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Determination of the carbon / hydrogen ratio in bitumen using prompt neutron gamma activation analysis

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Abstract

The paper presents a potential application of PGNAA method that allows the fast determination of colloidal index of bitumen compounds by a very fast analysis of hydrogen and carbon content. The H/C ratio thus determined is then correlated with colloidal index I_C. The regression line is given by the empirical relation $C/H = 5.9 + 34.1 * I_C$ with a correlation factor $R=0.99$ and a standard deviation $SD = 0.71$. The perspectives of on-line applications are discussed.

1. INTRODUCTION

Bitumen is very important industrial material whose quality is connected with its chemical composition, which is controlled mainly by the crude oil processing technology. Though it comprises a great number of chemical compounds the following model appear to be in general accepted: The high molecular weight asphaltenes which tend to form sterical colloids dispersed in a lower molecular weight oily medium (maltenes). This "see" of maltenes in its turn is constituted from saturates, aromatics, and resins. The proportions of these molecular groups give the physical properties of various bitumen samples /1,2/. The colloidal index of bitumen is defined as a ratio of the total amount of asphaltenes and saturates to the amount of resins and aromatics. It describes the stability of colloidal structure.

Using a Prompt Gamma Neutron Activation Analysis (PGNAA) Set Up developed and installed at IFIN-HH; Bucharest we present an industrial application of this nuclear method devoted to a fast estimation of colloidal index of bitumen.

2. THE EXPERIMENTAL SET-UP

The experimental set-up consists of an Am-Be neutron source (10^7 n/s) placed in a cylindrical vessel and a semiconductor Ge-Li detector outside the vessel. The experimental arrangement is presented in fig. 1. The prompt gamma spectrum is recorded and analysed using an integrated computerised system. The energy

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calibration was carried out using the known prominent gamma lines in the different parts of the spectrum. The MCA soft provides the digital spectrum stabilization (DSS) by choosing a few known references peaks.

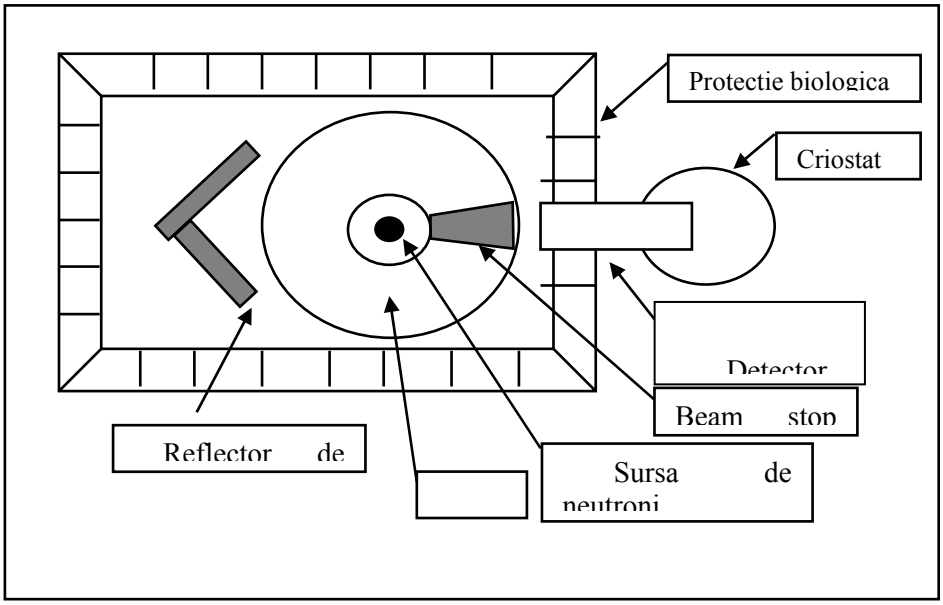

Fig. 1. PGNAA Schematic and view for experimental set up

3. PGNAA SPECTRA

The comments of the gamma lines obtained in such a geometry can be found in /3/.The PGNAA spectra were determined for three types of bitumen compounds. For exemplification in fig.2 the gamma spectrum for an ESSO sample is shown.

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The measuring time was one hour and the dead time was about 5 %. The inelastic scattering carbon lines are Doppler broadened.

