

1 **CaSO₄ SOLUBILITY IN WATER-ETHANOL MIXTURES IN THE PRESENCE**
2 **OF SODIUM CHLORIDE AT 25°C. APPLICATION TO A REVERSE OSMOSIS**
3 **PROCESS.**

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11 **Abstract**

12 Nowadays, the most common way to desalinate seawater is by reverse osmosis. As the
13 degree of conversion during this process increases more freshwater is recovered from
14 the feedwater. As a result, the salt concentration in the feed increases up to a point
15 where the solubility limit could be reached. Experimentally, it is known that adding an
16 organic substance such as ethanol to salty water induces salt precipitation. This work
17 investigated the solid-liquid equilibrium of the system water-ethanol-NaCl-CaSO₄ at
18 25°C. Results show that as the ethanol content is increased CaSO₄ solubility decreases.
19 On the other hand, brine from the reverse osmosis plant at the University of Alicante
20 was treated with ethanol to precipitate calcium sulfate and produce brine containing less
21 calcium and sulfate. The treated brine was analyzed and its calcium content was
22 compared with the predicted value based on the experimental data. The results suggest
23 that it is possible to use ethanol to precipitate the salts from brine in order to obtain a
24 higher degree of conversion in a reverse osmosis process. The obvious limitation of the
25 method is the cost of recovering the ethanol by separation.

26 **Keywords**

27 Ethanol, precipitation, reverse osmosis, higher conversion, CaSO₄, solubility

28 **1. Introduction.**

29 Desalination of seawater or brackish water is a technique used in regions facing water
30 scarcity in order to increase the amount of freshwater available for human consumption.
31 This avoids alternatives such as transfers from other regions that might involve greater
32 environmental impacts.

33 The term desalination is wide-ranging and encompasses a number of processes for
34 obtaining freshwater. Nowadays, the most common way to desalinate seawater is by
35 reverse osmosis (RO) (RO membrane plants constitute 80% of all desalination plants
36 worldwide) [1] since this method is the least energy intensive (about 2 kW/m³) [2].
37 Considering that freshwater is the desired product, the greater the degree of conversion
38 achieved the better. One of the limitations of reverse osmosis when brackish water is
39 desalinated is inorganic precipitation or scaling. As conversion increases more
40 freshwater is obtained from the feedwater and consequently salt concentration increases
41 up to a point where the solubility limit could be reached. If this limit is exceeded
42 precipitation over the membrane surface could occur (this is where a greater salt
43 concentration exists, i.e. a higher local salinity, due to transport limitations) [3]. Once
44 the membrane surface is covered with inorganic precipitate, reverse osmosis cannot
45 continue and a cleaning step is required.

46 Even though membrane cleaning makes reuse possible, irreversible fouling is inevitable
47 and shortens the life of the membrane. Therefore, it is essential to avoid inorganic
48 fouling for purposes of optimizing reverse osmosis processes. A question arises from
49 these observations: How does one increase conversion without reaching the inorganic
50 precipitation limit?

51 A possible solution to this problem is to pretreat the feedwater either by adding acid to
52 avoid carbonate precipitates or by adding antiscalants to slow down precipitation [4].

53 Nanofiltration before the RO step can be used to partially remove bivalent ions such as
54 calcium and magnesium that contribute to water hardness, as well as dissolved organic
55 material [5,6,7]. Nevertheless, the process remains limited by the presence of salts,
56 especially bivalent salts that act as scaling substances when the recovery rate is
57 increased. Some of the most important scaling substances are CaCO_3 , CaSO_4 , BaSO_4
58 and silica [8]. Of these salts, calcium sulfate is usually the first to precipitate when
59 brackish water undergoes reverse osmosis [9].

60 If bivalent salts could be eliminated from the feedwater during pretreatment, conversion
61 could be increased without risking precipitation. Experimentally, it is known that adding
62 an organic substance (C1-C5) such as ethanol to salty water induces salt precipitation
63 [10]. Thus, a pretreatment step might involve using ethanol to remove the bivalent salts
64 from brackish-water brines and then, in order to recover the ethanol, to separate it from
65 the water. In this way one could obtain brine that is low in bivalent salts, and thus
66 achieve a higher degree of conversion in a second RO process. This could be applied to
67 the brine produced in a typical brackish-water RO plant in order to obtain more
68 freshwater from the same feedwater after a regular filtration step [11]. Not only is this
69 promising in terms of increasing the recovery rate of the RO, but it could also result in a
70 Zero Liquid Discharge (ZLD) process [10]. ZLD is especially useful in the case of
71 brackish-water reverse osmosis (BWRO) as, on the one hand, it avoids the problem of
72 having to dispose of the RO concentrate without also causing environmental impacts
73 and, on the other, valuable byproducts are obtained (solid salts). These byproducts could
74 be put on the market to increase the economic viability of the process.

