# HYDROCHEMISTRY OF KARST SPRINGS FROM TWO CARBONATIC UNITS IN ZAGROSIDES OF IRAN

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## ABSTRACT

119 Karst Springs, all with electric conductivity of less than 500 μm/cm, discharging two carbonatic aquifers in Zagrosides of Iran are chosen and studied. The results indicate that the lithology of each Unit is well reflected in the chemistry of springs and the overall mineralogical composition of the aquifer can successfully be reconstructed from the hydrochemistry of the springs using a mass balance approach. The comparison of the chemistry of springs reveals that the significant difference are due to the dolomitic nature of one of the studied aquifers.

## INTRODUCTION

The hydrochemistry of ground water is mainly a function of the lithology and mineral composition of the aquifer that it passes through. In fact differences in the chemistry of aquifers is the main reason behind the observed differences in the ground water hydrochemistry (Flint, 1971; Palmer & Cherry 1985, Rogers 1989). In carbonatic units, as infiltrating rain and meltwater passes through pore spaces and secondary structures of various size, reaction takes place between the $CO_2$ bearing ground water and the carbonatic host. As a result the chemistry of ground water continuously changes as a function of time and the distance travelled by the water. Subsequently considerable dissolution of carbonatic and dolomitic units will also takes place. There is no doubt that if other soluble phases such as evaporitic minerals are also present as interlayers or some other form, these too will react and modify the major-ion chemistry of the ground water. This is why the chemistry of ground water is traditionally taken by the hydrogeologists as a good representation of the lithology of the aquifer through which the water flows. This approach is prefered to direct analysis of the geological units for the following reasons.

a) The lithology of sedimentary units is usually so variable that a Large number of samples should be analysed in order to obtain an average composition.

b) The exposed and available sections of the formations are generally weathered and thus analysis would not reflect the true chemistry of the fresh units.

c) Sampling from depth is expensive and uneconomical.

In this paper the hydrochemistry of springs discharging from two carbonatic units in Zagrosides of Iran, namely Sarvak and Asmari-Jahrum Formations is studied and compared.

## GEOLOGICAL SETTING

The stratigraphy of Zagros sedimentary sequence has been described in detail by James & Wynd (1965) and Falcon (1974). The stratigraphy of the study area is presented in fig 1. The formations of interest in a decreasing order of age consist of Kazhdomi Formation (Bituminous shale of Aptian to Cenomanian), Sarvak limestone (Albian to Turonion), Gurpi shales (sentonian to Maestrechtian), and Asmari. Jahrum limestone (Paleocene to Early Miocene).

Sarvak Formation with a thickness of about 800 m is a neritic, massive feature forming limestone contaning in some parts siliceous nodules and thin interlayers of marl. The Undifferentiated Asmari-Jahrum Formation with a thickness of 700 to 900 m in the study area is also a massive feature forming dolomitic limestone with shaly interlayers.

Considerable karstification occurs both in Sarvak and Asmari-Jahrum Formations and many karst springs can be found at the local base levels of erosion, especially at the contact between the carbonatic units and the impermeable marly and shaly formations that overlie and underlay these formations.

## DATA AND METHODS

72 karst springs from Asmari-Jahrum Formation and 47 karst springs from Sarvak formation were sampled. Fig. 1. represents the location of the sampled springs. The electric conductivity of all sampled springs is below 500 µm/cm and care was taken to select those springs that have no apparent connection with the adjacent evoporitic Formations. PH andelectric conductivity of the samples was measured and the major ions Na, K, Mg, Ca, $HCO_3$, $SO_4$ and Cl were also determined using standard wet chemical methods.

*Table 1 represents the mean, maximum and minimum of the measured ions in each formation. The contribution of each ion to the total disolved solids is also presented in percent values.*

## HYDROCHEMISTRY OF ASMARI-JAHRUM SPRINGS

Table 1 indicates that 85.7% of the total dissolved ions consist of Ca, Mg and $HCO_3$, the rest being made of $SO_4$, Cl, Na and K in that order.

The correlation coefficient of measured cations and anions are calculated using the student t-test and the results are presented in table 2. It is clear that in Asmari-Jahrum springs a good correlation exists between $HCO_3$ and Ca and Mg; $SO_4$ and Ca, Mg, Na; and between Cl and Na.

