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CONTACT (OIL) WATER DETERMINATION N TERRESTRIAL WATERS USING AN OCEANOGRAPHIC METHOD

ODREĐIVANJE KONTAKTNE (PETROLEJSKE) VODE U KOPNENIM VODAMA POMOĆU NOVE OCEANOGRAFSKE METODE

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CONTACT (OIL) WATER DETERMINATION IN TERRESTRIAL WATERS USING AN OCEANOGRAPHIC METHOD[1])

ODREĐIVANJE KONTAKTNE (PETROLEJSKE) VODE U KOPNENIM VODAMA POMOĆU OCEANOGRAFSKE METODE

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In some of our earlier papers (Buljan, 1962, 1963) we have shown that various natural waters may be usefully arranged into clearly distinguished groups according to some of their chemical properties.

This makes it possible for us to group together waters which, in the course of their past, came into contact with hydrocarbons in the earth's crust. This contact with oil or gas affected the chemical constitution of such waters and this is why they have been called »oil waters« or »petroleum waters«, the terms being synonimous with »edge waters« or »contact waters«. The existence of some other types of water, such as marine, rain and sulphate ones, as well as some transitory types (e. g. surface waters) was also discussed. Some of these waters are of great importance to us in connexion with present paper (Fig. 1. & Fig. 2.).

We have found that every natural water, including the contact waters, is marked by two important properties, viz. the balance of sulphate (SB) and the index of aeration (IA).

These two characteristics are represented with numerical values which can be calculated for every water from data of a routine chemical analysis (see Annex No. 1).

I *The sulphate balance (SB)*

The values of that parameter may vary from water to water to a considerable extent ranging from minus (—) several thousands to plus (+) several thousands.

A water with a negative value occupies a place on the Cl—SO_4 diagram lying *below* the »sea water line« (Buljan, 1962), the line corresponding to the equation

$$\log [Cl^-] = \log [SO_4^{2-}] + 0{,}8556$$

Such waters *are* indicative of oli. The higher the negative value of SB the better indication is for the presence of oil in the layers where that water was found.

A water with a positive SB values occupies a place on the graph lying *above* the »sea water line«, meaning that we are faced with a water that was not in contact with hydrocarbons. Such waters are not indicative of oil.

SB is a very significant characteristic parameter because it can, in some cases, give us some information even about the quantitative relations in the oil bearing strata.

II *The index of aeration (IA)*

For various waters the index of aeration (IA) ranges from 0 up to very high positive values. The values under 100 disclose the contact waters and they *do* represent indicators for the presence of petroleum or gas in the layers

[1]) This paper is partly read on the Symposium sur la Geodynamique de la région Méditerranéenne. Athens. Nov. 1972. Rapp. et proc. verb. des Reunions de la CIESM, Vol. 22, fasc. 2a p. 144, 1973.

where water was taken from. This is especially true of water with IA values under 20.

