{10}B /^{11}B isotope ratio and those determined by use of ICP-MS. Since diluted HNO_3 solutions (25 mM – 50 mM) are used as eluent, there no interference with the analysis. In all the boron enrichment experiments boric acid with at least 99.9% purity with low sulfate content is used which minimizes matrix effects. Therefore there is no need for matrix effect inspection on ^{10}B /^{11}B isotope ratio analysis. U.S.A. Department of Energy Lawrence Berkeley National Laboratory defines the natural ^{10}B/^{11}B isotope ratio for Boron as 19.92/80.12 = 0.2486 [5]. This natural ^{10}B/^{10}B ratio is defined as 19.9/80.1= 0.2484 in the software of Perkin Elmer ELAN 9000 ICP-MS used in this study. During the analysis, this value in the software is used.

3. Results and discussions

In Figures 4 and 5, the isotope percent analysis and boron concentration results given in ordinate axis belong to the solutions collected cumulatively during the experiment corresponding to the P-CAC outlet nozzle number given in the abscissa axis respectively for run 1 and 2. In run 1 the feed concentration is 0.1 M H_3BO_3, HNO_3 eluent concentration is 0.025M and feed flux (mM/cm2.s)/ eluent flux (mM/cm2.s) ratio is 0.107 whereas in run 2 all operation parameters, other than feed to eluent flux ratio, is kept constant.

For comparison, the feed solution analysis result with natural ^{10}B isotope percentage (19.9%) fed to P-CAC and boron concentration in the feed stream value that is calculated by taking account the dilution effect within the column also shown in the figures. The values given in these figures are the cumulative values of solutions collected in each eluent bottle.

To overcome any problems associated with the analysis of ^{10}B isotope enrichment with P-CAC experiment results which may result from ICP-MS instrument, isotope percentage of natural boric acid solution is also analyzed periodically during the analysis. It is seen that expected isotope percentage value of the natural solution is analyzed each time.

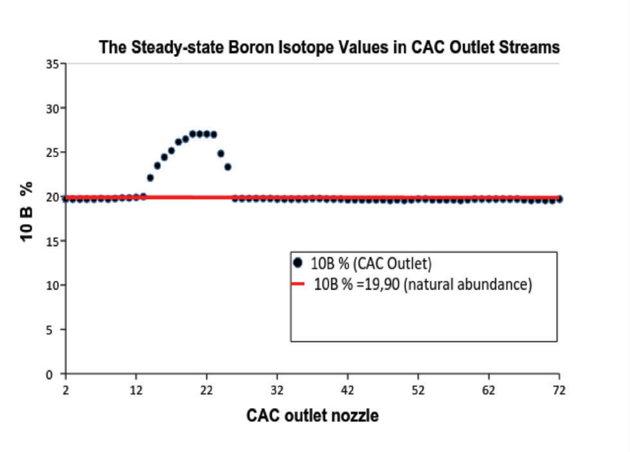

Figure 4a. Run 1. Steady-state ^{10}B isotope enrichment values at P-CAC outlet streams, feed concentration=0.1 M H_3BO_3, eluent concentration=0.025 M HNO_3, feed flux (mM/cm^2.s)/ eluent flux (mM/cm^2.s)=0.107

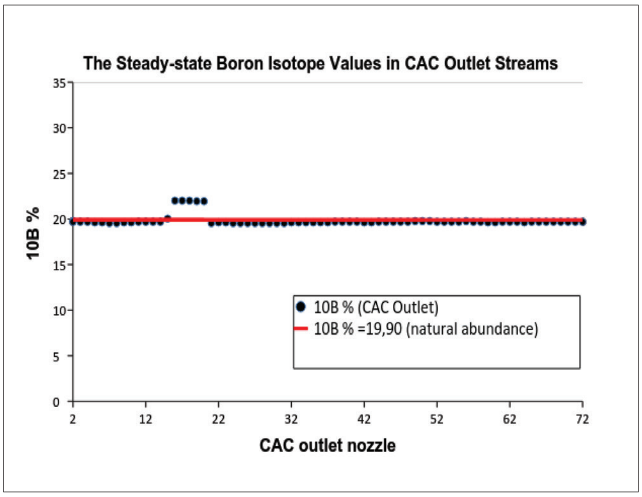

Figure 4b. Run 2. Steady-state ^{10}B isotope enrichment values at P-CAC outlet streams, feed concentration=0.1 M H_3BO_3, eluent concentration=0.025 M HNO_3, feed flux (mM/cm^2.s)/ eluent flux (mM/cm^2.s)=0.093

In Figure 4a and 4b, the ^{10}B isotope percentages are given for each CAC outlet nozzle. During the experiment, for every complete revolution of CAC column, samples are collected cumulatively from each outlet stream of CAC system and it was seen that after the fifth complete revolution of CAC column, system reached the steady-state both for run 1 and 2. From figure 4a it is clearly seen that, between the 14-25 outlet nozzles, 27% ^{10}B isotope enrichment is achieved. When run 1 and 2 are compared it is clearly seen from figure 4b that when feed to eluent flux ratio decreases, in other words eluent flux increases, the ^{10}B isotope enrichment decreases to 23% between the 17-21 outlet nozzles due to the low retention time of boron isotopes within the column. On the other hand, from other outlet streams, ^{10}B % is its natural values of 19.90% for run 1 and 2. It is obvious that this situation arises from the back-mixing problem within the annular column due to the pressure changes at the outlet of column.