Using a mass balance approach and assuming that all bicarbonate is used up by Mg and Ca, and that excess Mg and Ca is consumed by $SO_4$ anion, and also considering that Na is mainly used up by Cl, the source minerals of Asmari-Jahrum aquifer were reconstructed from the data in table 1 and are presented in table 3. Hence, the mass balance approach reveals that the mineralogical composition of the aquifer should predominantly consist of calcite and dolomite with minor amounts of gypsum, halite and probably epsomite. Although this is a rather perfect reflection of what is seen in the field, but it must be noted that this is a somewhat

*Table 1: Mean, Maximum, Minimum, Sum and percent of concentration of measured ions from karst springs of Sarvak and Asmari-Jahrum Formations.*

| | | Asmari Formation (N=72) | Sarvak Formation (N=47) |
|---|---|---|---|
| CA: | | | |
| | MEAN | 2.196 | 2.233 |
| | MAXIMUM | 3.800 | 3.700 |
| | MINIMUM | 1.000 | 0.800 |
| | % CA | 28.400 | 31.790 |
| MG: | | | |
| | MEAN | 1.386 | 1.059 |
| | MAXIMUM | 2.400 | 1.800 |
| | MINIMUM | 0.200 | 0.035 |
| | % MG | 17.928 | 15.074 |
| NA: | | | |
| | MEAN | 0.239 | 0.213 |
| | MAXIMUM | 1.050 | 1.120 |
| | MINIMUM | 0.029 | 0.026 |
| | % NA | 3.096 | 3.026 |
| K: | | | |
| | MEAN | 0.017 | 0.014 |
| | MAXIMUM | 0.097 | 0.110 |
| | MINIMUM | 0.000 | 0.000 |
| | % K | 0.219 | 0.203 |
| $HCO_3$: | | | |
| | MEAN | 3.046 | 2.668 |
| | MAXIMUM | 4.000 | 4.000 |
| | MINIMUM | 1.700 | 1.300 |
| | % $HCO_3$ | 39.394 | 37.985 |
| $SO_4$: | | | |
| | MEAN | 0.582 | 0.531 |
| | MAXIMUM | 1.900 | 1.824 |
| | MINIMUM | 0.000 | 0.060 |
| | % $SO_4$ | 7.530 | 7.560 |
| Cl: | | | |
| | MEAN | 0.265 | 0.306 |
| | MAXIMUM | 0.600 | 0.600 |
| | MINIMUM | 0.020 | 0.100 |
| | % Cl | 3.433 | 4.362 |
| PH: | | | |
| | MEAN | 7.387 | 7.544 |
| | MAXIMUM | 8.430 | 8.140 |
| | MINIMUM | 6.400 | 6.800 |
| EC: | | | |
| | MEAN | 377.514 | 347.532 |
| | MAXIMUM | 494.000 | 486.000 |
| | MINIMUM | 244.000 | 220.000 |

Concentration in m.eq/1; PH in Units; Ec is electric conductivity in μmhos/cm.

*Table 2: Correlation Coefficient between the chemical Variables*

| | | $HCO_3^-$ | $SO_4^{2-}$ | $Cl^-$ |
|---|---|---|---|---|
| As-Ja | $Ca^{++}$ | 0.58*. | 0.27* | 0.12 |
| | $Mg^{++}$ | 0.39* | 0.46* | -0.08 |
| | $Na^+$ | 0.12 | 0.74* | 0.52* |
| | $K^+$ | 0.08 | 0.03 | 0.044 |
| Sa | $Ca^{++}$ | 0.67* | 0.02 | -0.06 |
| | $Mg^{++}$ | 0.06 | 0.37* | 0.29* |
| | $Na^+$ | 0.25 | 0.37* | 0.39* |
| | $K^+$ | 0.18 | 0.21 | 0.28 |

simplified picture of the true situation, as there are undoubtedly minor minerals of various composition that are present in insignificant amounts and are not accounted for here. The original composition of the rain water should also be considered.