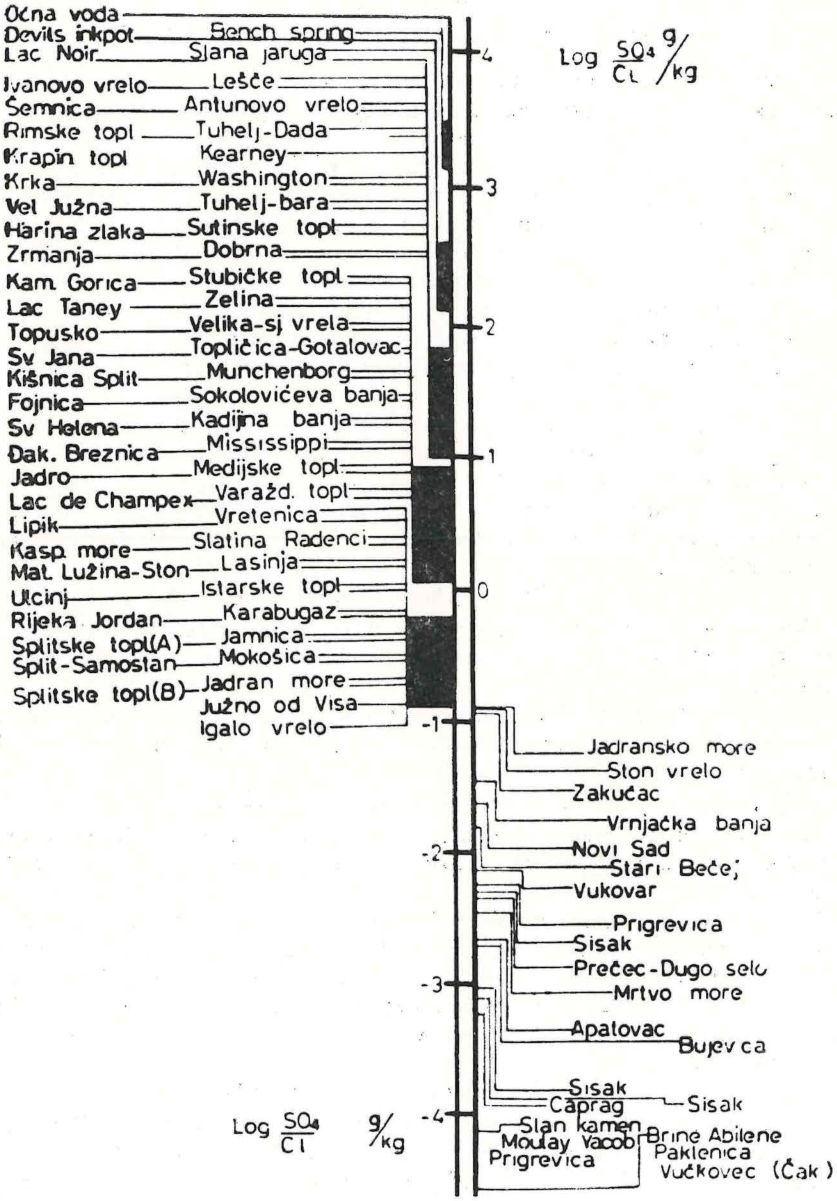

Fig. 1. Distribution of some natural waters when the values of log (SO_4/Cl) g kg^{-1} are considered. For detail see the paper B u l j a n, 1962.

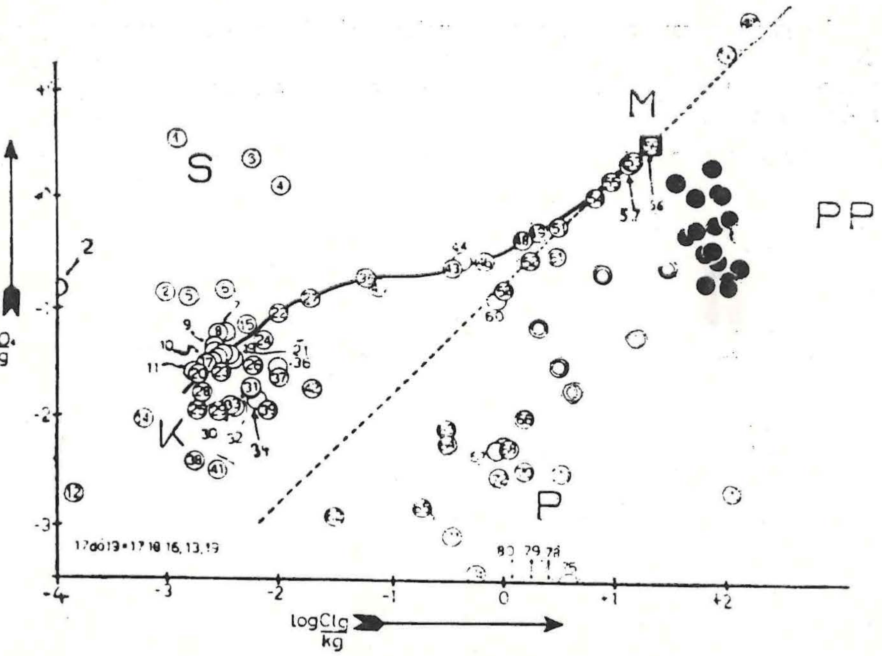

Fig. 2. Here are gathered various types of natural waters including the contact (petroleum) waters (PP and P). Those are placed *under* the diagonal line which has the equation: log $[Cl^-]$ = log $[SO_4^{2-}]$ + 0.8556. Full points on the right hand side (PP) represent a group of petroleum waters from »proved oil fields« in Near East (unpublished data). Close to the diagonal line are gathered the waters of recent marine origin (M). On the left hand side (K) of the graph, under the diagonal line, are placed various »surface waters« like rain waters, lake waters, river waters and some of mineral spring waters (B u l j a n, 1962).

The IA values, on the other hand, which are above 100, or especially > 1000, show that the water concerned is well aerated. They also mean that the water concerned neither has been in contact with organic matter nor has it ever been under a significant influence of bacteria. The IA of such water did then not undergo changes. Such waters *are not indicative* of oil.

