

Testing the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio measured by ICP-MS as a tracer for inter-well investigation in oil reservoirs

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Abstract. The use of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio has been tested as a natural tracer for inter-well tests in oil reservoirs using standard mass-spectrometry equipment. Such an application can have a special interest to offshore oil fields. Strontium is a relatively abundant component of the dissolved solids in seawater and exhibits a rather constant concentration worldwide. It is also present in the formation water in oil reservoirs in a different concentration and with different isotopic signatures. Hence seawater injection procedures in secondary recovery of the oil can disturb the original isotope ratio in a way that may reflect what is happening inside the reservoir. This study is concerned with the breakthrough of the injected water in production wells. The capability of a single collector quadrupole internal coupled plasma mass spectrometer for detecting the small variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is evaluated. The strategy for dealing with isobaric interference is addressed. The isotope ratio approach is compared with the straightforward use of strontium concentration as the tracer.

1. INTRODUCTION

An interesting characteristics exhibited by strontium isotopes is the spatial variation in their relative abundances. The ^{87}Sr isotope is generated by decay of ^{87}Rb (half-life: 4.75×10^{10} a) present in rocks, and consequently is richer in waters that have been in contact with them for long periods of time. The Sr^{2+} ion can replace Ca^{2+} in such rock minerals as carbonates, sulphates, and feldspars, thus participating in the same interactions with water and being either dissolved or becoming isotopically equilibrated through the solid surface of sediments. Likewise the geochemistry of the ^{87}Rb parent is akin to that of potassium. Hence potassium rich rocks have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Thus, feldspars and micas dissolved from carbonate rocks may be much older than the matrix in which they were incepted and have had time to attain quite higher radiogenic ^{87}Sr concentrations.

These chemical affinities are reflected in the higher Sr isotope ratios characteristic of groundwater. It qualifies this specific isotope ratio to act as an apt tracer for studying groundwater dynamics. They actually have been used for defining the origin of groundwater salinity [1]. In particular, formation surface waters may attain high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios depending on the type of rock they have contacted throughout the entire lifetime of an oil reservoir.

On the other hand ocean waters have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios inasmuch as they do not have that intimate contact with rocks. Besides ocean waters display a rather constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709020, this being due to their relatively short mixing time compared with their renewal time (ca. 10^3 a and 4×10^6 a, respectively).

In contrast, this isotope ratio in oil field waters spans the range 0.707 – 0.730, whereas strontium concentrations vary from zero up to 7200%, the average in seawater being about 8%.

This isotope ratio can be used as a tracer to inform on the reservoir behaviour. Specifically it may be utilized to determine the breakthrough of the injected water in the production wells during secondary oil recovery in offshore

reservoirs in which seawater is used as the oil displacing fluid. Nothing has to be added; the injected water traces itself.

This naturally occurring stable tracer methodology has been proposed (and even patented) about two decades ago [2]. Despite its obvious advantages, the information output it provides is limited compared to other tracers, it requires a more sophisticated measurement analytical equipment and, depending on local conditions, may require a rather high analytical precision. Besides, isobaric overlap between ^{87}Sr and ^{87}Rb has to be dealt with. Registers of its application cannot be easily found in the literature. The main purpose of the present work was to evaluate its applicability especially by tracer teams not equipped with high precision analytical facilities. Specifically a practical ion-exchange separation step and a conventional single collector quadrupole internal coupled plasma mass spectrometer (SC-ICP-QMS) were assessed for this task and compare with a straightforward natural tracer approach.

2. FUNDAMENTALS

2.1. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer

Whenever values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the oilfield formation water and injected seawater differ by a magnitude that can be unmistakably resolved by the mass-spectrometer to be used, they can be used to trace secondary recovery. The values measured at the water fraction from samples collected in a production well will exhibit a characteristic profile. The samples collected shortly after seawater injection will have an isotope ratio that is representative of the formation waters. Given that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is normally higher in the oilfield water, when the pumped seawater reaches the sampled well there will occur a gradual decrease in the measured isotope ratios down to a level corresponding to pure seawater.

