# تقدير مستويات العناصر الثقيلة في منابع المياه الكبريتية الساخنة شمال غرب ليبيا

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**الملخص :**

تـــم تقدير مستوى العناصر الثقيلة الكروم والكادميوم والنحاس والرصاص والزنك المنجنيز والحديد في مياه الآبار الكبريتية الموجودة شمال غرب ليبيا، تاجوراء والعجيلات والعسة وبدر . تمثلت هذه الدراسة في إجراء تحليل عدد 32 عينة من المياه الكبريتية الساخنة ، حيث كانت تراكيز العناصر ضمن الحد المسموح مقارنة بالمواصفات الليبية والعالمية لمياه الشرب، بينما عنصر الحديد كان مرتفعا في بئر بدر خلال فصل الصيف وكان في حدود 8.85 mg/l.

كان معدل تركيز عنصر الكروم يتـــراوح ما بين (< 0.01 – < 0.45 mg/l)، اتضح من النتائج أن أعلى تركيز في فصل الشتاء، أما بالنسبة لعنصر الكادميوم فقد تراوح تركيزه ما بين (< 0.013 - < 0.02 mg//l) أما عنصر النحاس فقد بلغ تركيزه (< 0.04 mg/l) في كل فصول السنة. وأوضحت النتائج أن عنصر الرصاص قد تراوح ما بين (< 0.20 - < 0.41 mg/l) ، وقد سجل أعلى تركيز للرصاص خلال فصل الشتاء وهو أقل من (0.41 mg/l). أما عنصر الخارصين فقد تراوح تركيزه (< 0.01 – < 0.03 mg/l). وعنصر المنجنيز سجل تركيزا تراوح ما بين ( – 0.01 < 0.14 mg/l) حيث كان أعلى تركيز له خلال فصل الشتاء في بئر العسة وهو أقل من (0.14 mg/l). ومن خلال النتائج تبين أن عنصر الحديد هو التركيز الأعلى مقارنة بالعناصر الأخرى التي تم تحليلها.

**الكلمات الدالة** : مياه كبريتية ساخنة، معادن ثقيلة، مطيافية الامتصاص الذري.

# Estimation of heavy metals levels in hot sulfur water sources in northwestern Libya

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**Abstract**

The level of heavy metals chromium, cadmium, copper, lead, zinc, manganese and iron was estimated in the water of sulfur wells located in northwestern Libya, Tajoura, Al-Ajeilat, Al-Assa and Badr. This study was represented in conducting the analysis of 32 samples of hot sulfur water, where the concentrations of elements were within the permissible limit compared to the Libyan and international specifications for drinking water, while the iron element was high in Badr well during the summer and was within the range of 8.85 mg/l.

The average concentration of chromium ranged between (<0.01 - <0.04 mg/l), and it was clear from the results that the highest concentration was in the winter season. As for cadmium, its concentration ranged between (<0.013 - <0.02 mg/l), while copper reached (<0.04 mg/l) in all seasons of the year. The results showed that the element lead had ranged between (<0.20 - <0.41 mg/l), and the highest concentration of lead was recorded during the winter season, which was less than (0.41 mg/l). As for zinc, its concentration ranged (<0.01 - <0.03 mg/l). The manganese element recorded a concentration that ranged between (<0.01 - <0.14 mg/l), where the highest concentration was during the winter season in Al-Assa well which was less than (0.14 mg/l). Through the results, it was found that iron is the highest concentration compared to the other analyzed elements.

*Key words: Hot sulfur water, Heavy metals, Atomic Absorption Spectroscopy*

**Introduction:**

The quality of water varies in its natural and chemical properties from one region to another, according to its presence in the geological layers of the earth in which it seeps. These properties can be identified by studying the geological origin of the components of rocks and soil originally composed of rocks, which are sometimes known as incoherent rocks (and the chemical origin, which includes physical and chemical properties (Abdel Qader, 1996).

