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Stable Carbon Isotope Ratio ($\delta^{13}C$) Measurement of Graphite Using EA-IRMS System

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$\delta^{13}C$ values in non-irradiated natural graphite were measured. The measurements were carried out using EA-IRMS (elemental analyzer combined with stable isotope ratio mass spectrometer) in the continuous flow mode. The samples were prepared with ground and non-ground graphite, the part of which was mixed with $Mg(ClO_4)_2$. The best combustion of graphite in the oxidation furnace of the elemental analyzer was achieved when the amount of pulverized graphite ranged from 200 µg to 490 µg and the mass ratio $C : Mg(ClO_4)_2$ was more than 1 : 6. The method for the graphite burning down avoiding the isotope fractionation is proposed.

Keywords: $\delta^{13}C$, graphite, isotope ratio mass spectrometry.

1. INTRODUCTION†

Stable isotope ratio mass spectrometry (IRMS) is widely used for the isotope ratio determination in solid organic and inorganic samples [1]. Isotope ratio value measurements make it possible to ascertain the origin of the sample material and factors, which had affected its isotopic variation. The isotope ratio mass spectrometry is usually used for analysis of organic compounds in biomedical, environmental sciences [2–4]. It can also be used as one of the experimental methods to evaluate the total neutron flux through graphite stack of a nuclear reactor [5]. Although IRMS couplet to the elemental analyzer (EA-IRMS) can give high-precision measurement, the accuracy limits can depend on the processes during the online sample preparation in elemental analyzer [6]. For the materials such as graphite, which can be not quantitatively combusted in an elemental analyzer, the carbon isotope fractionation can occur leading to the inaccurate carbon isotope ratio determination. Fractionation can occur as a result of incomplete combustion where residues are enriched in ^{13}C (isotopically heavier carbon isotope), while evolving gases are enriched in the isotopically lighter carbon isotope having relatively more ^{12}C. ^{13}C enriched residues inside the oxidation tube can be released during the subsequent combustion of the next sample, standard or blank capsule and alter the corresponding $d^{13}C$ value by a so-called memory effect.

Graphite is used in various types of nuclear reactors as a neutron moderator. Although it is a very pure material nevertheless it contains some impurities of various elements, which can be activated by (n, γ), (n, p), (n, α) reactions [5, 7]. Therefore they can be classified as long-lived radioactive wastes after the shutdown of a nuclear power plant. There are several possible principal solutions for the management of used nuclear graphite: disposal of graphite in appropriate repositories, incineration of graphite as a combustible radioactive waste, or recycling and reuse. To choose the best way for the graphite management, it is a necessity to evaluate parameters such as the neutron flux and graphite activation level. ^{13}C is produced by the $^{12}C(n, \gamma)^{13}C$ reaction 3.7 times faster comparing with it destruction due to $^{13}C(n, \gamma)^{14}C$ reaction. And the total reaction rate (proportional to flux weighted microscopic capture cross-section and atomic density of the nuclide) of $^{12}C(n, \gamma)\,^{13}C$ is 330 times higher comparing with destruction of ^{13}C in the reaction $^{13}C(n, \gamma)^{14}C$. As the result enhanced accumulation of ^{13}C in comparison to ^{14}C for the given period of time is observed. The carbon isotope ratio in the pristine and irradiated graphite can be used for the estimation of the total neutron flux [5].

Traditionally samples from the environment can be prepared for the isotope ratio mass spectrometric measurements in the laboratory by milling, grinding and other techniques. There can be physical limitations due to radioactivity for the grinding of the graphite samples taken from the nuclear power plant. There is a need to experimentally determine the precision of the carbon isotope ratio mass spectrometric measurements of the pristine graphite and elaborate the method for the graphite carbon isotope ratio measurements avoiding fractionation effects during combustion of the graphite.

The purpose of this work is to determine the optimal conditions for the evaluation of the stable carbon isotope ratio in the natural, non-ground graphite and propose the method for the measurement of the true $\delta^{13}C$ values (without fractionation) in graphite.