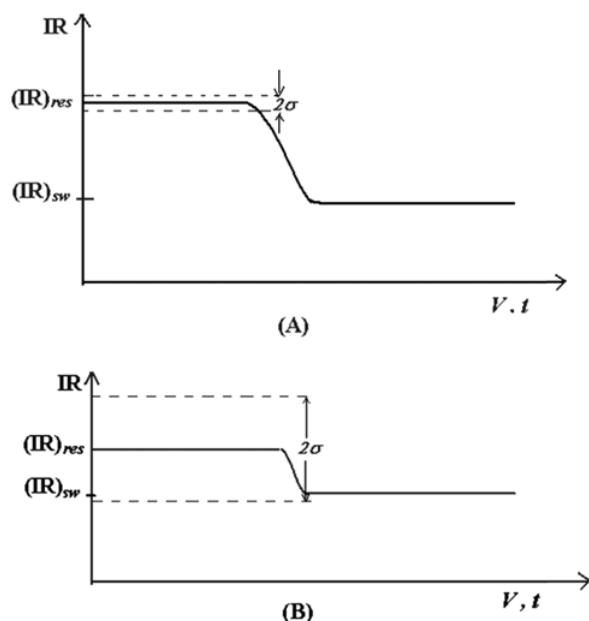


Figure 1. Isotope ratio tracer breakthrough record [3].

This means that the whole breakthrough curve will be sampled. This is illustrated in Figure 1.

The schematic plots of isotope ratio (IR) vs. injection time (t) or injected volume (V) show that at the start of the secondary recovery the reservoir (res) $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is measured. After a certain time breakthrough occurs and the ratio falls down to that corresponding to seawater (sw). Two cases are considered in the illustration. Figure 1A depicts a favourable situation in which production water and seawater isotope ratios greatly differ and the measurement equipment is very precise as indicated by the broken lines spanning two standard deviations. In the extreme case of Figure 1B the situation is reversed and the divergence in the two isotope ratios is completely engulfed by the large uncertainty in the measurement. The breakthrough cannot be defined and another tracer would be required. Hence highly precise equipment such as the multi-channel mass spectrometer (MC-ICP-MS) would be the best choice. Also, since formation water isotope ratios may have different magnitudes in different parts of the reservoir, a thorough sampling campaign should be performed prior to the injection of seawater.

A detailed discussion of analytical precision and its influence on accurate definition of the breakthrough is given by Smalley et al. [3]. The point to be stressed here in this connection is that the inverted sigmoid-like curve recording the breakthrough is the (negative) integral of the response to a tracer injected with the seawaters a pulse. Thus the breakthrough curve indicates not only the arrival and duration of the injected water front; it contains the whole information regarding the dynamics of the reservoir under secondary recovery. Of course this can only be recovered provided the favourable situation of Figure 1A prevails, which points to the importance of high precision and accuracy of the mass spectrometric measurement in any case.

Thermal Ionization Mass Spectrometers (TIMS) offer the highest accuracy and precision (relative standard

deviation down to about 0.005%) in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements. However, besides being costly, TIMS instruments require tedious sample pre-treatment procedures. Sector field instruments equipped with multi-collector detection systems (MC-ICP-MS) get near to the precision attained by TIMS but the cost of the equipment is considerably higher.

The precision of conventional SC-ICP-QMS instruments is of the order of $\geq 0.1\%$. Even though far from attaining the high precisions of TIMS and MC-ICP-MS do not require elaborate sample preparation and are introduced into the instrument via a nebulizer running at atmospheric pressure. Their quite lower cost and widespread availability makes them much more accessible to small institutions and academies. They may thus be a viable alternative whenever ultra-fine resolution levels are not exacted.

2.2. Isobaric overlap

Since radiogenic ^{87}Sr is generated by beta-decay or ^{87}Rb ($^{87}\text{Rb} \rightarrow ^{87}\text{Sr} + e^- + \bar{\nu} + Q$) the members of the parent-daughter pair $^{87}\text{Rb}/^{87}\text{Sr}$ has the same atomic mass they will not be differentiated by the mass spectrometer. Hence the two nuclides are always found together. A satisfactory resolution of these nuclides requires a mass resolution in excess of 300,000 which is unattainable even to a conventional quadrupole based sector-field or time-of-flight ICP-MS. Some additional step must take on the burden of their previous separation in each sample.