It is a good indication when both parameters (SB and IA), agree in showing the good qualites of a water in relation to oil, which is normally the case, because the low values of IA and the high negative values of SB mostly follow each other.

Tables are here enclosed reviewing the values of SB and IA of a number of waters in relation to their genetic connection with the occurrence of oil in strata. The waters referred to in the Tables 1 and 2 are but a small choice from hundreds of waters whose SB and IA values are avalable.

We can see from the Table 1 that from the decreasing SB values (column 3: higher and higher negative values) and also of decreasing IA values (column 4) we can guess upon the rate of change of properties of waters as of oil indicators (column 5).

In such a vay we start with waters which have no connecting with oil (Nos 1, 2, 3, and 4), and going over the intermediary group of waters we arrive to the group which contains really good waters accompanying rich oil fields (Nos 16 and 17).

TABLE 1. A survey of natural waters and some of their hydrological properties in genetic relation to the occurrence of oil in strata

Ord. No.	Name and origin	Sulphate Balance (SB)	Aeration Index (IA)	Description	Literature
1	2	3	4	5	6
1.	Caspi Sea	+2,294	405	a water of surface origin and of surface type: it is not an indicator for oil;	2
2.	1/11 well, Yugoslavia	+1,160	342	a spring water of the sulphate type: it is not an indicator for oil;	this paper
3.	Jordan River, Palestine	+112	125	a surface water;	13
4.	Tarfaya, Sahara	+89	137	a surface water: it is not an indicator for oil;	12
5.	Adriatic Sea	—2	101	the marine water;	5
6.	Igalo, Yugoslavia	—2	98	a marine water type; it is not an indicator for oil;	3
7.	A 3/2 well, Yugoslavia	—154	85	a weak contact (edge) water;	this paper
8.	Slankamen, art. well, Yugoslavia	—575	0.1	a contact water; it is an indicator for oil;	3
9.	Sisak art. well, Yugoslavia	—998	0.3	a contact water; it is an indicator for oil;	10
10.	A 3/7 Yugoslavia	—1,273	46	a good contact water: it is a good indicator for oil;	this paper
11.	Sea mud, Black Sea	—1,355	4	a recent contact water (287 cm under sea bottom);	16
12.	Tiberis Lake, Palestine	—2,220	14	a very good contact water and a good indicator;	11
13.	Moulay Jacoub, Morocco	—2,400	0.4	a spring water; a very good indicator for oil;	7
14.	Zohar Sulphur Spring, Palestine	—4,328	15	an extremely good contact water; it is a very good indicator for oil;	1
15.	A 7/1 well, Yugoslavia	—6,534	30.4	an extremely good contact water and a very good indicator for oil;	this paper
16.	BP 10. well, Near East	—10,546	1.4	an extremely good contact water from a »proved oil field«;	unpublished data
17.	BP 27. well, Near East	—11,074	3.1	an extremely good contact water from a »proved oil field«;	unpublished data

Note: The column 6 gives the source where the rough data were taken from.

Another group of examples is given in the Table 2 where a set of data covering various waters occurring in Rumanian oilfields (the area of Ploesti) are given. These values of our two geochemical parameters (SB and IA) were reckoned from the data published by Krejci-Graf (1963). The data in the Table 2 are rather instructive, showing a high degree of correlation (i) between the negative values of SB (the higher negative number the better!) with the occurrence of oil in the area, and similarly (ii) between the low numerical values of IA with the occurence of oil in the area. Very similarly behave also the data (Krejci-Graf, 1963) covering the Moldavian oil fields area.

TABLE 2. A survey of mutual connections of geochemical properties such as SB and IA of waters from South Rumania — Ploesti — and the presence of oil in the same area (the field data from Krejci-Graf, 1963).

