# Nuclear Science and Technology
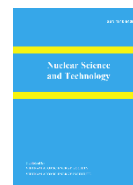
# Study on the removal of interferences for the determination of $^{87}$Sr/$^{86}$Sr isotopic ratio in petroleum drill-hole water samples using isotope dilution – inductively coupled plasma mass spectrometry (ID – ICP-MS)

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**Abstract**: $^{87}$Sr/$^{86}$Sr isotopic ratio is one of the useful tools that can authenticate the original source of the natural products from the earth-created and/or geological processes. However, the effect of interferences in petroleum drill-holes water sample such as thickness of sample matrix or isotopic signal of $^{87}$Rb might cause the low precision of $^{87}$Sr/$^{86}$Sr determination using quadrupole inductively coupled plasma spectrometry (ICP-MS). The elimination of these mentioned effects was thus studied by using the ion - exchange chromatography. Calcium in sample matrix was separated on anionite column (Bio-Rad AG1-X8 resin) in methanol medium with the high efficiency while rubidium was removed from strontium on cation exchange resin (Bio-Rad AG50-X8) with strontium recovery over 99%. The isotope dilution technique with $^{86}$Sr - enriched isotopic standard solution was used for the control of separation process. The $^{87}$Sr/$^{86}$Sr isotopic ratio was thus determined using ICP-MS with the signal correction by a strontium isotopic ratio standard reference material (NIST SRM 987).

**Keywords:** *$^{87}$Sr/$^{86}$Sr isotope ratio, petroleum drill-hole water, ion exchange chromatography, ID- ICP-MS.*

## I. INTRODUCTION

Natural occurring strontium has four stable isotopes, $^{84}$Sr , $^{86}$Sr , $^{87}$Sr , and $^{88}$Sr with relatively natural abundance variations of 0.55-0.58%, 9.75-9.99%, 6.94-7.14% and 82.29-82.75%, respectively, according to IUPAC [1]. The $^{87}$Sr isotope is generated by β decay of $^{87}$Rb: $^{87}$Rb = $^{87}$Sr + β$^-$ (haft life: $4.88 \times 10^{10}$ years) [2]. In the rocks and in water contacted with rocks/minerals for long time, concentration of $^{87}$Rb is rather high which consequently makes the radiogenic $^{87}$Sr isotope to be comparable [3]. $^{87}$Sr/$^{86}$Sr isotopic ratio of ancient water is thus higher than that from pumped surface seawater to the drill-holes to exploit the oil [4]. The average value of total strontium content in seawater is about 8 ppm around the oceans [4] whereas $^{87}$Sr/$^{86}$Sr isotopic ratio in the minerals and rocks spans the range 0.7-4.0 [5]. This isotopic ratio in the ocean water is constant of 0.7092 but it is in the range of 0.707-0.730 in the oil-field water [3]. From the co-relation between $^{87}$Sr/$^{86}$Sr ratio and concentration of total strontium dissolved in seawater, the original source of ancient water in the oil-fields would be authenticated [4,6]. It thus supports the

evaluation of petroleum potential [4] in the oil-fields.

The $^{87}$Sr/$^{86}$Sr isotopic ratio is commonly determined by thermal ionization mass spectrometry (TIMS) due to the high precision of method (from 0,01 to 1%) [2,7]. However, it requires the high cost equipment with sufficient skill of technician to prepare the sample and it is also the time-consuming method. Inductively couple plasma mass spectrometry (ICP-MS) also provides the capability to determine the isotopic composition of several elements in the periodic table together with their contents at high sensitivity and precision. ICP-MS (quadrupole type) and multi-collector (MC-ICP-MS) can measure many samples with high repeatability within short period of time, and the analyte price is rather inexpensive. ICP-MS is thus always a choice of researchers in the world to study stable isotope compositions [1-3,6,8,9].