Groundwater is found in the earth's layers at different depths between the grains of rocks or soil. There is the surface layer, which is the least deep and closest to the surface. Its depth ranges from (20-25 m), and its thickness does not exceed three meters in the western part and in the eastern part more than (50 m), and water is found in the semi-artesian layer at a depth of 25 m from the first layer, and its thickness is about (20 m) and is separated by a layer of limestone and clay rocks. On pollution by sea water, urbanization and agricultural and industrial activity depend on this water, and there is an artesian layer, at depths ranging from (250-450 m). It contains some minerals such as sulfur (Sharaf, 1971).

However, there are underground water springs, some of which are used for drinking and others are used for bathing only. Mineral water springs with curative properties are spread in many European countries, such as Kar Lovi Fadi in Chica, in the Republic of Hungary, in France and Germany, as well as in Egypt in the Helwan region, where they are used for drinking. There is a type that is used for bathing, and there are springs for treatment, such as the bath of our master Moses in southern Sinai (Hamida, 1991).

The source of heat is the hot igneous rocks, as they heat the water and bring out the water loaded with different materials, the most important of which is calcium carbonate, and during its arrival to the surface of the earth, gases come out of it, forming holes and pores in it (Sawalha, 2005).

It has been found through mineral exploration and drilling of oil wells that the temperature increases with depth at a rate of two degrees Celsius for every hundred meters. It expands the water and thus reaches the surface under less pressure and turns into water vapor, and then the cold groundwater seeps into the ground again to start the cycle again, and the hot water has a great ability to dissolve from cold water, and therefore it carries many dissolved substances such as silica and precipitate around the well, and travertine is a type of calcite that is characterized by hot water springs (Khalil, 2005).

In the limestone areas, the water of springs containing sulfur has an unpleasant taste for drinking and emits the smell of rotten eggs, which is the smell of sulfur gas (Sulaiman et al., 1984).

Such waters are found in the northwest of Libya in the areas of Tajoura, Al-Ajilat, Al-Assa and Badr. As these areas contain wells of high-temperature

sulfur water and an increase in its content of dissolved salts (Ansir, 2014). The Tajoura well for hot sulfur water is located 2 kilometers from the center of the city of Tajoura. The well of Al-Ajeilat is located in the south of the city of Al-Ajeilat three kilometers and is 80 kilometers from the capital, Tripoli. It is a treatment and tourist center that was established on an area of approximately 8 hectares (Al-Hashani, 2007). The water temperature in it is between (47-49°C). As for the well of Alasah, the well of Alasah for physiotherapy is located in the Alasah area, which is 40 km away from the city of Zuwara (Anseer, 2014). The Badr Well is located in the southwest of Tripoli, about 200 km. This well is located in the north of the city on the road linking Badr and Zuwara (Salem, 2011).

This study aims to detect the concentration of heavy metals (Cu, pb, Zn, Mn, Fe, Cr, Cd,) in hot sulfur water wells were located in Tajoura, Al-Ajilat, Al-Assa and Badr in northwestern Libya.

**Chemicals and Instruments**

**Chemicals:**

Nitric acid. Suitable standard solutions for each ingredient, Colored sample bottles.

**Instruments:**

Flame Atomic Absorption Spectroscopy (Analtik Jena GMbH- contra 700).

**Sample collection:**

The study was conducted between February and November of the year (2019-2020). (32) samples of sulfur water were collected from the wells of Tajoura, Al-Ajeelat, Al-Assa and Badr, with depths and distances ranging from 1549 - 904 m), following the scientific method of collecting samples to estimate the concentrations of heavy meatls.

**Results and discussion:**

The process of estimating heavy metals such as Cr, Cd, Cu, Zn, Pd, Fe, and Mn was carried out, and the results obtained are shown in the statistical analysis tables No. (1)

Table (1) shows the results of heavy metal concentrations in sulfur wells water in northwestern Libya (mg/l)