A commercial modular device is available to automatically perform this task, a reaction cell that can be inserted in the ion path between the plasma source and the quadrupole analyser in an ICP-QMS. It consists of a flow chamber within which a gaseous reagent, methyl fluoride (CH_3F), converts the strontium ions Sr^+ into SrF^+ thus shifting the ^{87}Sr signal to $m/z = 106$ with a high yield whereas $^{87}\text{Rb}^+$ remains unaffected. It is reported that this separation warrants the use of ICP-QMS even to such demanding MS applications as geochronology, thus doing without TIMS utilization.

The firm Perkin Elmer Sciex Instruments manufactures a reaction cell (Dynamic Reaction Cell[®]-DRC[®]) with this ability [4] that can be fitted to the ELAN ICP-MS model. However the cost of this module plus the methyl chloride may not be advantageous to small laboratories that perform ^{87}Sr analyses on an intermittent basis. More recently Perkin Elmer introduced a new ICP-QMS model (NexION 300) which incorporates a versatile combination of collision and reaction cell modes.

The alternative to instrumental separation of ^{87}Sr and ^{87}Rb is the proven ion-exchange chromatography. Other less competitive possibilities are provided by dissolution via fuming HNO_3 (only historic importance), liquid-liquid solvent extraction, chromatographic extraction, and selective precipitation [5].

The most widely used technique for strontium and rubidium separation is cation-exchange chromatography and acid elution. The AG50W-X8 resin, of the classical crosslinked polystyrene - divinylbenzene type is the most used; it is a highly acidic cation-exchange resin

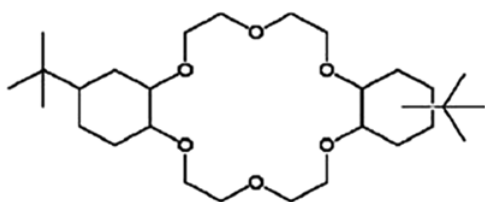


Figure 2. Crown ether in Sr spec resin.

composed of sulfonic acid functional groups attached to the copolymer lattice. Strontium is retained in this resin preferably to the other usual concomitants. Ideally rubidium should be completely extracted from the column before strontium is eluted. In practice however, if the rubidium concentration is too high a complete separation of these two elements is hard to attain. In this respect there is a similarity with the reaction cell. The ion exchange capacity, as informed by the manufactures is 1.7 meq/mL (74.8 mg Sr/mL).

More recently, selective extraction chromatography has become more frequently used for Sr/Rb separation [6]. This technique utilizes a solution of a crown ether in 1-octanol adsorbed in an inert substrate of a nonpolar aliphatic acrylic polymer to extract Sr^{2+} from nitric acid media. A commercially available selective resin (Sr spec[®], Eichrom Technologies) packed in micro-columns (<1 ml resin) is used. The technique adds the selectivity of solvent extraction to the dexterity of column chromatography. The structural formula of the crown ether 1.0M 4,4'(5')-di-*t*-butylcyclohexano 18-crown-6 is presented in Figure 2.

At a 1M concentration of the crown ether in the resin its exchange capacity is 8.9 mg Sr/ml, the highest capacity for alkaline and alkaline-earth metals. Besides, this resin permits a keen Ca/Sr separation, the selectivity varying with the HNO_3 concentration. The secret of this performance is the dimension of the negatively charged cavity inside the ring where the Sr^{2+} ion (132 pm ionic radius) fits in at ease.

Due to the slight incompleteness of that Sr/Rb separations, use of standards is always required to check separation yield and make due corrections. When using a standard the ^{86}Sr and ^{88}Sr isotopes (9.86% and 82.6% isotopic abundances, respectively) can be used as the MS reference signals (due to its much higher abundance, the ^{88}Sr signal is measured with the highest precision). Since the $^{86}\text{Sr}/^{88}\text{Sr}$ ratio is constant in nature, the measured $^{87}\text{Sr}/^{88}\text{Sr}$ ratio is directly converted to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

3. EXPERIMENTAL

3.1. Instrument

A Perkin Elmer ELAN DRC-e ICP – mass spectrometer installed at CDTN has been tested for measuring the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, besides determining the concentration of Sr, Rb, Ca, and other elements of interest.