Despite of its obvious advantages, ICP-MS still shows a disadvantage when determining the $^{87}$Sr/$^{86}$Sr isotopic ratio due to isobaric overlap of $^{87}$Rb signal at $^{87}$Sr isotope, which needs to eliminate. There exists several resolutions to correct the signal value for these two isotopes by using $^{85}$Rb and $^{88}$Sr [10,11] but the complete removal of Rb from Sr in analyzed sample is preferable with the use of ion-exchange chromatography [1,3,7,9-12]. In case of sample containing thick matrix due to high concentration of calcium and other alkaline earth elements such as rock or soil, it is necessary to remove these interfered major elements before the separation of strontium and rubidium [7,10-17]. The removal of calcium from sample matrices, especially from seawater was carried out with variety of reagents using solvent extraction or fractional precipitation or ion exchange [6, 8, 15-17]. Among them, the ion exchange technique was recently more applicable to separate calcium from different sample matrices [13-17] with

high recovery of strontium. Since calcium and strontium are adjacent elements in alkaline earth group with similar physical and chemical properties, the quantitative separation of each other is rather difficult even using ion exchange technique, except for the use of special resin to separate $^{90}$Sr trace from seawater [18].

In this study, the removal of matrix and isobaric interferences for the quantitative determination of $^{87}$Sr/$^{86}$Sr isotopic ratio using ICP-MS was focused. The matrix effect caused by calcium at high concentration in petroleum drill-holes water samples was eliminated by using anion exchanger (Bio-Rad AG1x8) in HNO$_3$-methanol (95%) medium, meanwhile the isobaric effect due to rubidium presented in sample was removed by cation resin Bio-Rad AG50x8. The isotope dilution technique (ID) with $^{86}$Sr enriched isotope standard solution was applied for the separation control and the NIST SRM 987 standard reference material was used for the signal correction of $^{87}$Sr/$^{86}$Sr isotopic ratio measurement on ICP-MS.

## II. EXPERIMENTAL

### A. Chemicals and reagents

All chemicals were of analytical grade: HNO$_3$ (d=1.4 g/mL), methanol (d= 0.972g/mL) and standard stock solutions of Rb, Ca and Sr (1000 mg.L$^{-1}$) for ICP-MS (Merck, Germany); Cation exchange resin (Bio-Rad AG50X8, 200-400 mesh) and anion exchange resin (Bio-Rad AG1X8, 200-400 mesh) supplied by Bio-rad Co., USA; Commercially available isotope enriched $^{86}$Sr (10.009 ± 0.073 mg.L$^{-1}$) standard solutions (Inorganic Venture-USA) and NIST SRM 987 (SrCO$_3$) $^{87}$Sr/$^{86}$Sr isotopic ratio standard reference material (National Institute of Standards and Technology, Gaithersburg, MD, USA) were used for isotope dilution analysis and signal

correction on isotopic ratio measurement, respectively. Purified water (18 MΩ.cm$^{-1}$) was used for preparation of aqueous solutions. High pure argon gas (99,999%, Messer) was used for ICP-MS measurement.

## B. Apparatus

The Agilent (USA) Model 7500a ICP-MS, controlled by Chemstation software, was used for the measurements. The optimized instrumental operating conditions are as follows: RF power, 1450 W; RF matching, 1.45 V; sample uptake time, 90 s; sample uptake rate, 0.4 rps; sample depth, 6.4 mm; Ar coolant flow rate, 15 L min$^{-1}$; carrier gas, 1.2 L min$^{-1}$; auxiliary gas, 0.9 L min$^{-1}$; water RF/TP flow rate, 2.4 L min$^{-1}$; water RF/TP, T = 293 K; analyzer pressure, $3 \times 10^{-4}$ to $2 \times 10^{-3}$ Pa.

Quart-glass chromatography columns are loaded resin (internal diameter of 12mm, 400mm height), which connected the peristaltic pump (Masterflex® L/S, Cole-Parmer Instrument Company, USA) to control flow rate and volume of fractions during loading and elution.

## C. Procedures

The experiments on chemical separation were performed at room temperature.