Ord. No of oil field	Code of water sample	Depth (m)	Sulphate Balance (SB)	Aeration Index (IA)	Total production of oil till 1942	Oil production (tons/ha)	Source of data
1	2	3	4	5	6	7	8
1.	*Moreni-Piscuri*				33,893,360	17,888	
	No. 3		—11,224	0.59			Table 9
	No. 4		—13,223	0.95			"
	No. 8	832	—1,867	2.0			"
	No. 34		—9,380	0.01			"
	No. 1		—22,296	2.0			Table 10
	No. 16	128	—15,732	0.2			"
	No. 19	1,138	—15,330	0.06			"
	No. 27	1,080	—14,400	0.01			"
2.	*Ochiuri*				7,658,830	25,529	
	No. 64		—13,050	0.01			Table 8
	No. 63	1,106	—15,967	0.33			"
	No. 62	1,083	—17,250	0.01			"
	No. 61		—3,440	3.3			"
3.	*Baiceiu*				2,812,090	31,245	
			—10,540	0.01			Table 12
4.	*Campina*				4,611,100	15,370	
	No. 13		—21,600	0.01			Table 13
	No. 6	258	—19,200	0.01			"
	No. 9	771	—15,330	0.01			"
	No. 14		—12,730	0.01			"
5.	*Bustenari*				14,450,310	15,370	
	No. 12	575	—2,170	0.46			Table 14
	No. 13	742	—16,634	0.01			"
	No. 14	751	—18,770	0.01			"
	No. 18	486	—13,870	0.01			"
	No. 20		—11,800	0.01			"

Note the high degree of correlation between the values in columns 4 and 5 on one hand and of the values in columns 6 and 7 on the other!

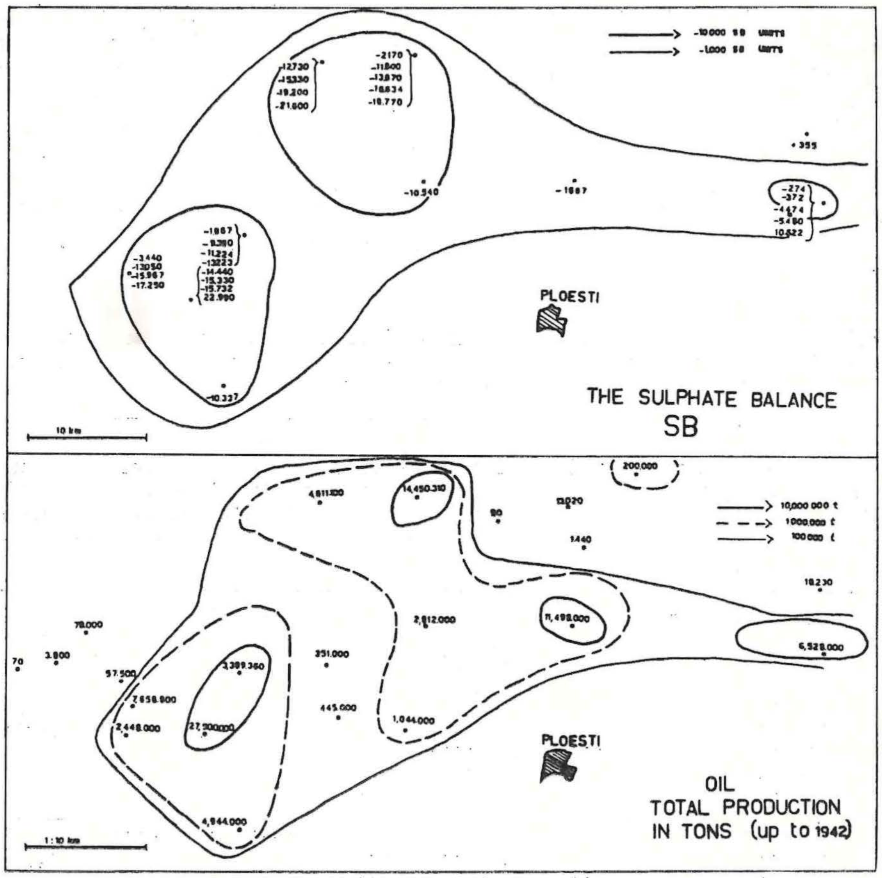

Fig. 3. The geographical distribution of: SB units in well waters and of oil richness of the oil fields in Ploesti area (Rumania). The two parameters are in a good agreement. The data are taken from K. Krejci - Graf (1963).

We may add here some graphs which can serve us further examples of how it works this new geochemical method for various places such as: Romania (Fig. 3), Jugoslavia (Fig. 4 & 5) and the Dead Sea area (Fig. 6).

It follows from what has been said above, that if a number of chemical analyses of various waters is available, one is able to identify »oil waters« by applying this method only, i. e. without the need of other help or information. It is clear enough, that if the locality where such a water was taken from is known, the datum can be useful to people prospecting for oil.

The advantage of this method is that it is applicable not only to water resulting from drilling for oil but to other ones too, such as mineral waters, normal source waters, artesian well waters, even to waters from lakes, rivers, brooks etc. Just because of this quality, precious information about the oil content in an area may be obtained by applying this method even prior to boring.