The quadrupole analyzer consists of 4 cylindrical bars of 20 cm length and 1 cm diameter, allowing mass spanning in the $1 < m/z < 240$ range in less than 0.1 s.



Figure 3. ELAN DRC-2 ICP-QMS and automatic sampler at CDTN.

3.2. Materials

Solutions, standards, and dilutions were prepared with ultra-pure Milli-Q water (18.2 MΩ cm), distilled HCL p.a., and trac-select $\text{HNO}_3 \leq 0.5 \mu\text{g/Kg}$ in Rb and Sr.

Argon gas 99.999% purity was used for the plasma, sample nebulisation, and as auxiliary gas.

Multi-element standards, N8125030 in HNO_3 2%, and N8125031 recommended by Perkin Elmer were used for daily performance evaluation and for lens calibration, respectively.

Mass discrimination effect was corrected the NIST SRM 987 (SrCO_3 , 99%) certified standard with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio = 0.71034 ± 0.00026 . Accuracy in Sr and Rb concentration measurements were checked with the NIST SRM 1643e ($\text{Sr} = 323.1 \pm 3.6 \mu\text{g/L}$, $\text{Rb} = 14.14 \pm 0.18 \mu\text{g/L}$) and NRC-CNRC SLRS-3 ($28.1 \mu\text{g Sr/L}$) standards.

Ion separations were carried with both Dowex AG59WX8-400 resin and Eichrom Technologies Sr spec SR-C50-A (100–150 μm) resin packed in 2 mL columns. A NaOH/EDTA solution (0.1M/1M) was used to regenerate the Sr spec resin.

3.3. ICP-MS analytical methodology

The linearity interval was verified and the accuracy of the elemental concentration measurements was checked with the standards.

The accuracy of the isotopic ratio measurement is automatically checked by the instrument using a built in software. A correction factor (f) is calculated taking into account the nominal ratio in the standard (S_i) and the measured ratios in the reference standard (S_n) and in a blank (S_j):

$$f = S_n[(S_i - S_j)/S_i]. \quad (1)$$

Using a 100 $\mu\text{g/L}$ solution of the SRM 987 SrCO_3 standard in HNO_3 0.1M the optimized acquisition condition in the MS instrument was obtained varying the operational

Table 1. Optimization of operational parameters for isotope ratio measurement.

Dwell time (ms)	50	75	100	200	250	300
Scans/reading	40	40	60	60	60	60
No. of scans	1	1	3	3	2	2
Replicates	6	6	6	6	6	6
RSD (%)	.475	.475	.260	.146	.132	.346
$^{87}\text{Sr}/^{86}\text{Sr}$	0.712	0.712	0.713	0.710	0.710	0.710

Table 2. Data acquisition parameters.

Parameter	Value	Parameter	Value
Plasma power	1400 W	Dwell time	250 ms
Ar flowrate in plasma	15 L min ⁻¹	Readings	180
Lens voltage	8.5 V	Replicates	6
Pulse phase voltage	1000 V	Dead time	60 ns
Discriminator threshold	19	Detector mode	dual

parameters to minimize the relative standard deviation (RSD). This is shown in Table 1.

A noticeable improvement can be noticed for dwell times in between 200 ms and 250 ms. The limiting factor for the improvement of RSD is the time spent in measuring the isotope ratio when output is a critical requisite.

The operational parameters adopted for the present study are summarized in Table 2.

Under these conditions, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in a 100 $\mu\text{g/L}$ solution of the SRM 987 standard was 0.71038 ($\sigma = 0.00301$, RSD = 0.42%). The average value of all the results from measurements performed during the tests in standard solutions was 0.7112 ($\sigma = 0.003179$, RSD = 0.45%). These RSD values are in agreement with those obtained when using similar equipment; the literature it is found that $0.10\% < \text{RSD} < 0.50\%$.