Petroleum drill-holes water samples received from Vietnam petroleum institute, which contained some oil and solid residue were filtered and stored in plastic bottle at 4°C for further treatment. A certain volume of this water sample was taken into a glass beaker, 2mL of concentrated HNO$_3$ was then added and this mixture was gently evaporated on a hot plate to dryness. This residue was dissolved in a mixture of 0.25 M HNO$_3$ in 95% methanol and made up a volume of 10 mL for separation experiment. A small amount of $^{86}$Sr enriched isotope standard was added in to sample

solution for the control of separation efficiency. Each type of ion exchanger (Bio-Rad AG50X8, Bio-Rad AG1X8) was pre-conditioned by immersing 5 grams in pure water for completely swelled up, then loading them on a column. Cation exchanger (Bio-Rad AG50X8, H$^+$ type) was equilibrated with 0.5M HNO$_3$ solution and this column was ready for separation experiment. Anion exchanger (Bio-Rad AG1X8, Cl$^-$ type) was washed with dilute HNO$_3$ at flow rate of 1mL/min until the Cl$^-$ trace was not detected in eluate by AgNO$_3$ solution. The excess of acid was then washed out with pure water for next step of sample loading. The separation procedure on both resins can be summarized in the following figures.

The concentration of all studied elements was determined by external calibrations on ICP-MS under the optimized operating conditions. The certified value of $^{87}$Sr/$^{86}$Sr isotopic ratio in NIST SRM 987 standard reference material as 0.71034 ± 0.00026 was applied for the control of isotopic ratio measurement on ICP-MS.
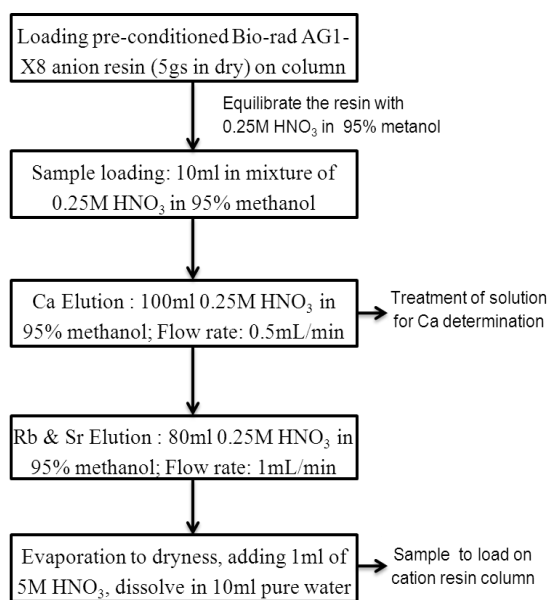


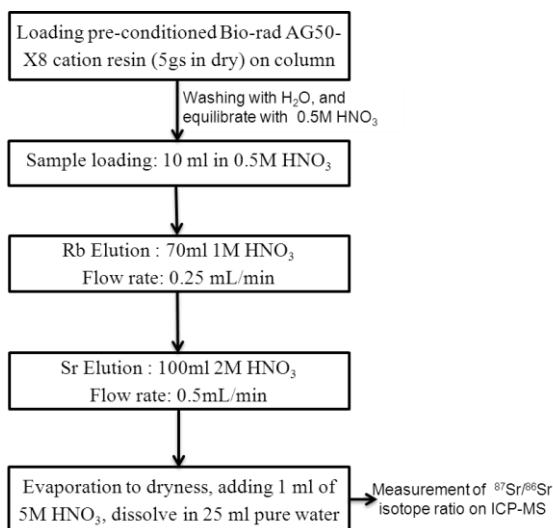**Fig. 1.** Separation of Ca from Sr and Rb on anion exchanger