This method is also characterized by the fact that it approaches the origin and distribution of oil in the earth's crust from an oceanographic aspect. This is justified when we consider the opinion prevailing today that the oil originates from *sea* organisms — from their organic matter through the action of *marine* bacteria in *marine* sediments. We have taken some rough data from Š i š k i n a 's papers (1959 a and 1959 b) and we have reckoned the values of our two parameters (SB & IA) for mud waters taken from Black Sea and from Pacific Ocean sediments of variuos depths under the sea bottom. From the results (Tab. 3) we have obtained a quantitative picture of the rate of diagenesis of interstitial sea mud water in recent time on two selected places where oil water is in statu nascendi. We can take for granted that these

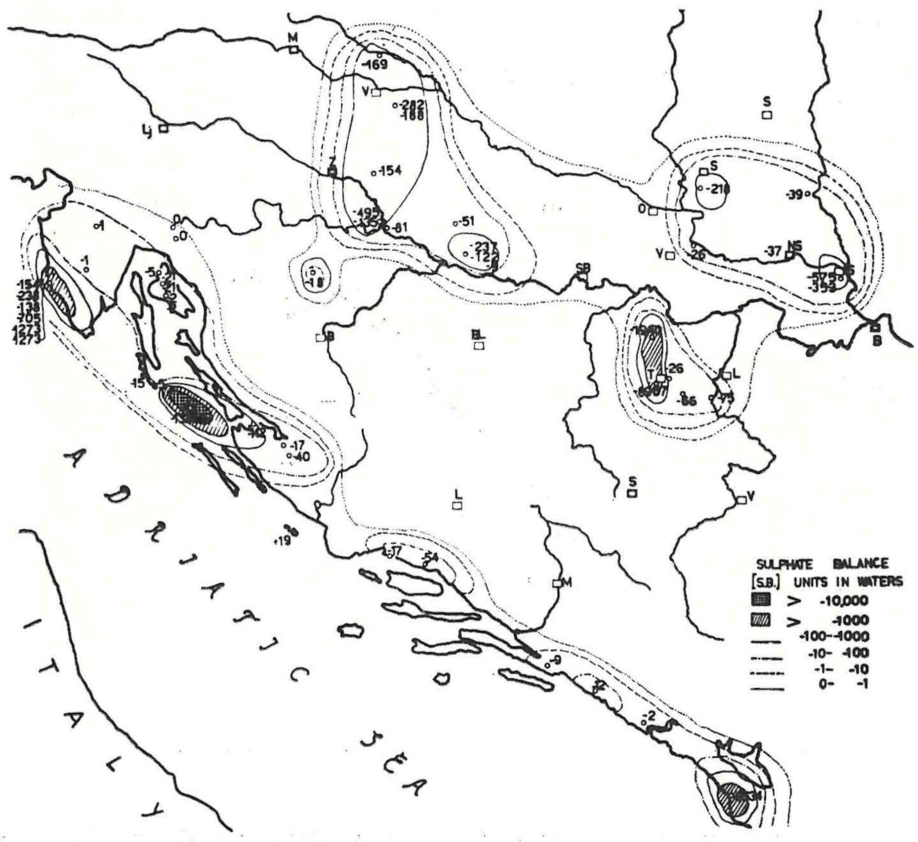

Fig. 4. The geographical distribution of SB characteristics of natural waters and of well waters in coastal area of the Adritic Sea and in Panonian Plain of Yugoslavia (M. B u l j a n, unpublished data).

waters were accompained with stoichiometric equivalents of produced hydrocarbons also in statu nascendi. (See also the Fig. 7).

The data from the same table probably reflect also the degree of bioproduction in the sea water above the respective sediments. However not all of the stations from the same author we have supervised showed such high degree of chemical change of water in sediments. Some of them had even positive SB values as e. g. St. No. 3154.

The marine orientation in the study of oil problem such as we have accepted has created, we think, the new possibilities being nov realized through the method expounded here.

Probably the most important quality of it is that using the vertical component of deep water natural courses the method can supply the valuable informations upon the qualities of these deep milieux and that is why this method will probably represent a new and useful geochemical tool in oil finding.