The relation between electric conductivity and the concentration of various ions is presented in fig 2. It can be seen that Ca, Mg, $HCO_3$, Na and $SO_4$ show good correlation with electric conductivity while Cl and K reveal a very poor correlation. Using a multiple regression method the relation between the dissolved ions and electric conductivity is calculated as logarithmic, semi logarithmic and non logarithmic equations. The F test and the coefficient of determination ($R^2$) show that the non logarithmic calculated equation is the best. The significant factor of F was also calculated and it was indicated that K and Cl hold no significance and so were ommited from the equation. After all these considerations, the equation of the line defining the relation between electric conductivity and the dissolved ions may be expressed as follow.

$$Ec = 41.42\,Ca + 39.25\,Mg + 72.85\,Na + 47.55\,HCO_3 + 46.56\,SO_4 + 42.1$$

## *HYDROCHEMISTRY OF SARVAK SPRINGS*

As it can be seen from table 1, Ca, Mg and $HCO_3$ comprise 84.80%

of the total dissolved solids, the rest being made of $SO_4$, Cl, Na and K respectivly. The same mass balance approach is used and the results are presented in table 4. It is obvious that the mineralogical composition of Sarvak aquifer should predominantly be made of calcite with some minor amounts of gypsum, epsomite, dolomite and halite. Here again we can see a perfect agreement between the reconstructed mineralogical compostion and field observations.

*Table 3: Reconstruction of Source Minerals for Asmari-Jahram Spring*

| | Ca + Mg | Na | K | $HCO_3$ | $SO_4$ | Cl |
|---|---|---|---|---|---|---|
| Concentration in Spring water | 2.20+1.39 | 0.24 | 0.02 | 3.05 | 0.58 | 0.27 |
| $CO_3Ca+CO_3Mg$ | 3.05 | | | -3.05 | | |
| | 0.54 | 0.24 | 0.02 | 0.00 | 0.58 | 0.27 |
| $SO_4Mg+SO_4Ca$ | -0.54 | | | | -0.54 | |
| | 0.00 | 0.24 | 0.02 | 0.00 | 0.04 | 0.27 |
| ClNa | 0.00 | 0.24 | | | | 0.24 |
| | 0.00 | 0.0 | 0.02 | 0.00 | 0.04 | 0.03 |

Concentration are in meq/L

*Table 4: Reconstruction of Source Minerals for Sarvak Springs*

| | Ca + Mg | Na | K | $HCO_3$ | $SO_4$ | Cl |
|---|---|---|---|---|---|---|
| Concentration of Spring Water | 2.23+1.06 | 0.21 | 0.01 | 2.66 | 0.53 | 0.31 |
| $CO_3Ca+CO_3Mg$ | -2.66 | | | -2.66 | | |
| | 0.66 | 0.21 | 0.01 | 0.00 | 0.53 | 0.0.31 |
| $SO_4Mg+SO_4Ca$ | 0.53 | | | | -0.53 | |
| | 0.13 | 0.21 | 0.01 | 0.00 | 0.00 | 0.31 |
| ClNa | | 0.21 | | | | 0.21 |
| | 0.13 | 0.00 | 0.01 | 0.00 | 0.00 | 0.11 |

Concentration are in meq/L

The relation between electric conductivity and the concentration of different ions is presented in fig 3. It can be seen that electric conductivity shows maximum correlation with $HCO_3$ while Ca, Na, $SO_4$ , K and Mg all show moderate correlation with Ec. Similar statistical treatment of the data as that of Asmari-Jahrum indicates that the non logarithmic equation of the line best defining the relation between Ec and dissolved ions is as follow.

$$Ec=42.97\ Ca+45.60\ Mg+68.22\ Na+45.18\ HCO_3+45.15\ SO_4+44.26$$

## *COMPARISON OF CHEMICAL CHARACTERISTICS OF ASMARI-JAHURM & SARVAK SPRINGS*

The measured ions, PH and electric conductivity of sampled karst springs from both formations were compared using non parametric Kruskal wallis and Mann-Whitney methods (Walpole & Myers). The results are presented in table 5. It can be seen that the differences in electric conductivity, Mg $HCO_3$ of karst springs of these two formations is significant while the difference between other determined ions and PH does not bear any important significance. The higher Mg, $HCO_3$ and electric conductivity values in Asmari-Jahrum formation seems to arise from its dolomitic lithology.