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┌─────────────────────────────────┐
│ Loading pre-conditioned Bio-rad  │
│ AG50-X8 cation resin (5gs in dry)│
│ on column                        │
└─────────────────────────────────┘
              │  Washing with H₂O, and
              │  equilibrate with 0.5M HNO₃
              ▼
┌─────────────────────────────────┐
│ Sample loading: 10 ml in 0.5M HNO₃│
└─────────────────────────────────┘
              │
              ▼
┌─────────────────────────────────┐
│ Rb Elution : 70ml 1M HNO₃        │
│ Flow rate: 0.25 mL/min           │
└─────────────────────────────────┘
              │
              ▼
┌─────────────────────────────────┐
│ Sr Elution : 100ml 2M HNO₃       │
│ Flow rate: 0.5mL/min             │
└─────────────────────────────────┘
              │
              ▼
┌─────────────────────────────────┐       ┌──────────────────────┐
│ Evaporation to dryness, adding 1 │──────▶│ Measurement of        │
│ ml of 5M HNO₃, dissolve in 25 ml │       │ ⁸⁷Sr/⁸⁶Sr isotope     │
│ pure water                       │       │ ratio on ICP-MS       │
└─────────────────────────────────┘       └──────────────────────┘
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**Fig. 2.** Separation of Rb from Sr on cation exchanger

## III. RESULTS AND DISCUSSION

### A. Study on the removal of calcium from sample solution using anion exchange chromatography

The analysis of petroleum drill-holes water samples showed that chemical composition of this sample type was rather complicated with high salt matrix, in which the average concentration of calcium was about 100 mg/L (ppm) but these values of rubidium and strontium were about 1 and 2 mg/L, respectively. It thus very much interferes with the mutual separation of small amount rubidium from strontium in that sample by ion chromatography due to the close distribution constants of calcium and strontium on cation exchange resin, which might cause the overlap on elution peaks of rubidium and strontium.

Previous report in literature [17] showed that the distribution constant of calcium on anionic exchanger much lower than that of strontium in alcoholic medium. Several cations can adsorb on strong base anion exchange resins, which contain the quaternary ammonium group with nitrate as counter-ion from solutions of nitric acid in alcohol [14] and the order of adsorption of these cations depends on the distribution coefficients [13, 14]. The phenomenon of adsorbed cations on anionic exchangers can only be obtained in solutions with highly polarized alcohol [17]. Hence, the mixture of 0.25 M HNO₃ in 95% methanol was selected for calcium separation on anion exchanger (Bio-rad AG1-X8) in our study. Mixed standard solutions with different ratios between Ca and Sr (1:1; 1:10; 1:100 and 1:1000) were respectively loaded onto the anion exchange columns. The eluted fractions (10 ml each) were collected with the flow rate of 0.5 mL/min for the determination of Ca concentration and that of 1 mL/min for Sr elution. Figures 3 and 4 below gave the examples of elution chromatographs on mutual separation of calcium from strontium at various concentration ratios.
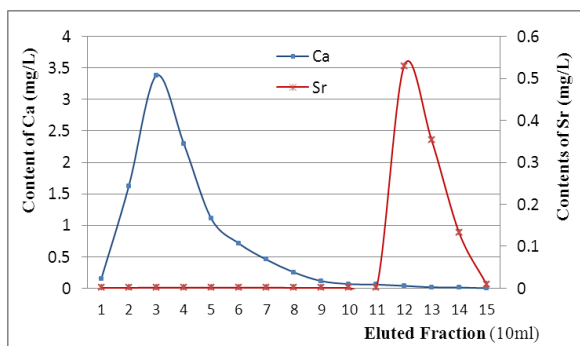


**Fig. 3.** Elution curve for mutual separation of Ca from Sr (Concentration Ratio between Ca and Sr = 10:1)
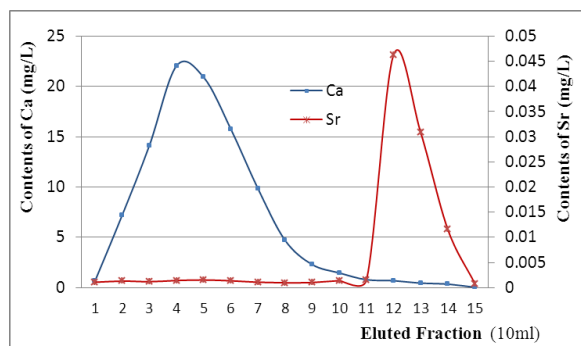


**Fig. 4.** Elution curve for mutual separation of Ca from Sr (Concentration Ratio between Ca and Sr = 1000:1)

Calcium and strontium in all four cases were well separated from each other when the elution was taken part with 0.25 M $HNO_3$ in 95% methanol at gradient flow rate (see Fig.1). However, a small amount of calcium in peak tailing exists in some early Sr eluted fractions at the cases of high ratios between Ca and Sr such as 100:1 and 1000:1. With 1:1 and 10:1 ratios, calcium was completely separated from strontium after 10 fractions of elution (100 mL). The recovery of strontium in all cases was about 98%. This result is similar to other study with different anion exchangers [13,14,17].