75 In order to simulate and optimize the separation of calcium sulfate from water using
76 ethanol, solubility data on calcium sulfate in ethanol-water mixtures is required.
77 Moreover, the presence of other salts in the water modifies the solubility of calcium

78 sulfate because of ionic strength changes. In the case of a real brine, it is necessary to
79 understand the influence of the other salts on this solubility.

80 As far as real brines are concerned, which are commonly produced during reverse
81 osmosis and contain a wide variety of salts, sodium chloride is usually the most
82 abundant salt component, especially when it comes to seawater RO.

83 The objective of the work presented in this paper was to determine calcium sulfate
84 solubility data in water-ethanol mixtures at different concentrations of NaCl and at the
85 same time, to contribute to the compilation of an experimental database of stable
86 equilibriums for extremely low solubility brine type minerals in mixed solvents, which
87 can subsequently be used in the formulation of thermodynamic models. At the time of
88 writing of this paper, this equilibrium data was not available in the literature.

89 Furthermore, a study at the laboratory scale was conducted to ascertain the viability of a
90 process to induce gypsum precipitation by adding ethanol to a real brine (the product of
91 a reverse osmosis plant). The calcium content after this process was analyzed and
92 compared with the calculated value based on previously determined solubility data.
93 With this, it is possible to estimate how much improvement in reverse osmosis
94 conversion can be expected once the scaling substances have been eliminated.

95 **2. Materials and methods**

96 2.1. Chemicals

97 The sodium chloride used was provided by Merck at a purity of higher than 99.5%.
98 Calcium sulfate was in the form of calcium sulfate dihydrate (gypsum), and was
99 provided by Merck at a purity of more than 99.5%. Ethanol was provided by Merck at a
100 purity of higher than 99.8%. It exhibited no impurities besides water by gas

101 chromatography (TCD) and contained less than 500 ppm of moisture (Karl Fisher water
102 determination technique). The water used was ultrapure and was purified by means of a
103 MilliQPlus system.

104 2.2. Apparatus and procedures

105 Equilibrium measurements were made by preparing mixtures of known overall
106 compositions by mass, stirring vigorously and allowing to settle for 24h at a constant
107 temperature of 25.0 ± 0.1 °C to ensure that equilibrium had been reached.

108 The mixtures were prepared by adding known masses of the different compounds used
109 up to a total mass of 20g. The samples contained four different concentrations of NaCl:
110 0, 2.5, 5 and 7.5% by weight. The maximum NaCl concentration (7.5% wt.) is low
111 enough to avoid precipitation of salt up to the maximum ethanol concentration used
112 (50% wt.) [12]. Different mixtures were prepared for each of the NaCl concentrations
113 by varying the proportion of water/ethanol by mass from 0 to 50% of the total ethanol
114 mass composition. Enough $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was introduced into each mixing tube to
115 ensure that calcium sulfate was always in the solid state after equilibrium had been
116 reached. A measured amount of 0.3g of calcium sulfate dihydrate was added to the 20g
117 mixtures, which was enough for the salt to remain in the solid state once equilibrium
118 was reached.

119 Once equilibrium had been attained, liquid phase samples were extracted from the tubes
120 using syringes that contained a filter. The filter was a Millipore Swinney 13 mm
121 Stainless Steel filter with a 13 mm cellulose acetate filter on its support screen. This was
122 done to ensure that any micro particles that might not be decanted would go into the
123 syringe. The extracted samples were diluted with water to ensure that their

124 concentrations were compatible with the methods of analysis. Up to 2% by mass nitric
125 acid was also added.

126 The analysis to determine the salt content was done by means of the inductively coupled
127 plasma (ICP) mass technique. It was carried out using an Agilent 7700x ICP-MS
128 coupled with an HMI (high matrix introduction) in order to dilute the aerosol with argon
129 before it reached the interphase where it might cause obstruction problems. Scandium
130 was added and used as internal standard for the ICP analysis.