*Table 5: Nonparametric comprison of Chemical Characteristic of Karst Spring from Asmari-Jahrum and Sarvak formations.*

| | Z | \|Z\| | H' | Result of Comparison |
|---|---|---|---|---|
| Ca | +0.23 | 0.23 | 0.052 | $Ca_{Sa} = Ca_{As-Ja}$ |
| Mg | -3.49 | 3.49* | 12.205* | $Mg_{Sa} < Mg_{As-Ja}$ |
| Na | -1.92 | 1.92 | 3.694 | $Na_{Sa} = Na_{As-Ja}$ |
| K | -1.89 | 1.89 | 3.560 | $K_{Sa} = K_{As-Ja}$ |
| $HCO_3$ | -3.28 | 3.28* | 10.743* | ${HCO_3}_{Sa} < {HCO_3}_{As-Ja}$ |
| $SO_4$ | -1.20 | 1.20 | 1.431 | ${SO_4}_{Sa} = {SO_4}_{As-Ja}$ |
| Cl | +1.91 | 1.91 | 3.633 | $Cl_{Sa} = Cl_{As-Ja}$ |
| PH | +1.59 | 1.59 | 2.532 | $PH_{Sa} = PH_{As-Ja}$ |
| Ec | -2.05 | 2.05* | 4.200* | $Ec_{Sa} < Ec_{As-Ja}$ |

* Indicates that the compared parameters in the two formations are Unequal.

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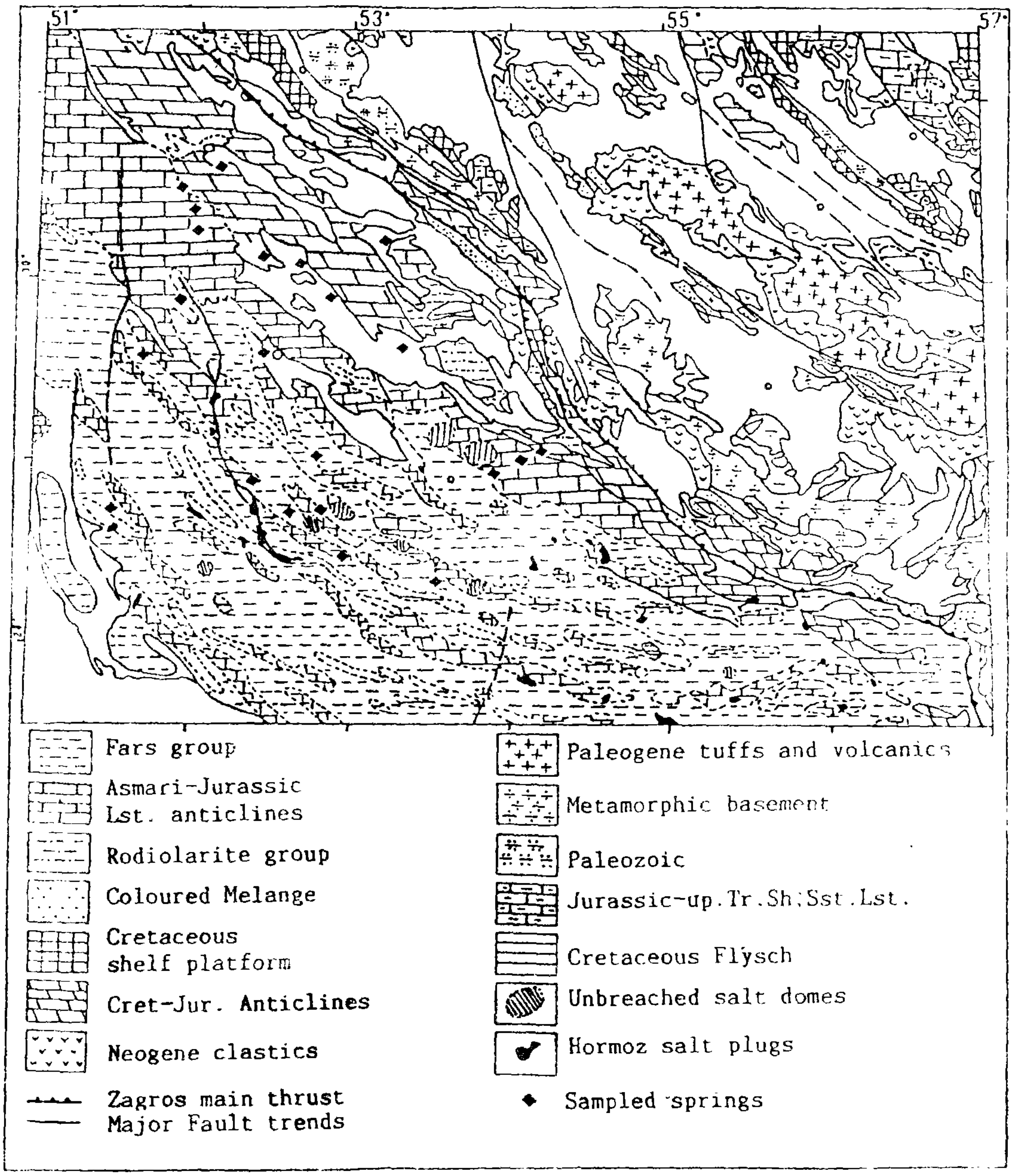