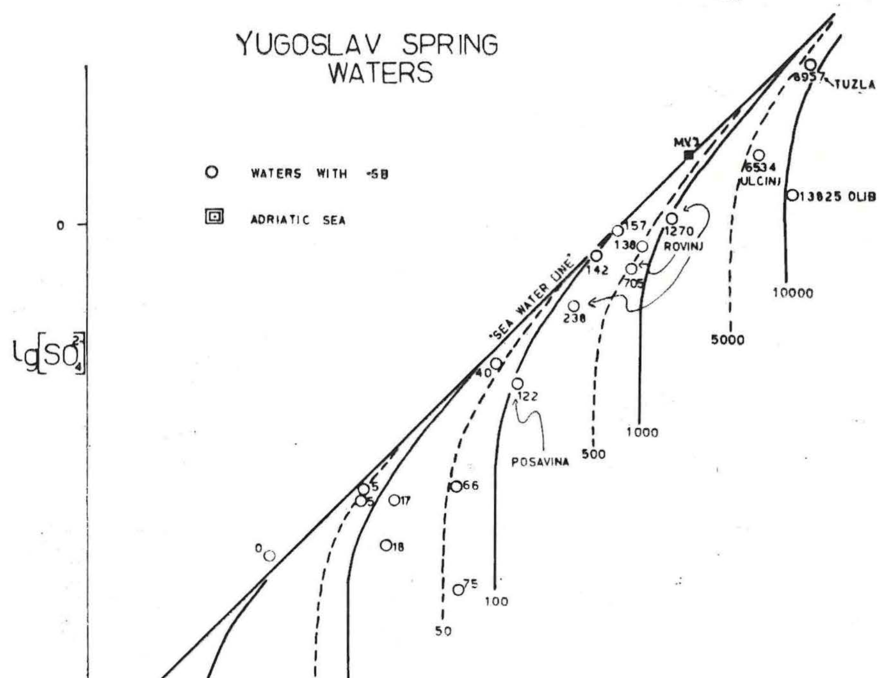

Fig. 5. The waters from some Yugoslav drilling holes. Each vertical curve is signed with the corresponding number of SB units: 10, 100, 1000, and 10.000. The points on the right hand side represent very good contact waters (unpublished data).

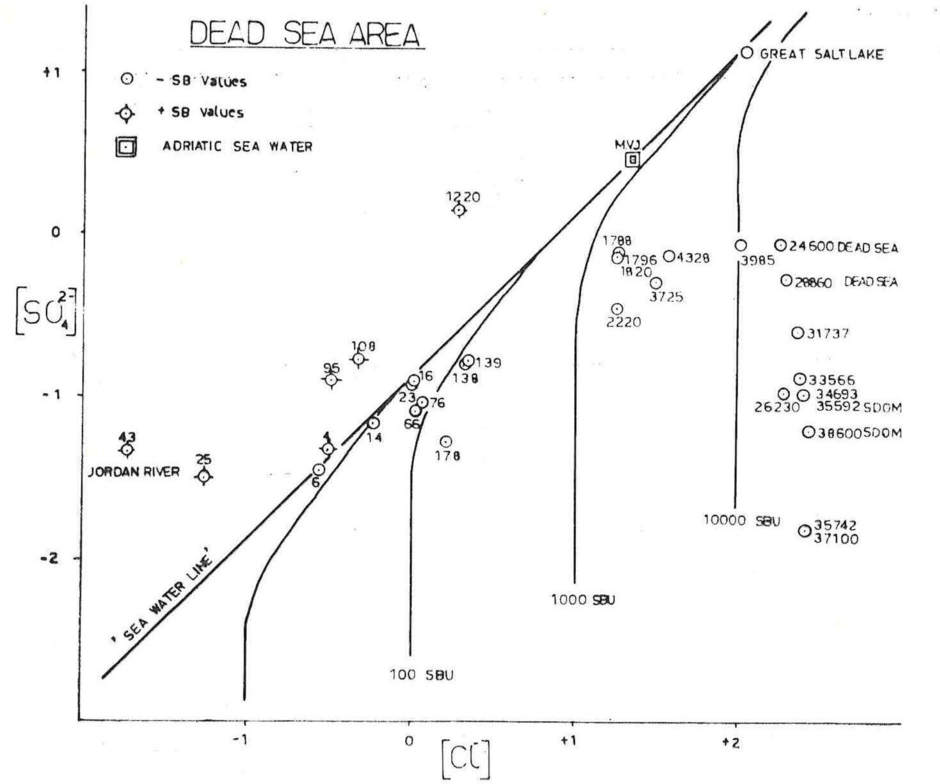

Fig. 6. The waters of Dead Sea area. Each vertical curve is signed with the corresponding number of SB units (SBU). The points on the right hand side represent extremely good contact waters. Data taken from K. Y. Bentor (1961) and O. H. Oren (1962).