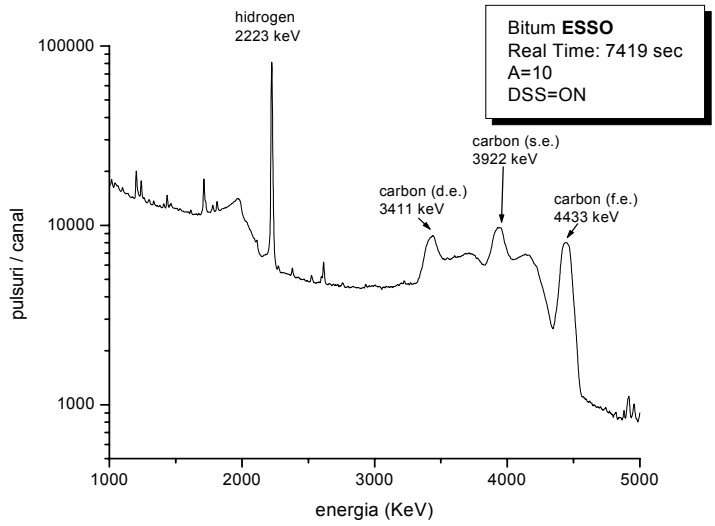

Fig.2. The PGNAA spectrum for ESSO bitumen sample

4. C/H RATIO

In order to determine the C/H ratio for bitumen by PGNAA method we used the thermal capture line of hydrogen at 2.22 Mev and the inelastic scattering (n, n',γ) of carbon at 4.43 Mev. The concentration of hydrogen will be given by:

$$\nu_H = \frac{A_H . R_H}{\varepsilon(E_{H,\gamma}) . I_{H,\gamma} . \sigma_{\gamma,H}} \tag{1}$$

where A_H stands for atomic mass, R_H-the peak area of hydrogen capture line, ε(E) is the detector efficiency at energy E of the line, I-the photon emission probability per captured neutron, while σ stands for thermal neutron capture cross section of hydrogen. In the case of carbon we deal with an averaged cross section on the fast neutron flux that is present in the sample:

$$\nu_C = \frac{A_C . R_C}{I_C . \varepsilon(E_{C,\gamma})} \tag{2}$$

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where A_C is the mass of the carbon nucleus , R_C is the carbon line area, ,ε(E) is the detector efficiency at 4.43 Mev while I_C, the sensitivity factor is given by the following integral

$$I_C = \int_0^{E_{max}} S'(E).\sigma(E).dE \tag{3}$$

It represents the averaged cross section on effective fast neutron flux S'(E) normalised to unity. The value of this integral for an Am-Be neutron source placed in moderator medium, composed especially from carbon and hydrogen (like hydrocarbons, coal, or polymers) was calculated by Wormald.

$$I_C = 0{,}11029$$

The aromatic factor C/H will be given by the ν_C/ν_H ratio:

$$\frac{C}{H} = \frac{A_C.R_C}{A_H.R_H}\frac{\varepsilon(E_H)}{\varepsilon(E_C)}\frac{I_C}{\sigma_{\gamma,H}} \tag{4}$$

Here the value of σ_H is 0,332 barn, A_C = 12, A_H= 1, while the efficiencies ratio $\varepsilon(E_H)$ / $\varepsilon(E_C)$ was obtained from the efficiency function of Ge-Li detector calculated by us by Monte Carlo simulations:

$$\frac{\varepsilon(E_H)}{\varepsilon(E_C)} = 1{,}23$$

The calibration of the experimental system was realized by using an graphite-alum mixture:

$$(NH_4)\ Al.(SO_4)_2\ 12.H_2O$$

This compound contains:

H	6.2%
O	70.6%
N	3%
S	14.0%
Al	6.2%

The measurements were carried out on two such mixtures:

50% graphite	50% alum	C/H ratio = 16,13
70% graphite	30% alum	C/H ratio =24.19

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In order to have a good homogeneity the two materials were very well chewed and the geometry of the system was kept identical. On the other hand the bitumen has a composition dominated by carbon (81÷86%), hydrogen (9.5÷10.8%), and sulfur (1.3÷6.9%).The comparison of PGNAA data with real mixture composition gave the following results:

Table 1. The main data of the calibration mixtures for check

Sample Number	Graphite / Alum ratio	C/H ratio mixture	C/H ratio PGNAA	Deviation (%)
1	50(%) / 50(%)	16,13	15,54	3,6
2	60(%) / 40(%)	24,19	25,48	5,06

The aromatic factor C/H will be given by the ν_C/ν_H ratio:

$$\frac{C}{H} = \frac{A_C.R_C}{A_H.R_H}\frac{\varepsilon(E_H)}{\varepsilon(E_C)}\frac{I_C}{\sigma_{\gamma,H}} \tag{5}$$

In the last relation σ_H is 0.332 barn, $A_C = 12$, $A_H = 1$, while the ratio $\varepsilon(E_H) / \varepsilon(E_C)$ was evaluated from Monte Carlo simulations

$$\frac{\varepsilon(E_H)}{\varepsilon(E_C)} = 1,119 \text{ (for second escape line of carbon)}$$

Replacing these values in (5) we obtain a very simple empirical formula for the evaluation of the aromatic factor C/H.

$$\frac{C}{H} = 40.5 \times \frac{R_C}{R_H} \tag{6}$$

For a given experimental arrangement the relation (6) allows the fast determination of this parameter that characterises the bitumen sample. This can be correlated with other technical parameters like viscosity, thermal susceptibility, and hardness if the correlation functions are apriori known. In the present work we correlated this ratio with colloidal index I_C, a technical parameter that is connected with bitumen composition that in its turn gives the microscopic structure. /1,2/. It is defined as a ratio of the total amount of asphaltenes and saturates to the amount of resins and aromatics. It describes the stability of colloidal structure.

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5. COLLOIDAL INDEX

Bitumen is composed generally by carbon (81÷86%), hydrogen (9.5÷10.8%), sulphur. (1.3÷6.9%). Small amounts of other elements are also present: oxygen, (1÷2 %), nitrogen (1÷2 %). Though the hydrogen content of bitumen is greater than in the case of our calibration mixture we used the same value of integral I_C. We can not appreciate the errors of this effect. The results are presented in the table 2.

Sample	Hydrogen peak area (counts/sec)	Carbon peak area (counts/sec)-double escape	Aromatic factor	Colloidal index
ARPECHIM	46,9	24,0	21,17	0.45
ESSO	93,33	30,94	13,4	0.23
EKO	96,07	13.45	3,31	0.29

Table 2. The results of PGNAA analysis correlated with colloidal index.

In the first column are given the type of the sample. The final results were presented in fig. 3. The regression line can be described by an empirical relation.

$$C/H = 5.9 + 34.5 * I_C$$

with a correlation factor R = 0.99 and a standard deviation SD = 0.71

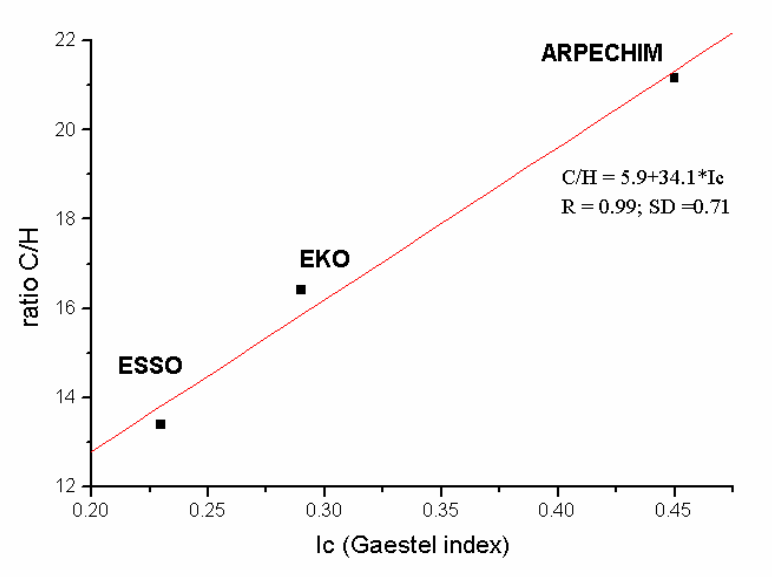

Fig.3. The aromatic factor C/H as a function of colloidal index.

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