4. RESULTS AND DISCUSSION

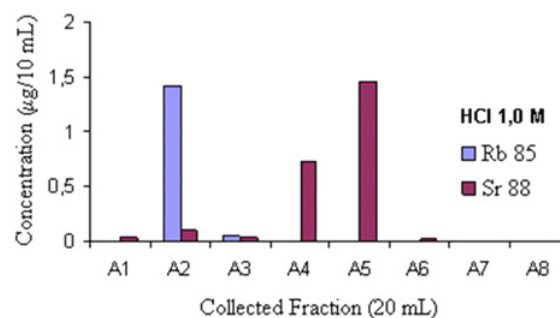
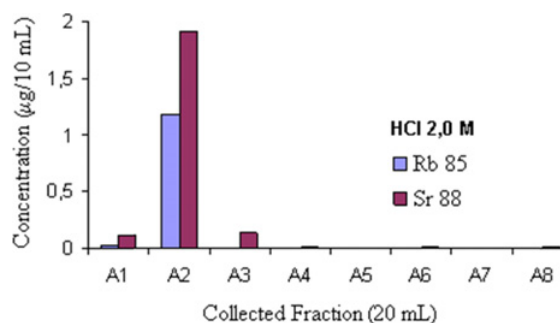
4.1. Rb/Sr separation by ion exchange

4.1.1. Separation by ion exchange

It was known beforehand that the Dowex AG50WX8-400 resin would perform poorer than the Sr spec resin. Nonetheless tests were carried with the AG50WX8-400 in order to measure the performance and provide a basis for cost/benefit analysis (Sr spec is not as available as AG50WX8-400; besides the cost procurement from abroad may take some time). Preparing the column is a hindrance; obtaining a homogeneous column packing is not an easy task.

Both the NIST and NRC-CNRC standards were used in the tests. The tests mainly tried to define the influence of the HCl eluent concentration on the separation of Rb and Sr. Concentrations down from HCl 6M were tested. Figures 4 and 5 plainly demonstrate the influence of the eluent concentration.

A reasonable separation was achieved with HCl 1M, but failed with HCl 2M (higher concentrations produced even worse results). However, there is still some Rb mixed

**Figure 4.** AG50WX8 resin eluted with HCl 1M.**Figure 5.** AG50WX8 resin eluted with HCl 2M.**Figure 6.** Sr spec column.

with Sr in the first fractions. Sr recoveries of 99.665% were obtained.

The pre-packed 2 mL columns containing Sr spec resin has been used for chromatographic extraction. The work has been developed stemming from the road map proposed by Brach-Papa et al. [7] and optimized for the conditions at the CDTN laboratory.

4.1.2. Optimization of the chromatographic extraction

Figure 6 stresses the dimensions of the pre-packed Sr spec column.

Solutions with Sr and Rb in the proportions 1 : 2, 1 : 1, and 2 : 1, prepared from the Sr NIST SRM 987 standard and from the Rb Perkin Elmer standard to be used in the tests with the Sr spec resin. These tests were carried passing the solutions once and twice in the column (one and two steps tests).

In the first step the test solution was eluted with 20 mL of HNO₃ 8M at <1 mL min⁻¹ followed by 10 mL of ultra

Table 3. Sr recovery and Rb left over after separation.

Standard solution	⁸⁵ Rb (µg/L)	⁸⁸ Sr (µg/L)	Sr recovery (%)	Rb residual (%)
SP12 – 1 step	28.2	985.8	93.4	1.4
SP11 – 1 step	18.4	965.8	91.5	1.8
SP21 – 1 step	6.3	1896.8	89.8	0.6
SP12 – 2 steps	1.2	897.3	85.0	0.06
SP11 – 2 steps	2.6	663.6	62.8	0.26
SP21 – 2 steps	1.9	1391.7	65.9	0.19

Table 4. Isotope ratios in solutions used in Sr spec resin.

Solution	[Sr] (µg/L)	[Rb] (µg/L)	⁸⁷ Sr/ ⁸⁶ Sr	RSD (%)
SP	264	-	0.71287	0.53532
SP12	1056	2000	0.85876	6.15919
SP11	1056	1000	0.78622	2.13206
SP21	2112	1000	0.74997	2.25873
SP12-1P	1056	2000	0.71336	0.60739
SP11-1P	1056	1000	0.71470	0.55241
SP21-1P	2112	1000	0.71655	0.88807
SP12-2P	1056	2000	0.71006	0.58038
SP11-2P	1056	1000	0.71271	0.77072
SP21-2P	2112	1000	0.71567	0.41026

pure water to remove the Sr. This eluate was evaporated and the residue dissolved in 5 mL of HNO₃ 8M.

This solution was reintroduced in the column in the second step, which just repeated the operations of the first step.