The separation test was also carried out with a mixed solution of 100 ppm Ca, 1 ppm Sr, 1 ppm Rb under the same conditions in order to learn about the rubidium removal. The following figure performs the result. The recovery was calculated according to the content of each element in eluted solution and the result was shown in Table I.
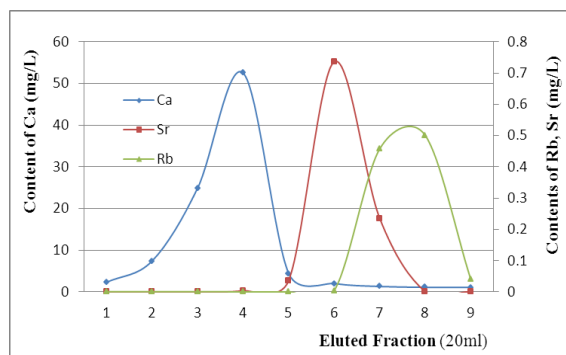


**Fig. 5.** Elution curve of a mixed solution

As can be seen in Fig.5, the elution peak of Rb appeared latter than that of Sr in the same elution condition. The present finding is somewhat different to the former study [13] when other alkali metals were separated from mixed elements sample at higher flow rate and lower $HNO_3$ concentration.

**Table I.** Separation efficiency and recovery of elements

| Elem. | Total amount (mg/L) | Content in eluted solution (100 ml) (mg/L) | Content remained in column (mg/L) | Separation Efficiency (%) | Recovery (%) |
|---|---|---|---|---|---|
| Ca | 100.64 | 93.33 | 10.10 | 92.74 | 102.77 |
| Rb | 0.999 | 0.054 | 0.95 | 94.58 | 99.16 |
| Sr | 0.998 | 0.043 | 0.95 | 95.50 | 98.92 |

The data in Table II show that the removal of calcium from studied sample reaches rather high efficiency after 5 fractions (100 mL) of elution, and the next 4 eluted fractions (80 mL) contains almost Sr and Rb, which will be used for the separation of Rb on cation exchanger.

**B. Study on the removal of rubidium from strontium using cation exchange chromatography**

Mixed standard solution of rubidium and strontium in 0.5 M $HNO_3$ medium (1ppm of each element) was loaded onto the cation exchanger column. The elution of mutual rubidium from strontium was carried out under gradient $HNO_3$ concentration (1.0 M and 2.0 M) solutions at the rate of 0.25 and 0.5 mL/min for Rb and Sr, respectively. The elution curves for these elements were shown in below figure.
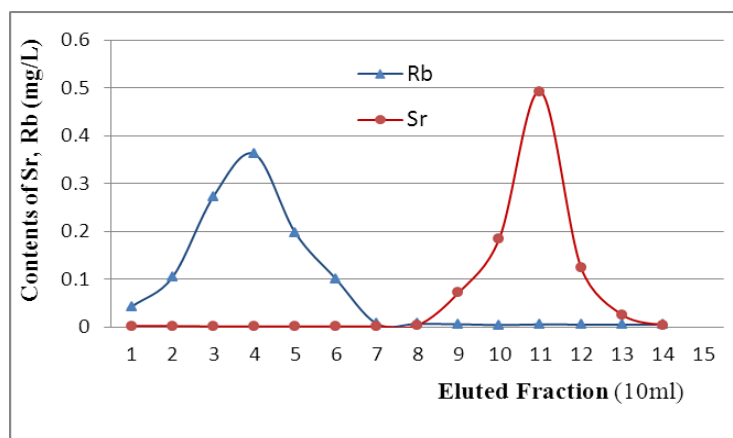
**Fig. 6.** Elution curves of Rb, Sr under gradient conditions (1M $HNO_3$ within first 7 fractions, 2M $HNO_3$ for next 7 fractions)