| Elements | Loation | Seasonal classes | | | | |
|---|---|---|---|---|---|---|
| | | Summer | Autumn | Winter | Spring | Annual rate |
| Chrome (Cr) | Tajoura | < 0.01 | < 0.01 | < 0.45 | < 0.01 | < 0.12 |
| | Al-Ajilat, | < 0.01 | < 0.01 | < 0.45 | < 0.01 | 0.12< |
| | Al-Assa | < 0.01 | < 0.01 | < 0.45 | < 0.01 | < 0.12 |
| | Badr | < 0.01 | < 0.01 | < 0.45 | < 0.01 | < 0.12 |
| Overall average (annual) | | | | | | 0.12 |
| Cadmium (Cd) | Tajoura | < 0.02 | < 0.01 | < 0.01 | < 0.02 | < 0.015 |
| | Al-Ajilat, | < 0.02 | < 0.01 | < 0.01 | < 0.02 | < 0.015 |
| | Al-Assa | < 0.02 | <0.02 | <0.02 | < 0.02 | < 0.02 |
| | Badr | < 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.0125 |
| Overall average (annual) | | | | | | < 0.0156 |
| Cupper Cu | Tajoura | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 |
| | Al-Ajilat, | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 |
| | Al-Assa | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 |
| | Badr | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 |
| Overall average (annual) | | | | | | < 0.04 |
| Lead Pd | Tajoura | < 0.18 | < 0.18 | < 0.2 | < 0.1 | < 0.165 |
| | Al-Ajilat, | < 0.18 | < 0.18 | <0.15 | <0.1 | < 0.1525 |
| | Al-Assa | < 0.18 | < 0.18 | < 0.41 | <0.1 | < 0.2175 |
| | Badr | < 0.18 | < 0.18 | < 0.23 | < 0.1 | < 0.1725 |
| Overall average (annual) | | | | | | 0.1769 |
| Zinc Zn | Tajoura | < 0.02 | < 0.01 | < 0.02 | < 0.01 | < 0.015 |
| | Al-Ajilat, | < 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.0125 |
| | Al-Assa | < 0.02 | < 0.01 | < 0.03 | < 0.01 | < 0.0175 |
| | Badr | < 0.02 | < 0.01 | < 0.02 | < 0.01 | < 0.015 |
| Overall average (annual) | | | | | | < 0.0150 |
| Manganese Mn | Tajoura | < 0.03 | < 0.02 | < 0.09 | < 0.01 | < 0.0375 |
| | Al-Ajilat, | < 0.03 | < 0.01 | < 0.08 | < 0.03 | < 0.0375 |
| | Al-Assa | < 0.03 | < 0.02 | < 0.14 | < 0.01 | < 0.05 |
| | Badr | < 0.05 | < 0.05 | < 0.07 | < 0.01 | < 0.045 |
| Overall average (annual) | | | | | | < 0.0425 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Iron Fe | Tajoura | < 1.12 | < 0.1 | < 0.01 | < 0.01 | < 0.31 |
| | Al-Ajilat, | < 0.83 | < 0.1 | < 0.01 | < 0.02 | < 0.24 |
| | Al-Assa | <0.84 | < 0.64 | < 0.1 | < 0.44 | < 0.5050 |
| | Badr | 8.85 | 5.43 | 9.1 | 6.23 | 7.4025 |
| Overall average (annual) | | | | | | 2.1144 |

**1- Chromium (Cr)**

Through the results in Table (1) and Figure (1) the concentration rates of chromium (Cr) during the seasons of the year in the hot sulfur water wells in (Tajoura, Al-Ajeelat, Al-Asa and Badr) was less than (0.12) ppm, and it appeared equal in the concentration rates.

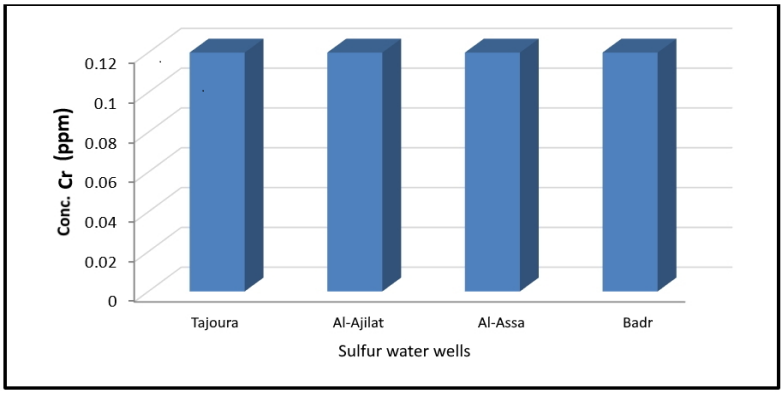


Figure (1) shows the concentration of chromium (Cr) in hot sulfur well water (ppm).