131 The above device was used to determine the calcium and sodium content. As the
132 presence of ethanol in the samples modifies the output signal, it was necessary to
133 prepare standards. These standards contained the same concentrations of ethanol and
134 sodium chloride as the analytic samples. Several standards of different calcium sulfate
135 concentrations were prepared until one was obtained for which the output signals of the
136 standard and sample were similar. In that case it could be asserted that the sample had
137 the same calcium concentration as the standard.

138 The absolute uncertainty in the ethanol and NaCl weight fraction measurements was
139 0.0001. In the case of the CaSO_4 concentrations, the absolute uncertainties varied as
140 much as the measured values themselves. These uncertainties are reported with the
141 results.

142 For the experiments with brine, two samples of the brine obtained from the RO plant at
143 Alicante University were mixed with ethanol at concentrations of up to 10 and 30%
144 w/w ethanol. Those two mixtures were placed in a thermostatic bath at 25°C for long
145 enough to ensure that all the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precipitated completely. Employing the
146 same procedure as the solubility determination described earlier, the liquid mixture was
147 analyzed by the ICP technique.

148 **3. Results and discussion**

149 3.1. Equilibrium data

150 Table 1 shows the experimental data obtained for the solid-liquid equilibrium of the
151 system water + ethanol + NaCl + CaSO₄ at 25°C. The compositions are reported in
152 weight fractions (w_i). In all cases, CaSO₄·2H₂O was the equilibrium solid phase since it
153 is the stable mineral at 25°C. It was also the compound used to prepare the global
154 mixtures.

155 Figure 1 shows the solubility of CaSO₄ versus ethanol concentration for all the NaCl
156 concentrations used. The experimental data collected [12] at zero NaCl concentration
157 has also been plotted in this figure. There is good agreement between both sets of
158 experimental data.

159 Conversely, figure 2 shows the effect that increasing NaCl content has on CaSO₄
160 solubility at different ethanol concentrations (from 0% to 50%). Experimental values
161 [13, 14,15] for the solubility of CaSO₄ in the presence of NaCl have also been plotted in
162 this figure.

163 From figure 1 it can be seen that as the ethanol content increases, CaSO₄ solubility
164 decreases. This effect occurs at all NaCl concentrations. As a result, adding ethanol to
165 brine may induce CaSO₄ precipitation.

166 On the other hand, as figure 2 shows, CaSO₄ solubility increases with the amount of
167 NaCl present. When the NaCl content of an aqueous phase is raised, the ionic strength
168 of the solution increases. As a consequence, a higher concentration of CaSO₄ can be
169 obtained in a saturated phase. If it is desired that the CaSO₄ precipitates on addition of

170 ethanol then, depending on the concentration of the other salts, more ethanol would
171 have to be added before precipitation will occur.

172 Modeling work on aqueous electrolyte solutions is rather extensive and reviews on the
173 progress of thermodynamic modeling that includes the simulation of industrial
174 processes are available [16]. For example, figure 2 shows the solubility curve of
175 calcium sulfate in sodium chloride solutions obtained by means of the code PHREEQC
176 [17] with the option of using a modified version of the Debye-Huckel equation [18,19]
177 to calculate the activity coefficients. The code also takes into account ion association
178 reactions that involve formation of ion pairs or aqueous complexes, as well as their
179 corresponding stability constants. The latter quantity gives the portion of the total
180 concentration of a given ion that is not free but associated to other ions. As figure 3, 4
181 and 5 show, in the case of the solubility of calcium sulfate, these two corrections are
182 very important. Here, the activities of the free ions Ca^{2+} and SO_4^{2-} and the percentage of
183 several related ions relative to total sulfate and calcium have been plotted against the
184 concentration of sodium chloride.

185 Figure 3 shows the activity coefficients of the free ions Ca^{2+} and SO_4^{2-} and the mean
186 γ_{+-} (product of the activity coefficients of the two free ion $\gamma_{\text{Ca}^{2+}} \cdot \gamma_{\text{SO}_4^{2-}}$). Figure 3
187 shows that the activity of the free SO_4^{2-} decreases with the sodium chloride
188 concentration down to 0.1 of the total concentration. On the other hand, the activity
189 coefficient correction of Ca^{2+} goes down to 0.25 as the concentration of sodium chloride
190 rises to 4.3 %, but then increases for higher NaCl concentrations of up to 0.3. Finally, in
191 γ_{+-} decreases whenever the NaCl concentration rises.