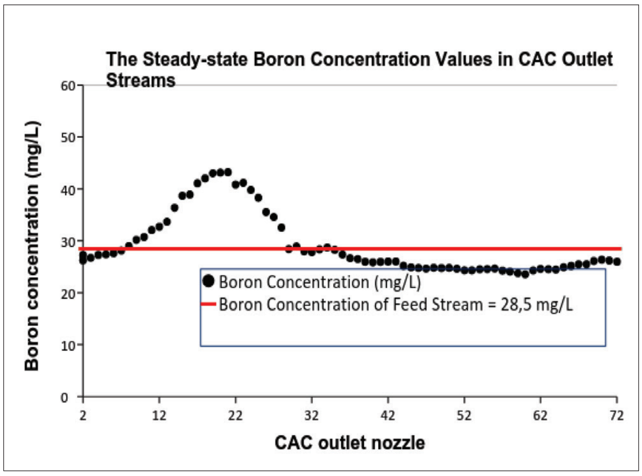

Figure 5a. Run 1. Steady-state boron concentration values at P-CAC outlet streams, feed concentration=0.1 M H_3BO_3, eluent concentration=0.025 M HNO_3, feed flux (mM/cm^2.s)/ eluent flux (mM/cm^2.s)=0.107

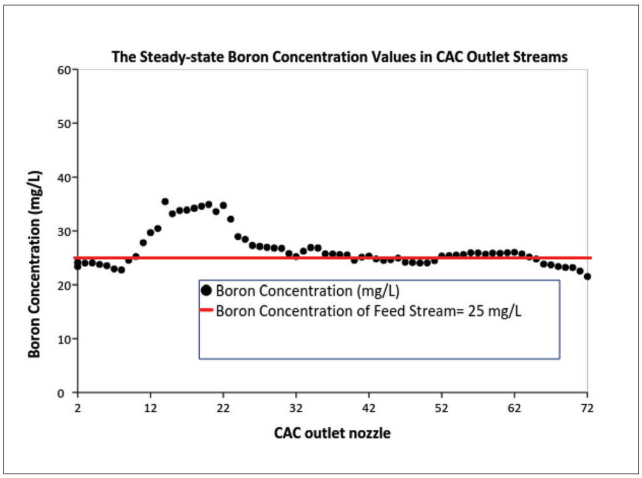

Figure 5b. Run 2. Steady-state boron concentration values at P-CAC outlet streams, feed concentration=0.1 M H_3BO_3, eluent concentration=0.025 M HNO_3, feed flux (mM/cm^2.s)/ eluent flux (mM/cm^2.s)=0.093

In Figure 5, steady-state boron concentration values are given for each CAC outlet nozzle after the fifth complete revolution of CAC column for run 1 and 2. When investigated with Figure 4, it is seen that boron concentration increases at the region where ^{10}B percent increases. On the other hand, at the 14-25 outlet nozzles for run 1 and 17-21 outlet nozzles for run 2, the boron concentration is greater than the boron concentration of the feed stream while the dilution effect of feed stream is taken into consideration.

As a result, from Figures 4a and 5a, it is clearly seen that that P-CAC is an effective instrument for ^{10}B isotope enrichment such that in some eluent collection bottles, ^{10}B isotope values of 27% are obtained at high concentration values. Regarding the amount of feed separated to 27% isotope ratio, it should be stated that the process is continuous. The data expressed in Figure 4 and 5, is collected during the operation interval between 23 hour – 27 hour, commencing from the experimentation. During which time interval the cumulative volume of injected feed and eluent was 9.24 l. During this time interval of experimentation, ^{10}B isotope which is enriched to 27% constitutes 7% (v/v) of input stream. These results when compared with natural ^{10}B isotope ratio of 19.9% indicate the significance of use of P-CAC instrument for continuous chromatographic method of isotope enrichment process.

Sonoda et al. [26], carried out batch studies where they first boron loaded an ion exchange column, containing glucamine functionalized resin under pH > 7.5. Later, carried out reverse breakthrough studies with dilute acidic solutions. They observed fractionation of ^{10}B isotope in the stationary phase and explained it due to the tetrahedral coordination geometry of the ^{10}B isotope boron complex in the stationary phase and its planar trigonal coordination geometry in the mobile phase. Whereas, they stated that, regarding ^{11}B isotope the reverse case holds. Nevertheless our repeated observations with Continuous Annular Chromatography system shows that the mechanism might be different since column pH is always on the acidic side during the operation (competitive simultaneous adsorption and elution of boron isotopes) of the CAC system.

Zhou et al. [29] also investigate the separation performance of continuous annular chromatography technology and in their study, they reached 21.45% ^{10}B isotope enrichment from boric acid solution with 820 mm continuous annular chromatography by using weak base anion exchange resin, Diaion WA21J.

4. Concluding remarks

In this study, it is determined that ^{10}B isotope ratio can be increased over 27% in a single pass CAC operation. According to the best of our knowledge, in the open literature, this figure is the highest ^{10}B isotope enrichment ever reported in a single pass chromatographic separation study. We concluded that ^{10}B isotope enrichment ratio can be further increased with P-CAC apparatus either operating in recycle mode or with the employment of P-CAC apparatus having longer bed height or both. Furthermore, since P-CAC is a continuous process, very large volumes of feed solution can be processed for ^{10}B isotope enrichment that cannot be matched by conventional chromatography.

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