**2- Cadmium (Cd)**

It appears from the results presented in Table (1) and Figure (2) that the rates of cadmium concentration during the seasons of the year in the hot sulfur water wells range from ppm (< 0.0125 – < 0.02 ppm), and it showed an increase in the Al-Assa well, where the general annual rate was less than (< 0.02 ppm) and the average concentration of the element during the seasons was about less than (< 0.02 ppm).

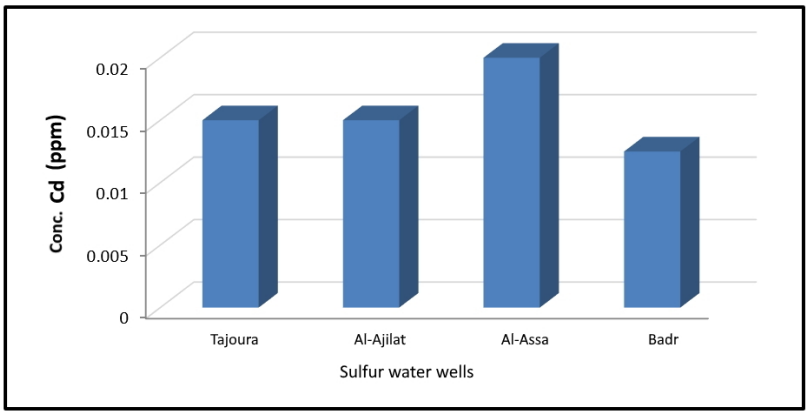


Figure (2) Concentration of Cadmium (Cd) in Hot Sulfur Well Water (ppm)

**3- Copper (Cu)**

Through the data in Table (1) and Figure (3), it was found that the copper concentration rates during the seasons of the year in the sulfur water wells in (Tajoura, Al-Ajeelat, Al-Asa and Badr) amounted to less than (0.04) ppm. Less than (0.04 ppm) for all seasons.

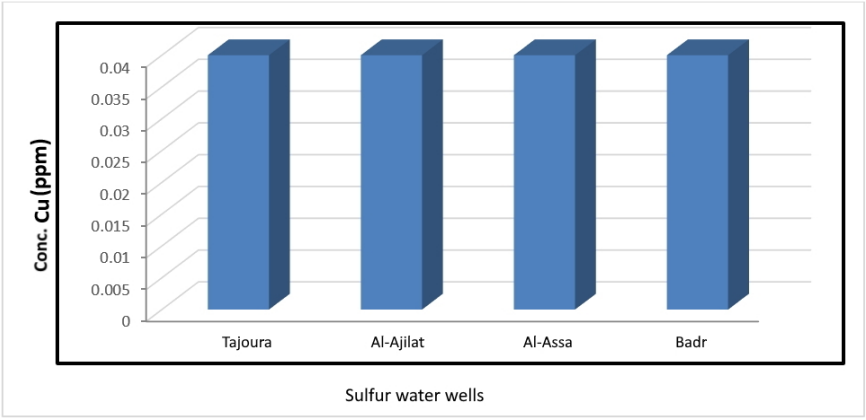


Figure (3) Concentration of copper (Cu) in hot sulfur well water (ppm)

**4- Lead (Pd)**

It appears from the data in Table (1) and Figure (4) that the concentration rates of lead during the seasons of the year in the hot sulfur water wells in (Tajoura, Al-Ajeelat, Al-Assa and Badr) range between (< 0.1525 - < 0.2175 ppm), as the variation appears in the rates of the concentration of lead where it rises in the well of Al-Assa to less than (< 0.2175ppm) and the highest rate of the element was recorded during the

winter season, which is less than (< 0.41ppm), and the lowest annual rate of the element was recorded in the well of Al-Ajeilat, where it reached less than (< 0.1525ppm) ) And the highest concentration of the element was recorded during the summer and autumn seasons less than (< 0.18 ppm).