192 The importance of complexing corrections for SO_4^{2-} is shown in figure 5. It can be seen
193 that only 50% of sulfate occurs as free SO_4^{2-} . More than 5% exists as the CaSO_4^0

284 complex in solution, and more than 40% as NaSO_4^- . Figure 4 shows that the complexes
285 of calcium are not as important since most of it (more than 90%) exists as free Ca^{2+} and
286 only about 5% as CaSO_4^0 complex.

287 These considerations highlight the importance of complexing and activity corrections in
288 the calculation of the solubility of aqueous solutions since the value calculated by taking
289 the corrections into account produces agreement with experiment. In conclusion, the
290 increase in the solubility of calcium sulfate with the concentration of sodium chloride is
300
353 Δ as well as to the formation in solution of aqueous complexes such as NaSO_4^- .

354

355 However, in contrast to aqueous electrolyte solutions, the calculation of the solubility of
356 solid electrolytes in pure organic solvents or water + organic mixed solvents has
357 received much less attention: the thermodynamic modeling thereof is still very
358 challenging and various researchers are still trying to establish a thermodynamic
359 framework as a basis for the calculation [19-21]. Those models that do calculate activity
360 coefficients for such systems don't take into account the effect of the complexing
361 correction that can be important in such extremely low solubility brine type minerals.
362 Therefore, the influence of ethanol on the solubility curves in figures 1 and 2 can be
363 explained qualitatively based on the salting out effect produced by the ethanol: the
364 higher the concentration of ethanol, the lower the solubility of the salt.

365

366 3.2. RO application

367 In order to determine by how much the degree of conversion in a RO process can be
368 increased if ethanol is added to precipitate CaSO_4 , a practical case was analyzed. The

369 reverse osmosis plant located on campus at the University of Alicante was used for this
370 purpose. This plant treats water from an aquifer to produce a permeate and a brine of
371 compositions shown in table 2. Water from an aquifer (the brackish water from the
372 aquifer under the University of Alicante) has been treated in this plant to produce a
373 permeate and a brine of compositions shown in Table 2. This was achieved by the
374 following procedure. Firstly, the water is subjected to a pretreatment step involving the
375 addition of an antiscalant substance that serves to slow down the precipitation,
376 minimizing scaling risk to a certain extent. Then, to eliminate solid particles, the water
377 is passed through a sand bed, and a 5 μm membrane filter cartridge. Finally, the
378 pretreated water undergoes reverse osmosis using different pumps to maintain the
379 pressure difference across the membrane. The permeate, consisting of essentially water
380 and a number of ions, is able to pass through the reverse osmosis membrane because of
381 this pressure difference. What remains, the brine containing almost all the ions and less
382 water, is then subjected to reverse osmosis repeatedly until the ion concentration in the
383 brine has nearly reached the precipitation point. The permeate is used to irrigate the
384 university gardens and the brine is treated as wastewater. The plant achieves a 63%
385 conversion and is limited by the precipitation of CaSO_4 .

386 Calcium sulfate precipitation in a real brine on addition of ethanol. The first part of this
387 study served to verify whether the experimental equilibrium data presented in this paper
388 could be used to approximately calculate how much gypsum would precipitate if
389 ethanol was added to a real brine containing other ions aside from Ca^{2+} , Na^+ , Cl^- and
390 SO_4^{2-} , such as Mg^{2+} , K^+ or HCO_3^- .

391 The obtained calcium concentration was 141 ppm in the 10% ethanol mixture and 10.1
392 ppm in the 30% ethanol mixture, which translates, respectively, into a reduction of 6
393 and 85 times the calcium concentration in the brine.

