

## THE DETERMINATION OF THE $\delta^{13}\text{C}$ IN PETROLEUM AND NORMALIZATION OF ITS VALUE

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**Abstract :** Carbon consists of two stable isotopes, carbon 12 and carbon 13. Carbon isotope ratios are determined by the CO<sub>2</sub> sample using the gas mass spectrometer, so, the carbon of petroleum is transformed to the carbon dioxide. The carbon isotope ratios are reported as  $\delta$  - values, where the  $\delta$ - value is the difference between the isotope ratios of a sample and a standard, related to the isotope ratio of the standard used. To resolve the confusion due to expression of the isotopic data, we have expressed the data versus international PDB – standard, so, we have normalized these data. Normalization is the process of stretching or shrinking an isotope ratio scale, so, that a second reference material is set to a defined  $\delta$  - value relative to the first reference material.

**Introduction :** The acquaintance of the isotopic composition of the carbon of the petroleum and natural gases there was an important problem the last years. Natural variations in carbon isotopes are caused by equilibrium exchange and kinetic fractionation processes in the different carbon cycles. In this way, carbon isotopes give information on the generation, maturation and genetic correlation of hydrocarbons and their precursors which can be used in oil and gas exploration [ 1 ].

The isotopic analyses of the carbon, usually, were fulfilled by the carbon dioxide gas using a mass spectrometer with gas equilibrium; the equipment must be with entry double system and a system multi collectors.

Generally, in the geochemical studies and the data interpretation, there are important the  $\delta$  - value , which for the carbon is : [ 2 ]

$$\delta^{13}\text{C} (\text{‰}) = \left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sam.}} - \left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{ref.}} / \left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{ref.}} (\text{‰})$$

where :  $^{13}\text{C} / ^{12}\text{C}$ , represent the isotope ratio of the carbon for the sample and for reference.

The  $\delta$ - values there are expressed in ‰ with respect to the international standard PDB ( amerikan Belemnite ).

**Object and study method :** The preparation of the carbon dioxide from the petroleum, isotopic analyses of the carbon dioxide and the determination of  $\delta^{13}\text{C}$  ‰ of the petroleum have been the objects of the study. The generation of the CO<sub>2</sub> is fulfilled through the combustion of the natural petroleum using the elementary analyzer Model 1106; the combustion of the petroleum is fulfilled in the presence of the convey gas Helium enriched with the clear Oxygen. The gases of the combustion pass into the chromatography column filled with chromium oxide and cobalt oxide which are in the role of catalizators. At the exit of the chromatography column, there are pass one by one the different gases of the petroleum combustion, so, there is the possibility to gather the CO<sub>2</sub> in the glass test – tube and in the presence of the liquid nitrogen trap.

The isotopic analyses of the CO<sub>2</sub> generated were realized using the mass spectrometer SIRA 10, with the double entry system, with three collectors system and with the system of the CO<sub>2</sub> gas equilibrium.

*Experimental results:* During the experimental study there were the objectives of : the generation of the clear carbon dioxide; the determination of the smallest quantity of the sample for isotopic analyses; the isotopic analyses of the carbon and the determination of the  $\delta^{13}\text{C}$ .

a ) The generation of the clear carbon dioxide : At the beginning there have been some experiments for the investigation of the combustion process of the petroleum and the carbon dioxide generated. For the experiments were used the petroleum samples of Vlorë 10 and two samples of asphaltens. In the glass test - tube, probably, will had the carbon dioxide gas and convey gas Helium. The glass test - tube is connected at the entry system of the mass spectrometer, is putted into the liquide nitrogen trap and after this process is evacuated the Helium gas.