Results of Sr recovery and Rb contamination after these steps are shown in Table 3.

The isotope ratio of the solutions prepared in the three described proportions was measured in the ICP-MS. These measurements were done before the solutions suffered separation, after the first step, and after the second step of the separation, in order to verify if and how much the presence of Rb in the three different proportions would affect the isotope ratio measurement. The results of these measurements are listed in Table 4.

The SP designation means that the first solution is the NIST Sr standard. The 1P and 2P suffixes stand for one and two separation steps. Absence of suffix indicates that the solution has not been submitted to separation. Isotope ratios determined following chromatographic extraction are shown in Figure 7.

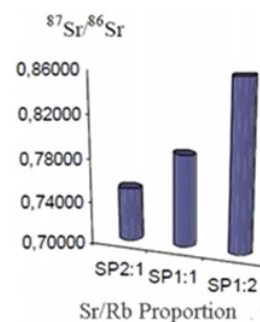
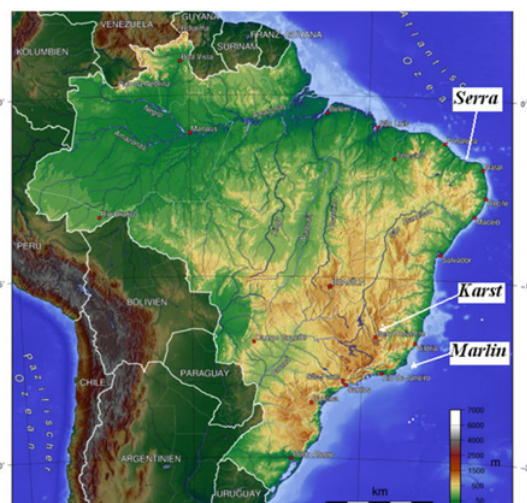
The measured isotopic ratio values of solutions SP12, SP11, and SP21 did not change after one and two steps. Besides, the recovery lowered when two steps were processed. It was thus decided to proceed with just one step in subsequent work.

The pre-packed columns were regenerated 10 mL of a EDTA 1M – NaOH 0.1M mixture followed by 10 mL of ultrapure water. This procedure was repeated at most twice inasmuch as after the third regeneration the column sorption efficiency falls below 90%. A further advantage of this resin is that it requires only two eluents (water and nitric acid), significantly simplifying the procedure and taking less time. Once the separation has been tested,

Table 5. Groundwater from karstic region

Sample	Sr (µg/L)	Rb (µg/L)	pH	Conductivity (µS/cm)
Lagoa Santa	1.6	204	8.2	326
Jaboticatubas	1.5	564	6.0	143

Sample	⁸⁷ Sr/ ⁸⁶ Sr	σ	RSD (%)
Lagoa Santa	0.71093	0.0041	0.57
Jaboticatubas	0.71140	0.0049	0.69


Figure 7. Sr/Rb proportions and respective isotope ratios.

Figure 8. Map of Brasil showing sampling locations.

the method was used for the analysis of environmental samples.

4.2. Application to environmental samples

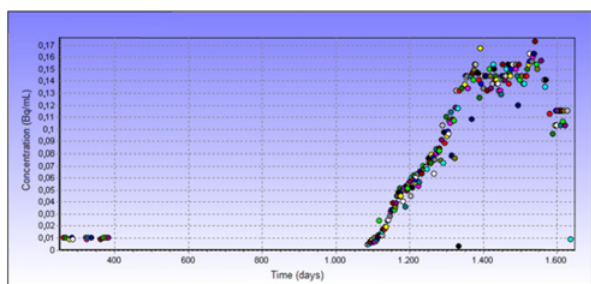
4.2.1. Rb/Sr in karst waters

Two samples of groundwater from a karstic region at Lagoa Santa and Jaboticatubas, about 40 Km north of Belo Horizonte. The locations of the collected samples are indicated in the map in Figure 8. Analytical results are summarized in Table 5.

Following the measurement of each third sample a new calibration of the spectrometer was performed to check the steadiness of the correction factor with time.

Table 6. Oilfield produced waters.