As can be seen from Fig. 6, rubidium could well be separated from strontium with 1.0 M $HNO_3$ eluant at the low flow rate as 0.25 mL/min. The faster elution would remove small amounts of strontium that cause the lower separation efficiency and recovery. Under this condition, the recovery of rubidium was quantitatively over 99%. On the other hand, the elution of strontium was successful with using 2.0 M $HNO_3$ eluant at 0.5 mL/min flow rate and the recovery nearly completed. That is the reason why the gradient conditions of eluant concentration and flow rate of elution should be applied for the quantitative removal of the isobaric interference caused by Rb on the determination of strontium isotope ratio.

However, the small amount of calcium remained in sample solution at this stage was also considered when using cation chromatography technique for removal of Rb interference. The mixed solution containing 1.5 ppm Ca, 0.5 ppm Sr and 0.25 ppm Rb was loaded on the cation exchanger column. The elution was carried out under the same condition as above mentioned. The elution curve is shown in Fig. 7.
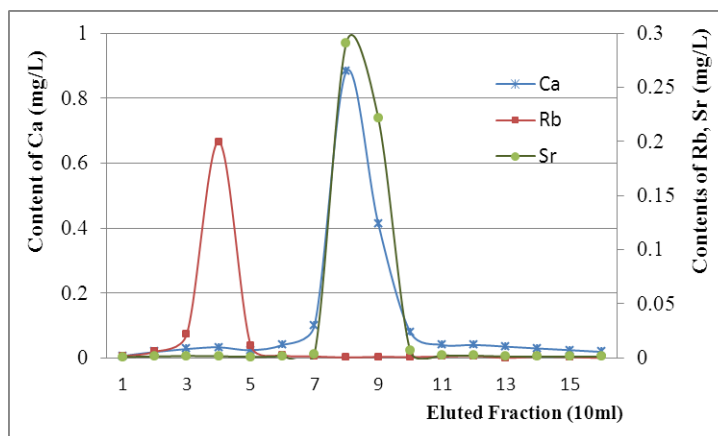


**Fig. 7.** Elution curves of Rb, Ca and Sr under gradient conditions

The elution peaks from Fig. 7 depict that almost Ca presented in mixed solution was eluted together with Sr meanwhile Rb was completely removed within the first 7 eluted fractions. It confirms that the small amount of Ca in sample solution does not interfere with the quantitative separation of Rb, and that the isobaric effect caused by Rb can be completely removed.

## C. Validation of separation procedure

The recovery of strontium through separation procedure was studied by using Sr isotopic standard solutions, in which total concentration of strontium was fixed as 100 µg/L but the isotope ratio $^{86}Sr/^{87}Sr$ was various with the addition of a certain amount of $^{86}Sr$ isotope standard solution in to the natural Sr standard solution (see Table II) in a matrix (100 mg/L Ca and 50 µg/L Rb). The separation procedure was repeated for all synthesized samples under the same conditions as reported above. The results were given in Table II.

**Table II.** Recovery of Sr in synthesized samples

| Total Sr (µg/L) | Spiked $^{86}Sr$ (µg/L) | $^{86}Sr/^{87}Sr$ (by theory) | $^{87}Sr$ found (µg/L) | Total Sr found (µg/L) | Recovery (%) |
|---|---|---|---|---|---|
| 100 | 0 | 1.40857 | 7.80047 | 103.605 | 103.61 |
| 90 | 10 | 2.98187 | 6.35607 | 90.801 | 100.89 |
| 80 | 20 | 4.90220 | 5.72470 | 81.781 | 102.22 |
| 60 | 40 | 10.4921 | 4.40357 | 62.908 | 104.85 |
| 40 | 60 | 21.9123 | 2.92630 | 41.804 | 104.51 |

The data in Table II show that the recovery of strontium for whole cases (from 100.89% to 104.85%) seemed reliable for Sr analysis through the long procedure of mutual separation. It is thus suitable for the application of Sr isotopic ratio analysis in petroleum drill-holes water samples.