TABLE 3. The rate of diagenesis of mud water in sea sediments

Ordin. No.	Depth in sediment (cm)	Sulphates Balance (SB)	Aeration Index (IA)	Literature
1	*Black Sea, Eastern part, Stat. No 4. Depth 2150 m*			
	2	—120	93	16
	5	—660	61	
	72	—611	64	
	97	—949	43	
	120	—1,223	26	
	162	—1,238	16	
	204	—1,329	11	
	226	—1,478	6.5	
	287	—1,355	4.3	
	325	—1,290	10	
	351	—1,254	12	

Cont. of Table 3.

2	*Pacific Ocean. near Kuril Is., Stat. No. 3177. Depth 6860 m*			
	50	—144	94	15
	160	—614	77	
	232	—1,040	62	
	320	—1,640	40	
	395	—2,120	23	

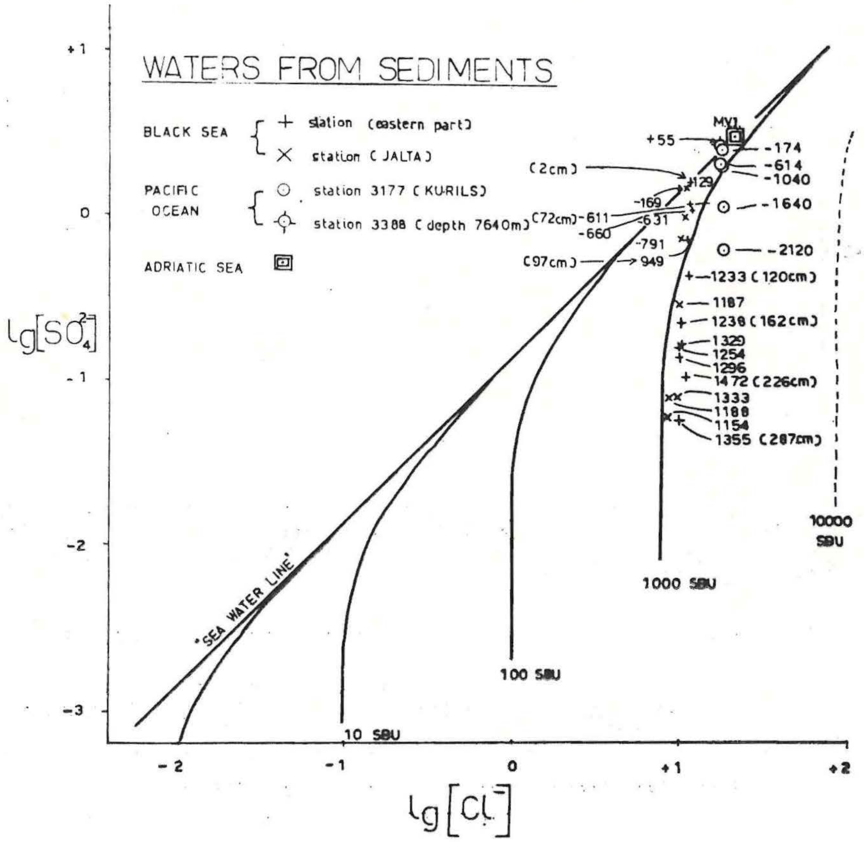

Fig. 7. The waters from sea sediments. Water in sediments changes its chemical composition depending of the place and the depth in the sediment. The Sulphate Balance (SB) can sometimes serve as a measure of the rate of diagenesis of such interstitial water. The deeper the water (the earlier buried) — the higher SB value. Such is the rule at least up to a certain depth. Each vertical curve is signed with corrensponding number of SB units. All the values of the SB units for waters *under* the diagonal line are negative although negative sign (»-«) is partly ommited. Data taken from O. V. Šiškina (1959 a, and 1959 b).

ANNEX No. 1

Two principles were adopted while preparing the present paper, (1) the relative uniformity in the composition of the sea water as established by Dittmar (1884), and (2) the mutual genetic connection between all kinds of water on the earth's crust as claimed by Vernadski (1933). We have earlier concluded (Buljan, 1962) that, by its origin and through the action of cyclic salts, the rain is closely connected with the sea water, influencing, on the other hand, most of the waters existing in the earth's crust (mineral and other springs).

According to G. N. Kamenski (1958) the presence of mineral waters in the earth's crust may be explained by the solving of salts contained in the upper rock strata through the action of infiltrating water. M. P. Tolstoy (1958) considers many mineralized waters to be of marine origin.