Fig 1: General geological map of the study area showing the location of the sampled springs

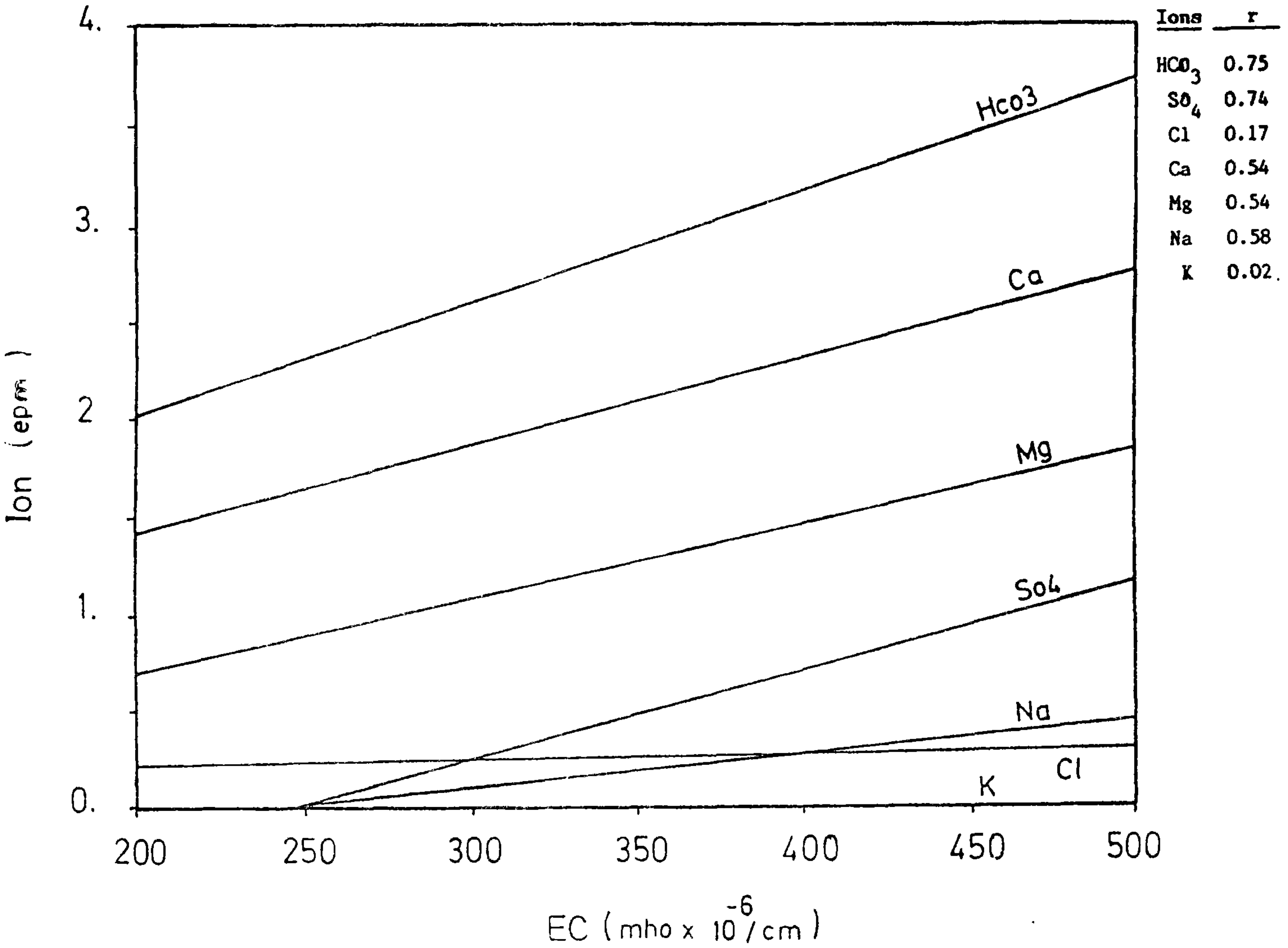
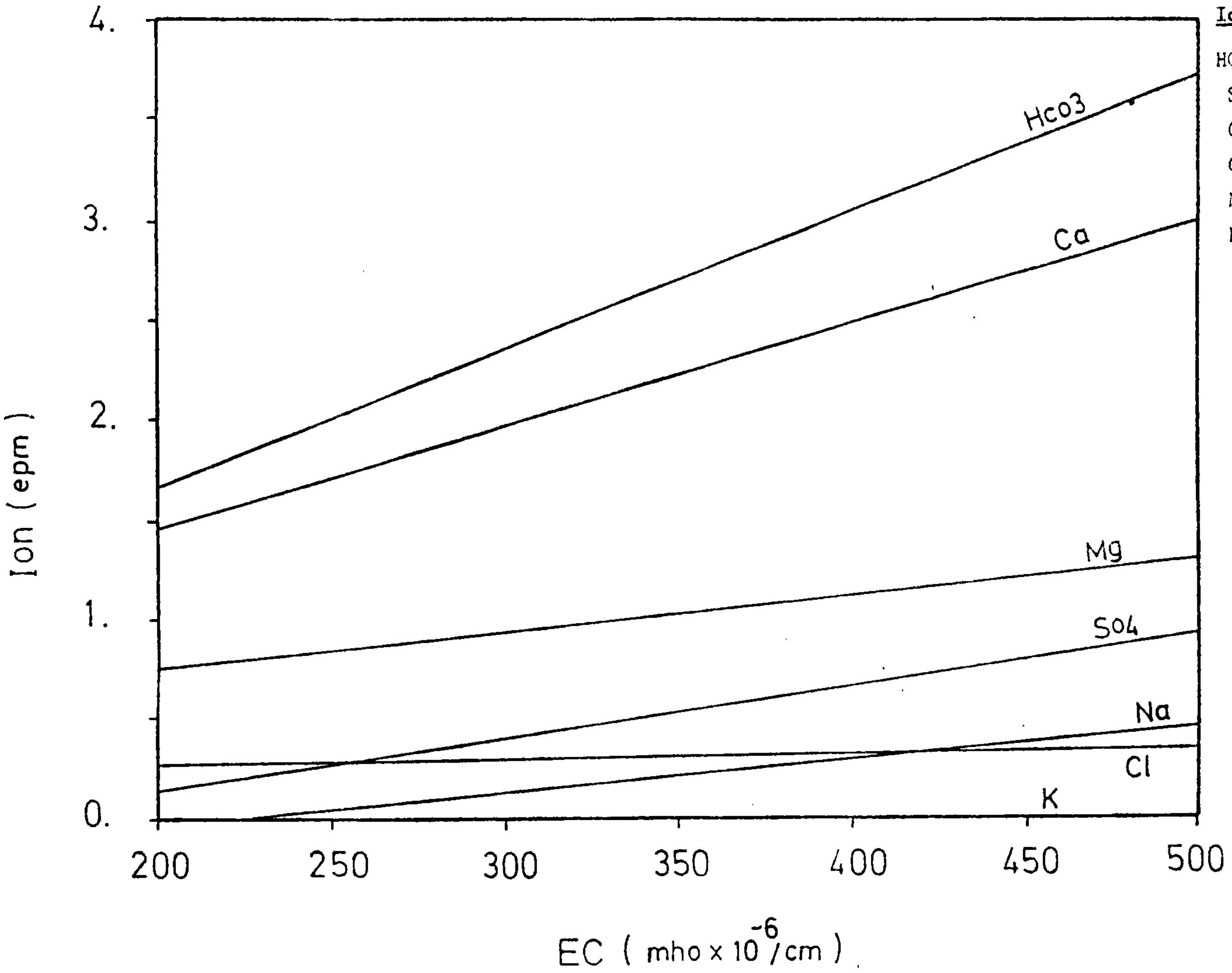


*Fig. 2: Relation between electric conductivity and the concentration of various ions in Asmari-Jahrum Karst Springs.*



| Ions | r |
|---|---|
| $HCO_3$ | 0.76 |
| $SO_4$ | 0.45 |
| Cl | 0.21 |
| Ca | 0.57 |
| Mg | 0.32 |
| Na | 0.53 |
| K | 0.37 |

*Fig. 3: Relation between electric conductivity and the concentration of various ions in Sorvak Karst Springs.*