The accuracy of separation method was studied by the use of NIST SRM 987 (SrCO$_3$) isotopic standard reference material. The isotopic standard solution was prepared by dissolving a certain amount of standard reference material in dilute HNO$_3$ and a small portion of this solution containing 100 µg/L (as total Sr concentration) was loaded on anion

exchanger column. Whole separation procedure was carried out for this standard sample and the final elution fractions were collected for the determination of $^{87}Sr/^{86}Sr$ isotopic ratio on ICP-MS. Five replicates of experiment were done and the results were given in Table III.

**Table III.** Analysis of the standard sample SRM 987

| $^{87}Sr/^{86}Sr$ certified value | $^{87}Sr/^{86}Sr$ analyzed value | Absolute Error (%) |
|---|---|---|
| 0,71034 ± 0.00026 | 0.71453 ± 0.00836 | + 0.59 |

The relative correctness of analyzed value is 99.41% to that of the certified value for NIST SRM 987, which seems reasonable in

this study due to the contribution of signal measurement deviation of instrument to the error. That is also the reason why the more precision of the isotopic analysis can be obtained from MC-ICPMS [1].

## D. Analysis of petroleum drill-holes water samples

Petroleum drill-holes water samples were pretreated to remove the oil and suspended solid particles as denoted in procedure. The chemical composition of sample was analyzed using ICP-MS in order to preliminary classification of the solution matrix. The sample solution was diluted with pure water as needed before applying the separation procedure, followed by the isotopic ratio measurement on ICP-MS. The analytical data were given in Table IV together with total concentrations of Rb and Sr and relative standard deviation (RSD) of $^{87}$Sr/$^{86}$Sr isotopic ratio measurement.

**Table IV.** Analysis of petroleum drill-holes water samples

| Sample Code | Total Rb (µg/L) | Total Sr (µg/L) | $^{87}$Sr/$^{86}$Sr Isotopic ratio | |
|---|---|---|---|---|
| | | | Value | RSD (%) |
| EW02 | 36.6 | 989.8 | 0.70715 | 1.17 |
| EW05 | 45.3 | 3502.5 | 0.70734 | 2.78 |
| EW17 | 34.5 | 1240.1 | 0.70699 | 1.52 |
| PW03 | 80.0 | 824.0 | 0.70686 | 1.45 |
| PW04 | 60.2 | 423.5 | 0.70639 | 1.63 |
| PW14 | 120.0 | 1980.0 | 0.70674 | 2.46 |

Analytical results showed that, $^{87}$Sr/$^{86}$Sr isotopic ratio of petroleum drill-holes water samples was various with different sample matrix. These data relatively agreed with those, which were obtained from similar study [4] of drill-holes water in Vietnam Petroleum Institute, where the water samples were pretreated and the analysis of $^{87}$Sr/$^{86}$Sr isotopic was carried out by TIMS in over-sea laboratory.

## IV. CONCLUSIONS

The removal of calcium in matrix from petroleum drill-holes water samples and the elimination of rubidium isobaric interference with strontium isotopic ratio determination were successfully achieved by using ion exchange chromatography. The anion exchange resin (Bio-Rad AG1X8 200-400 mesh) was employed for the separation of major calcium by 0.25 M HNO$_3$ in 95% methanol with Sr recovery over 99%. The mutual separation of rubidium and strontium by gradient conditions of HNO$_3$ concentration and flow rate on cation exchanger (Bio-Rad AG50X8 200-400 mesh) was taken part with nearly complete Sr recovery. The validation of method was also studied using isotopic standard solution and standard reference material with relative correctness of the analyzed value about 99.41% to the certified value of NIST SRM 987 reference material. The analytical procedure was then applied for the determination of $^{87}$Sr/$^{86}$Sr isotopic ratio in

petroleum drill-holes water samples using ICP-MS, which would contribute to the development of an analytical method to supply the demand of petroleum research and exploitation in Vietnam.

## ACKNOWLEDGEMENT

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