Our own investigations involving natural waters (Buljan, 1963) have shown that Cl^- and $SO^{2}_{4}{}^{-}$ are perhaps the most important pair of anions in such waters.

As regards ocean water it has been found (Sverdrup & al., 1946) that to each quantity of 19,010 g/kg Cl (including some Br^-) corresponds a quantity of 2,649 g/kg $SO^{2}_{4}{}^{-}$.

It is indispensable, in the application of our method, te make use of data referring to the Cl mg/kg quantities contained in the water under investigation. The established quantities of Cl mg/kg present in a water will serve us to calculate the theoretical content of sulphates (tSO_4) corresponding to the quantities of chlorides (+ bromides) in that water:

$$\text{Cl mg/kg} : SO_4 \text{ mg/kg} = 7.18 \quad (1)$$

$$\text{Cl mg/kg} \times 0.1394 = t\,SO_4 \quad (2)$$

This again is the basis for the calculation of the sulphate balance (SB):

$$SB = SO_4 - t\,SO_4 \quad (3)$$

and for the calculation of the aeration index (IA):

$$IA = \frac{SO_4 \cdot 100}{t\,SO_4} \quad (4)$$

Here are a few examples illustrating the calculation of our parameters SB and IA:

TABLE 1.

	Cl mg/kg	SO_4 mg/kg	tSO_4	$\frac{SO_4 \cdot 100}{tSO_4}$ = IA	$SO_4 - tSO_4$ = SB	Literature
Ocean	19,010	2,649	2,650	100.0	0.0	Sverdrup & al, 1942
Sisak, well, Yugoslavia	3,585	0.003	998	0.3	—988	Miholić & al., 1952
Arbanasi, well, Rumania	108,130	0.00	15,060	0.01	—15,060	Krejci-Graf, 1963
Jordan river	3,192	556.0	444	125.0	+112	Sahama & Rankama, 1950

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CONTACT (OIL) WATER DETERMINATION IN TERRESTRIAL WATERS USING AN OCEANOGRAPHIC METHOD

ABSTRACT

A method is described making it possible to disclose contact waters among a number of natural waters of all types. Two new properties for every waters has to be found: the sulphate balance (SB), what equals to the loss of sulphate during the diagenesis of the water, and the index of aeration (IA). A number of data from various countries including Rumania, Yugoslavia & Near East is given indicating the strong correlation between the negative values of sulphate balance and the occurrence of oil in the layers where water samples were taken from. A similar correlation is found also for the other parameter: the aeration index (IA) of water from one side and the oil occurrence in the strata from the other. Informations are added to show how the sulphate balance and the aeration index disclose the recent formation of contact water in the sea sediments. The usefulness of the method is emphasized because in can sometimes give prior to boring for oil important informations which regard the content of oil in the strata.

The way how to reckon the values of two new parametars is given also.

ODREĐIVANJE KONTAKTNE (PETROLEJSKE) VODE U KOPNENIM VODAMA POMOĆU NOVE OCEANOGRAFSKE METODE

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KRATAK SADRŽAJ

U radu je opisana nova metoda koja je u stanju da, između raznih tipova prirodnih voda (marini, kišnički, sulfatni i neprozračni tip) pronađe petrolejsku ili fosilnu vodu tj. vodu koja u svom kemijskom sastavu pokazuje da je nedavno bila u dodiru sa ugljikovodicima. U tu svrhu je potrebno odrediti dva važna svojstva svake prirodne vode; indeks prozračenja (IA) i sulfatni bilans (SB). Ovi se mogu izračunati iz podataka normalne kemijske analize. Upotreba ovih dvaju parametara je rastumačena kada se oni ponašaju bilo kao pozitivni indiktori bilo kao negativni indikatori za prisutnost nafte u slojevima.

U tabeli br. 1. su dati podaci (stupci br. 4 i 5) koji ukazuju na jaku korelaciju koja postoji između visokih negativnih vrijednosti SB s jedne strane i pojave ugljikovodika u slojevima odakle su bili uzeti uzorci voda.

Metoda ima oceanografski pečat pa je izneseno mišljenje da je upravo ova marina orijentacija donijela nove mogućnosti kod rješavanja problema kao što je traženja nafte koja je i sama proizvod marine sredine.

Opisana su i druga svojstva metode između ostalih i to da nekada može da dade važne informacije u vezi sadržaja ugljikovodika u nekom terenu i prije bušenja na naftu.