394 On the other hand, the equilibrium data presented in the first part of this paper were
395 used in a theoretical calculation to see how much calcium remains in solution after the
396 ethanol is added to the brine. Because the brine contains other ions apart from Ca^{2+} ,
397 Na^+ , Cl^- and SO_4^{2-} , the calculation of the solubility of CaSO_4 has been done using the
398 ionic strength of the solutions. To make this possible, the solubility data presented in
399 this paper have been correlated against ionic strength for each of the ethanol
400 concentrations, based on the assumption that all the calcium, sulfate, sodium and
401 chloride present in the solution occur as the free ion. From the ion composition of the
402 brine (table 2) and the ethanol added, the ionic strength of the liquid mixture is
403 determined and is used to calculate by interpolation the calcium sulfate (gypsum)
404 solubility and with it the remaining calcium once precipitation has set in. As the calcium
405 sulfate precipitation affects the ionic strength of the solution (the calcium and the sulfate
406 concentration decreases), an iterative method has been used to calculate the solubility,
407 ionic strength and final concentrations of calcium and sulfate.

408 Following this procedure, the calculated calcium in solution was 141 and 8.3 ppm for
409 10% and 30% of ethanol added, respectively, which are very similar to the values found
410 experimentally (141 and 10.1 ppm) in spite of the presence of different types of ions.
411 This demonstrates the validity of the method for calculating the final composition of the
412 brines after the precipitation of the CaSO_4 (gypsum) due to the addition of ethanol.

413 Improvement of RO conversion using an intermediate precipitation step. The
414 conversion of the RO plant could be raised if the brine obtained in a regular step of the
415 RO process is treated with ethanol to decrease the amount of dissolved sulfate and
416 calcium, it is filtered to eliminate the solid CaSO_4 (gypsum) and the ethanol is
417 recovered to separate it from the water. In this way one could obtain brine that is low in
418 bivalent salts, and thus achieve a higher degree of conversion in a second RO process to

419 obtain more freshwater from the same feedwater. In order to estimate the improvement
420 in the conversion of a RO process when ethanol is added, the final compositions of the
421 mixtures after adding 10% and 30% ethanol, precipitating and filtering the CaSO_4 and
422 eliminating the added ethanol, were used to calculate the maximum conversion of a RO
423 plant that is limited by the precipitation of CaSO_4 (gypsum).

424 The mixtures to be treated in the second step would have the composition shown in
425 Table 3. If this product were used as a feed to a RO plant it would in theory be possible
426 to achieve a conversion of up to 73% on addition of 10% w/w ethanol before CaSO_4
427 precipitation over the membrane. That would translate into a global conversion of 90%
428 after both steps. Furthermore, in the case of 30% w/w ethanol we could theoretically
429 achieve 91% conversion in the second step, thus achieving a global conversion of up to
430 96.5%. It would actually be difficult to attain such levels of conversion because the
431 process would have come up against other design limits long before then, such as water
432 quality index (Langelier Index,...), hydrodynamic or mechanical limits (maximum/
433 minimum flux, pressure,...), etc. However, at least the precipitation would no longer be
434 the limiting factor.

435 Even though this analysis relies on a number of simplified calculations (as stated
436 previously), the increase in the degree of conversion obtained after an intermediate step
437 of precipitation with ethanol is an incontrovertible fact.

438

439 **4. Conclusions**

440 To conclude, both the literature [11] and our investigation suggest that it is possible to
441 use ethanol to precipitate salts from brine in order to obtain a higher degree of
442 conversion in a RO process. The obvious limitation of the method is the cost of

443 recovering the ethanol by separation. The next step, aside from reducing ethanol
444 production costs, would be to find an efficient way to separate ethanol from the water
445 once the salts have precipitated and have been filtered out, with a view to obtaining a
446 final process resulting in zero liquid discharge.

447

448 **5 Bibliography**

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512

513

514 **FIGURE CAPTIONS**

515 Figure 1. CaSO_4 solubility at 25°C versus ethanol concentration for different NaCl
516 concentrations (weight fraction). All concentrations are expressed as weight fraction.

517 Figure 2. CaSO_4 solubility (weight fraction) at 25°C versus NaCl concentration (weight
518 fraction) for different ethanol concentrations.

519

615 \square CaSO_4 vs. NaCl concentration in Na-Ca-Cl- SO_4 - H_2O solutions (PHREEQC
616 calculation).