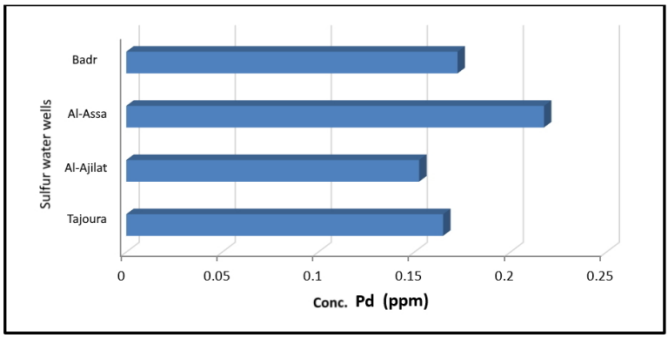


Figure (4) Concentration of lead (pd) in hot sulfur well water (ppm)

**5- Zinc (Zn)**

Through the results presented in Table (6) and Figure (18), it was found that the concentration rates of zinc during the seasons of the year in the sulfur water wells (Tajoura, Al-Ajeelat, Al-Asa and Badr) ranged between (< 0.0125 - < 0.0175 ppm), and the results showed a discrepancy in the concentration rates. Zinc, where it showed a rise in the well of Al-Assa and its rate is less than (0.0175 ppm), and the highest rate of the element was recorded in the winter season with a concentration of the lowest (ppm0.03), and the lowest annual rate was recorded in the well of Al-Ajeilat where it reached (< 0.0125 ppm) and the highest concentration was recorded for the item during the summer when the item reached less than (0.02 ppm).

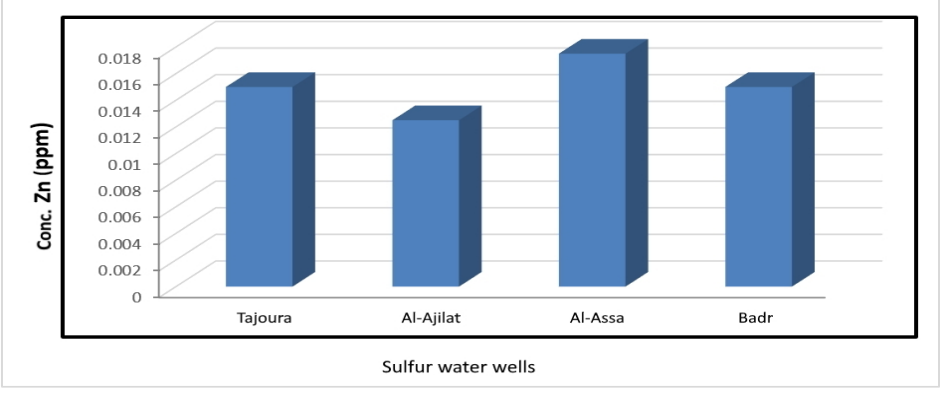


Figure (5) shows the concentration of zinc (Zn) in hot sulfur well water (ppm)

**6- Manganese (Mn)**

It is clear from the results in Table (1) and Figure (6), it was found that the rates of manganese concentration during the seasons of the year in the sulfur water wells (Tajoura, Al-Ajeelat, Al-Asa and Badr) ranged between (< 0.0375 - < 0.05 ppm), and it is noted that the manganese concentration rates vary according to the regions, It showed an increase in the Al-Assa well, where the annual rate was (< 0.05ppm) and the highest rate was recorded during the winter season with a concentration (< 0.14ppm), and the lowest annual rate was recorded in the Tajoura and Al-Ajailat wells, where it reached the lowest (< 0.0375ppm).

The highest concentration of the element was recorded in the wells during the winter season, where the concentration of the element was respectively (< 0.08 - < 0.09 ppm), and it is noted that the concentration rates are similar during the seasons of the year.