2. EXPERIMENTAL DETAILS

Natural, non-irradiated graphite from Poland was used as a test graphite sample for the carbon isotope ratio (Fig. 1). Natural graphite was obtained from the Mr. Mateusz Ciszewski from the Silesian University of Technology, Gliwice, Poland. The samples for the isotope analysis were prepared using ground and non-ground

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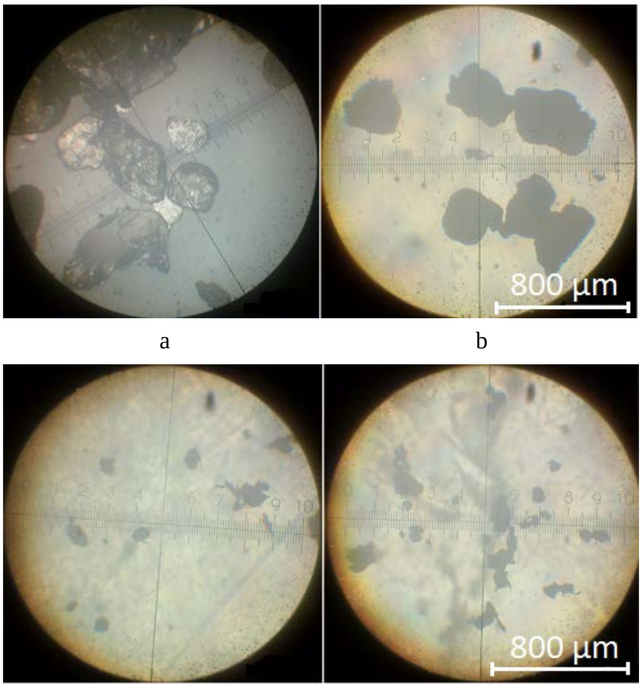
graphite, mixed with oxidant $Mg(ClO_4)_2$. Graphite (ground or non-ground) was mixed with the oxidant before introducing it into a tin capsule. Pulverizing was performed using a manual grater to achieve a larger active surface area of graphite. The approximate diameter of ground and non-ground graphite particles was respectively about 35 µm and 250 µm.

The magnesium perchlorate in elemental analyzer decomposes at high temperature producing oxygen [8]:

$$2Mg(ClO_4)_2 = [MgO{\cdot}Mg(ClO_4)_2] + Cl_2 + 3.5O_2; \quad (1)$$

$$[MgO{\cdot}Mg(ClO_4)_2] = 2MgO + Cl_2 + 3.5O_2. \quad (2)$$

The measurements were performed using the elemental analyzer FlashEA 1112 connected to the stable isotope ratio mass spectrometer ThermoFinnigan Delta Plus advantage. The samples were combusted in the oxidation furnace at the temperature of 1020 °C with the oxygen excess. Carbon of the sample was oxidized into CO_2 gas and transferred through several additional stages of the elemental analyzer before passing it to the mass spectrometer. Carrier He flow in the EA was 80 mL/min, oxygen added for the 4 s with the flow of 180 mL/min. For more details see [9].



a b

c d

Fig. 1. The view of graphite particles through optical microscope: a, b – non-ground graphite; c, d – ground graphite.

The CO_2 gas with the known isotopic ratio was delivered to the spectrometer before and after the analysis of a sample. This allows to calculate the carbon isotope ratio in the sample.

The carbon isotope ratio of the sample is expressed using the dimension of δ specifying the deviation from the international standard [10]:

$$\delta^{13}C = \frac{\left({}^{13}C/{}^{12}C\right)_{sample} - \left({}^{13}C/{}^{12}C\right)_{sandard}}{\left({}^{13}C/{}^{12}C\right)_{sandard}}, \quad (3)$$

where $({}^{13}C/{}^{12}C)_{sample}$ is the carbon isotope ratio of the sample, $({}^{13}C/{}^{12}C)_{standard}$ is the carbon isotope ratio of the international standard.

The system was calibrated using graphite USGS24 ($\delta^{13}C = -16.05$ ‰$_{V\text{-}PDB}$, SD = 0.035 ‰) as a reference material.

Magnesium perchorate (6 – 18 mesh, CAS N 10034-81-8) was obtained from Thermo Electron Corporation (Italy). Tin capsules pressed standard weight 5 mm×3.5 mm were obtained from the Sercon Ltd (UK). High purity gases He 5.0, CO_2 4.5 and O_2 4.5 were used during the analysis.