By the isotopic analyses of the  $\text{CO}_2$  which is used as equilibration gas to the mass spectrometer SIRA 10, the intensity  $I = 6\text{E}-09\text{A}$  of the highest peak ( mass number 44 ) is arrived for the pressure of the ionization chamber  $p = 2.1\text{E}-08$  torr; the same intensity of this peak is arrived for the same pressure and for the  $\text{CO}_2$  gas prepared from petroleum and asphaltens, so the sample gas is clear from other gases.

b) The treatment and isotopic analyses of international standards NBS 22 and PEF 1 : The  $\delta^{13}\text{C}$  ‰ is expressed with respect to international standard PDB, but it is not effective to use it in each measurement [ 3 ]. We have used two standards, NBS 22 and PEF 1, distributed by the International Atomic Energy Agency ( IAEA ), for the determination of  $\delta^{13}\text{C}$  ‰ value of the equilibration gas  $\text{CO}_2$  of the mass spectrometer. The  $\delta^{13}\text{C}$  values, versus to PDB, of the standards NBS 22 and PEF 1, there are respectively :

$$\begin{aligned} \delta^{13}\text{C} \text{ ‰} &= - 29.73 \text{ ‰} \\ \delta^{13}\text{C} \text{ ‰} &= - 31.77 \text{ ‰} \end{aligned} \quad [ 4 ]$$

Generally, for the  $\delta^{13}\text{C}$  ‰ value, versus to PDB, we can write :

$$\delta^{13}\text{C} \text{ ‰}_{\text{PDB}} = A \cdot \delta^{13}\text{C} \text{ ‰}^* + B \quad ( 1 )$$

where : A and B there are two constants which must determinated, while  $\delta^{13}\text{C} \text{ ‰}^*$  is the value of the sample, versus laboratory standard, taking into the consideration the Craig corrections [ 6 ] and the fact that the our mass spectrometer there are a system with three collectors.

The treatment of the  $\text{CO}_2$  gas from the standards NBS 22 and PEF 1 were realized the same line and the same parameters of the treatment of the  $\text{CO}_2$  gas from the petroleum; the isotopic analyses, also, were realized at the same parameters of the mass spectrometer. Referring the formula ( 1 ) for the two standards, the values of constants A and B there are :

$$A = 1.02 ; \quad B = - 42.53.$$

The mean value of the  $\delta^{13}\text{C}$  ‰ of the carbon dioxide, used as laboratory standard gas, there is :  $\delta^{13}\text{C} \text{ ‰} = - 42.49 \text{ ‰}$ .

Using the standards NBS 22 and PEF 1, have determinated the smallest quantity of the samples for isotopic analyses, taking into the consideration that the high vacuum of the analyzer to change with one or two times at the moment of the sample input to the analyzer. Referring the results of our experiments and our measurements, the smallest quantity of the sample or standard for isotopic analyses there is 0.5 mgr.

c ) The determination of the  $\delta^{13}\text{C}$  ‰ of the petroleum and comparison of the results : Taking into the consideration the method of the elaboration of the sample, the method of the treatment of the carbon dioxide from the sample and the isotopic analyses of the  $\text{CO}_2$  gas, we have determinated the  $\delta^{13}\text{C}$  ‰ value of the petroleum versus to PDB standard; for two petroleum samples we have had the possibilities to compare the results with the values of one other laboratory [ 5 ]; the results there are in the Table No.1 :

Table No.1

Sample	$\delta^{13}\text{C} \text{ ‰}$ ( our lab. )	$\delta^{13}\text{C} \text{ ‰}$
Ba 20	- 28.2	- 28.9
Bu 42	- 27.7	- 28.6

The values of the  $\delta^{13}\text{C} \text{ ‰}$  of the petroleum samples of two different laboratories there are in good correspond.

#### Conclusions :

1 - The our method of the treatment of the carbon dioxide from the petroleum is correct because it is created possibilities to gather the  $\text{CO}_2$  and Helium convey gas into the glass test - tube. Also, the our method of separation of the carbon dioxide from the helium is effective, because the  $\text{CO}_2$  sample is clear.

2 - It is presented a way of the  $\delta^{13}\text{C} \text{ ‰}$  calculation of a sample gas dioxide versus PDB, using two other known standards versus PDB.

3 - The good correspond of the  $\delta^{13}\text{C} \text{ ‰}$  values of the same petroleum samples between two laboratories confirm the right way of : the treatment of the carbon dioxide from petroleum; the cleaning of the carbon dioxide from other gases; the calculation of  $\delta^{13}\text{C} \text{ ‰}$  versus PDB, using two known standards.

#### References :

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