Sample	Rb ($\mu\text{g/L}$)	Sr ($\mu\text{g/L}$)	$^{87}\text{Sr}/^{86}\text{Sr}$	RSD
Mrl-1	171	9,638	0.70882	0.32
Mrl-2	166	15,468	0.70969	0.26
Mrl-3	189	14,508	0.71448	0.33
Mrl-4	248	27,545	0.71353	0.26
Mrl-5	172	7,872	0.70758	0.13
Mrl-6	190	20,471	0.70553	0.22
Mrl-7	197	21,432	0.71081	0.36
Mrl-8	183	20,501	0.70689	0.15
Mrl-9	190	21,464	0.71164	0.50
Mrl-10	184	21,777	0.70840	0.11
Mrl-11	187	20,341	0.70743	0.19
Mrl-12	179	19,876	0.70774	0.33
Mrl-13	159	8,428	0.70576	0.18
Mrl-14	204	21,155	0.70608	0.58
Serra	58	1,654	0.71071	0.20

**Figure 9.** Tritium breakthrough observed at Mrl-84 well.

4.2.2. Rb/Sr in oilfield produced water

The samples used in these measurements had been previously collected during an interwell tracer test in which tritium had been pulse injected into two offshore oilfields: Marlin and Serra in the southeast and northeast coast of Brasil. The results are recorded in Table 6, where the samples from Marlin oil field are identified by the prefix Mrl.

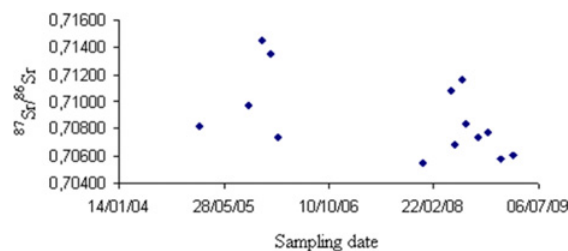
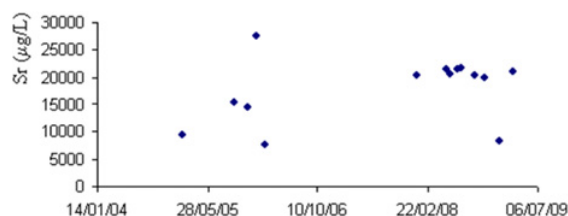
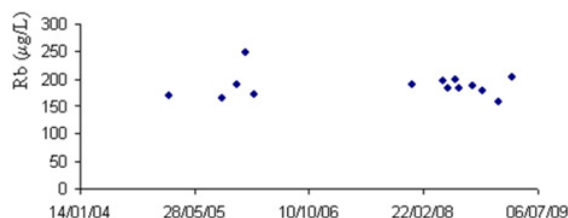
The fourteen samples from the Marlin oilfield were collected at the same producer well but at different moments during the tritium monitoring campaign. This was a quite long experiment. It took nearly three years for the tritium to arrive at the monitored well, and then sixteen more months for the peak to pass by.

Two more months after that sampling was discontinued as the contractor would not bear having his personnel carrying an additional task and handling a supposedly dangerous material for a so extended period.

The results of the tritium injection are plotted in Figure 9.

Out of the multitude of collected samples, fourteen were selected, five of them collected before the tritium signal arrived, and the remaining nine samples at different times during the period in which the tritium activity at the well was rising.

Since this did not coincide with the breakthrough of the injected ocean water following the start of secondary

**Figure 10.** $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in samples collected at well Mrl-84.**Figure 11.** Strontium concentration at well Mrl-84.**Figure 12.** Rubidium concentration at well Mrl-84.

recovery, the results are not supposed to define the actual shape of the breakthrough.

The test was rather intended to detect any trends during this lengthy period and observe if this technique was sensitive enough to reveal them. The ratio results are plotted in Figure 10.

There is too much scatter, but it seems to be a trend towards decreasing ratios, whereas the trend of the Sr concentration (Figure 11) is towards a slight increase.

It is known fact that formation waters from different parts of the reservoir can have distinct compositions; so different formation waters could have been pumped in the two periods analyzed.

Differently from strontium, the rubidium concentrations scarcely varied throughout the sampled period, as evidenced in Figure 12. The Rb concentration in seawater is uniform and amounts to $120 \pm 10 \mu\text{g/L}$ [8]. Hence the Rb content in the produced water is significantly higher, indicating that there are Rb containing rocks in the reservoir and that they are interacting with the formation waters.