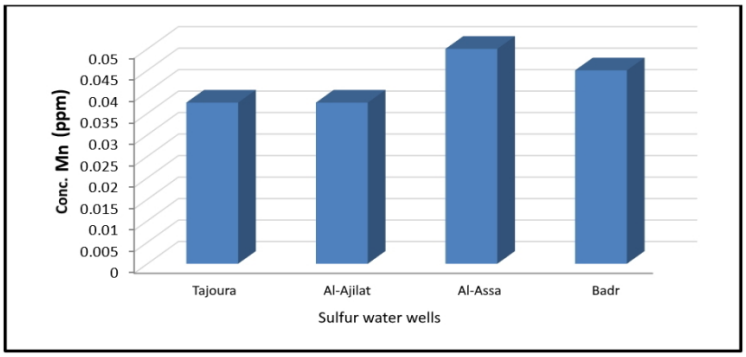


Figure (6) shows the concentration of manganese (Mn) in hot sulfur well water (ppm)

**7- Iron (Fe)**

Through the results presented in Table (1) and Figure No. (7), iron concentration rates during the seasons in sulfur water wells (Tajoura, Al-Ajeelat, Al-Asa and Badr) range between (< 0.24 - 7.40 ppm), and the results showed a variation in iron concentration rates according to regions. And it showed the rise in Badr well at an annual rate of (7.40 ppm), and the highest rate was recorded in the summer with a concentration of (8.85 ppm), and the lowest annual rate was recorded in the well of Al-Ajeilat, which amounted to (< 0.24 ppm), and the highest concentration of the element was recorded in

the summer Where it reached (0.83 ppm) and it is noted that the concentration rates of the element are equal during the winter and spring seasons.

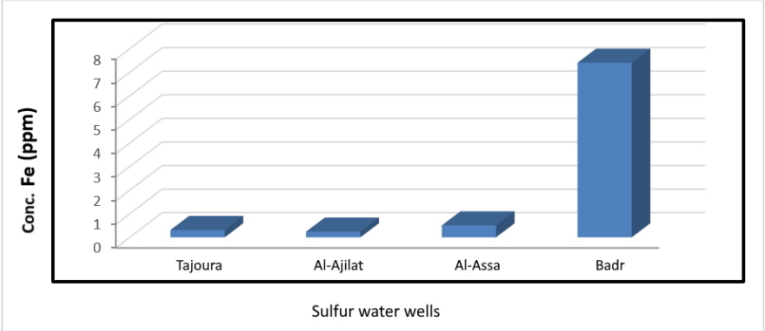


Figure (7) shows the concentration of iron (Fe) in hot sulfur well water (ppm)

Table (2) shows the general (Annual rate) of heavy metal concentrations in the hot sulfur wells water in northwestern Libya (the element concentration rate mg/l).

| Location / Element | Tajoura | Al-Ajilat | Al-Assa | Badr | Annual rate | International Standards WHO (mg/l) |
|---|---|---|---|---|---|---|
| **Cr** | **< 0.12** | **< 0.12** | **< 0.12** | **< 0.12** | **< 0.12** | **0.05** |
| **Cd** | **< 0.015** | **< 0.015** | **< 0.02** | **0.0125 <** | **0.0156 <** | **0.003** |
| **Cu** | **< 0.04** | **< 0.04** | **< 0.04** | **< 0.04** | **< 0.04** | **1.0** |
| **Pd** | **< 0.165** | **0.1525 <** | **0.2175 <** | **0.1725 <** | **0.1769 <** | **0.05** |
| **Zn** | **< 0.015** | **0.0125 <** | **0.0175 <** | **< 0.015** | **0.0150 <** | **5.0** |
| **Mn** | **0.0375 <** | **0.0375 <** | **< 0.05** | **< 0.045** | **0.0425 <** | **0.5** |
| **Fe** | **0.31** | **0.24** | **0.5050** | **7.4025** | **2.1177** | **0.3** |
| **Annual rate** | **0.10** | **0.088** | **0.138** | **1.115** | **0.36** | |

## Conclusion

This study has presented the levels of heavy meatls such as Cu, Pb, Zn, Mn, Fe, Cr, Cd in the hot sulfur water wells samples. The results showed that, the concentrations of heavy metals were within the permissible limits locally and internationally (WHO, 1984), with the exception of iron, where the general average of its concentration was (2.11 mg/l), the reason for the

rise is due to the rust and erosion of water pipes and to the nature of the rocks that make up the ground, and the lead is less (0.18 mg/l). Chromium concentration was less than (0.12 mg/l), Cadmium and Zinc less than (0.02 mg/l), Manganese less than (0.04 mg/l), followed by Copper with the lowest concentration rate (0.04 mg/l).

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