617

618 Figure 4. Contribution of aqueous calcium species $\text{Ca}^{2+}(\text{aq})$ and $\text{CaSO}_4^0(\text{aq})$ to the total
619 calcium concentration vs NaCl concentration in Na-Ca-Cl- SO_4 - $\text{CaSO}_4^0(\text{aq})$ - H_2O
620 solutions at 25°C (PHREEQC calculation)

621 Figure 5. Contribution of aqueous calcium species $\text{SO}_4^{2-}(\text{aq})$, $\text{CaSO}_4^0(\text{aq})$ and NaSO_4^-
622 to the total sulfate concentration vs NaCl concentration in Na-Ca-Cl- SO_4 - $\text{CaSO}_4^0(\text{aq})$ -
623 H_2O solutions at 25°C (PHREEQC calculation)

624

625

626 **TABLES**

627 Table 1. Solid-liquid equilibrium data (weight fraction) of the system water-ethanol-

628 NaCl-CaSO₄ at 25°C. The solid phase is CaSO₄·2H₂O¹.

629

W_{ethanol}	W_{NaCl}	W_{CaSO4}	^aCaSO₄ unc.
0.00000	0.0000	0.00218	0.0001
0.09996	0.0000	0.00071	0.00005
0.20020	0.0000	0.00025	0.00001
0.29973	0.0000	0.00007	0.00001
0.40009	0.0000	0.00003	0.00001
0.50001	0.0000	0.00002	0.00001
0.00000	0.0249	0.00421	0.0001
0.09986	0.0249	0.00228	0.0001
0.19997	0.0250	0.00107	0.0001
0.30042	0.0251	0.00062	0.00005
0.39997	0.0250	0.00035	0.00002
0.49942	0.0249	0.00019	0.00001
0.00000	0.0497	0.00513	0.0001
0.09994	0.0499	0.00272	0.0001
0.19966	0.0501	0.00145	0.0001
0.29982	0.0499	0.00082	0.00005
0.39980	0.0499	0.00051	0.00005
0.49967	0.0500	0.00033	0.00002
0.00000	0.0745	0.00598	0.0001
0.09975	0.0746	0.00336	0.0001
0.19951	0.0748	0.00189	0.00005
0.29930	0.0750	0.00098	0.00005
0.39978	0.0749	0.00073	0.00005
0.49960	0.0749	0.00049	0.00002

630

631 ^aCaSO₄ unc = Absolute uncertainties in the CaSO₄ measurements. ¹ Standard
632 uncertainties *u* are *u*(ethanol) = 5·10⁻⁵, *u*(NaCl) = 1·10⁻⁴

633

634

635

636 Table 2. Ionic content^b of the input and output water streams in the reverse osmosis
 637 process carried out on the RO plant at Alicante University. Feed: brackish water from
 638 the aquifer under Alicante University (Spain).¹

639

	Feed	Permeate	Brine
pH	7.04	5.56	7.34
Conductivity (μS)	5900	327	13630
CO ₃ (ppm)	0	0	0
HCO ₃ (ppm)	327	13	854
Cl (ppm)	1150	73	2994
SO ₄ (ppm)	1677	11	4539
NO ₃ (ppm)	206	38	475
Na (ppm)	1016	73	2619
K (ppm)	22	0	53
Ca (ppm)	293	3.4	844
Mg (ppm)	205	2.5	526
Fe (ppm)	0.0	0.0	0.0
B (ppm)	5.2	3.3	6.6

640 ¹ Standard uncertainties u are $u(\text{pH}) = 0.01$, $u(\text{conductivity}) = 1\mu\text{S}$, relative standard uncertainty

641 u_r (uncertainty/measurand) $u_r(\text{ion}) = 0.03$

642

643

644 Table 3. Composition of the brine after treatment with 10 or 30 % w/w ethanol,
645 precipitation and elimination of the ethanol¹

	10% ethanol	30% ethanol
pH	7.30	7.30
CO ₃ (ppm)	0.0	0.0
HCO ₃ (ppm)	854.0	854.0
Cl (ppm)	2993.6	2993.6
SO ₄ (ppm)	2890.7	2545.1
NO ₃ (ppm)	474.8	474.8
Na (ppm)	2619.2	2619.2
K (ppm)	53.2	53.2
Ca (ppm)	156.0	11.9
Mg (ppm)	526.3	526.3
Fe (ppm)	0.0	0.0
B (ppm)	6.6	6.6

646 ¹ Standard uncertainties u are $u(\text{pH}) = 0.01$, relative standard uncertainty u_r
647 (uncertainty/measurand) $u_r(\text{ion}) = 0.03$.