The strontium content of the produced water is also above seawater concentration, this last being also quite uniform at $8, 100 \mu\text{g/L}$ [9]. This is consistent with the Rb concentration, supports the utilization of radiogenic ^{87}Sr as a natural tracer for these waters.

Even though the Sr concentration did not show a remarkable variation there is some correlation between the trends in the variations of Sr and Rb, as indicated in Figure 13. These findings demonstrate that the whole ensemble of results is consistent.

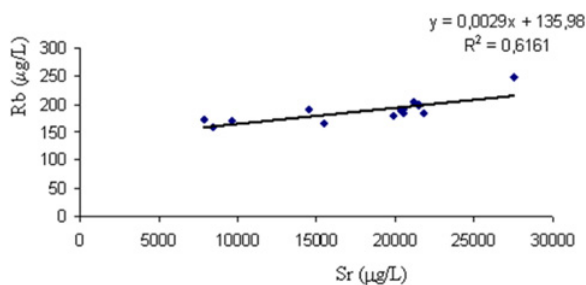


Figure 13. Correlation of Sr and Rb variations.

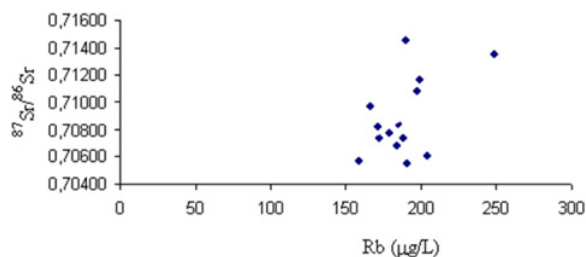


Figure 14. Strontium concentration at well Mrl-84.

In principle an increase in the Rb content of the produced water should mean more radiogenic ^{87}Sr and a corresponding increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

However no correlation could be detected between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the Rb content in the samples (Figure 14), however much the trend seems to be visually in the right way.

5. CONCLUSIONS

The possibility was tested of using the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio as a tracer for injected seawater breakthrough in oil reservoirs under secondary recovery using a conventional single detector ICP-MS. The average standard deviation obtained with the NIST SRM 987 standard in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measurements with this equipment was $\text{RSD} = 0.45\%$.

The methodology was applied in groundwater from karstic regions and in produced waters from offshore production platforms.

Due to isobaric overlap, separation of rubidium and strontium is a pre-condition for mass spectrometric measurements.

The Sr recovery in the eluate with the AG50WX8-400 and HCl 1M resin was 74.2%. This increased to over 90% when Sr spec was used. Besides, the procedure is much simpler using the late (no column preparation, only two elutions required).

The precision of the method as indicated by the range of standard deviations obtained throughout the work, $0.5\% < \text{RSD} < 0.69\%$, average value $\text{RSD} = 0.45\%$ would not qualify it as applicable to the samples studied,

given the small difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured in the produced water from the tested oilfield and in seawater (0.7111 and 0.7092, respectively). This would require that the difference between the isotopic ratios of seawater and produced water were at least $2\sigma = 0.0064$. This means that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the produced water should be ≥ 0.7156 .

According to Smalley and Raheim [3] the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in oilfield waters varies in the range 0.707 – 0.730. Hence it is admissible that SC-ICP-IQMS instruments might be used to trace the variations in the Sr isotope ratio during the breakthrough of injected seawater. (Actually the samples used did not reflect the seawater breakthrough; they only detected changes in the isotope ratio during part of a well-to-well radiotracer test. The formation water was already diluted by seawater at the time).

A technique for improving both accuracy and precision of isotope ratio measurements with ICP-MS instruments has been reported by Al-Ammar and Barnes [10]. Corrections were obtained by measuring several internal reference isotope ratios simultaneously with the analyte; precision was improved to 0.05% and accuracy to 0.02%, using an instrument identical to the one in which the present work was carried. The authors intend to use this technique in the near future.

One other possibility to be explored is the use of the Sr concentration itself. Strontium in seawater shows a uniform concentration of 7.74 mg/L. This value is precisely measured by an ICP-MS and can be unmistakably contrasted to those of produced waters found in this work, of the order of 20 mg/L.

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