3. RESULTS AND DISCUSSION

During the conventional elemental analyzer burning event no memory effect is observed, but graphite in this case burns down incompletely. This can be caused by insufficient amount of oxygen, small surface area or structural characteristics of grahite. The tailing is observed during the analysis of graphite (Fig. 2).

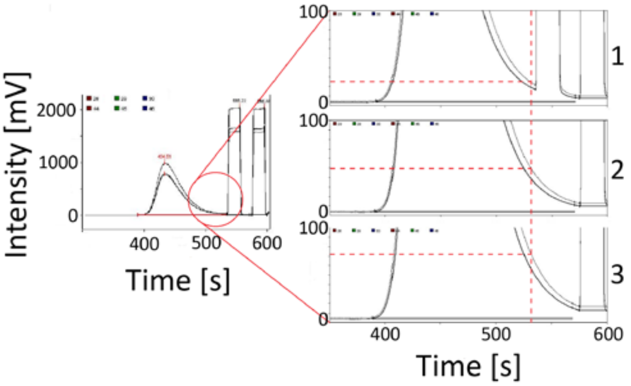


Fig. 2. Chromatograms of three consecutively measured ground graphite samples. Tailing indicates incomplete combustion of the sample and can have effect on carbon isotope ratio values for the next sample

Figure 2 shows chromatograms of three graphite samples that were measured consecutively – each after another – are presented. The signal intensity at the same time point, which is marked by the perpendicular dotted line, is steadily growing with each sample measurement. This indicates the growing amount of graphite residues in the oxidation furnace.

Grinding practically leads to complete burning, but when dealing with the radioactive materials, the sample preparation is not always possible. We carried out carbon isotope ratio mass spectrometric measurements using ground as well as non-ground graphite. Experimental data are presented in Table 1.

Small amount of the ground graphite (<100 µg) burnt down completely during a single run, but the carbon isotope ratio calculation cannot be precise due to a low mass of the sample. The impurities of the tin capsule should be taken into account since they can have influence on the measured δ value [11]. A small amount of the residue is left in the elemental analyzer oxidation column after increasing weight of the ground graphite sample. This residue is isotopically heavier (Fig. 3), and it indicates that during incomplete combustion of the graphite sample the isotopically lighter carbon forms CO_2 gas.

Table 1. $\delta^{13}C$ values of the non-irradiated graphite. A residue represents the graphite, which was left in the column after the run

No.	Graphite preparation	Amount of graphite, µg	Amount of $Mg(ClO_4)_2$, µg	$\delta^{13}C$, ‰				
				Initial sample	Residues I	Residues II	Residues III	Residues IV
1	Ground	70	–	–21.1				
2	Ground	480	–	–21.5	–20.7	–20.3		
3	Ground	200	230	–21.4	–20.0			
4	Ground	230	310	–21.6	–20.6			
5	Ground	410	460	–21.5	–20.7			
6	Ground	490	2930	–21.7	–21.3			
7	Ground	490	3430	–21.5	–19.6			
8	Ground	360	3100	–21.5				
9	Non-ground	70	–	–20.7	–21.0	–21.2	–20.2	
10	Non-ground	480	–	–21.2	–21.7	–20.8	–20.9	–20.7
11	Non-ground	340	340	–21.3	–20.3	–20.0		
12	Non-ground	760	740	–21.3	–21.1	–20.8	–20.8	
13	Non-ground	660	4120	–21.9				
14	Non-ground	280	560	–21.3	–20.1			
15	Non-ground	390	3560	–21.4				
16	USGS24	320		–16.0				
17	USGS24	210		–16.1				
18	USGS24	210		–16.1				

To burn down graphite residues from the oxidation furnace, subsequent measurements with no sample were performed. If some graphite is still left in the furnace, it burns down during the subsequent measurement and the EA detector records CO_2 signal. The more graphite was left after initial measurement, the more repeated measurements were needed (Fig. 3).

For the estimation of the true carbon isotopic ratio in the same graphite sample, isotope mixing equation was applied:

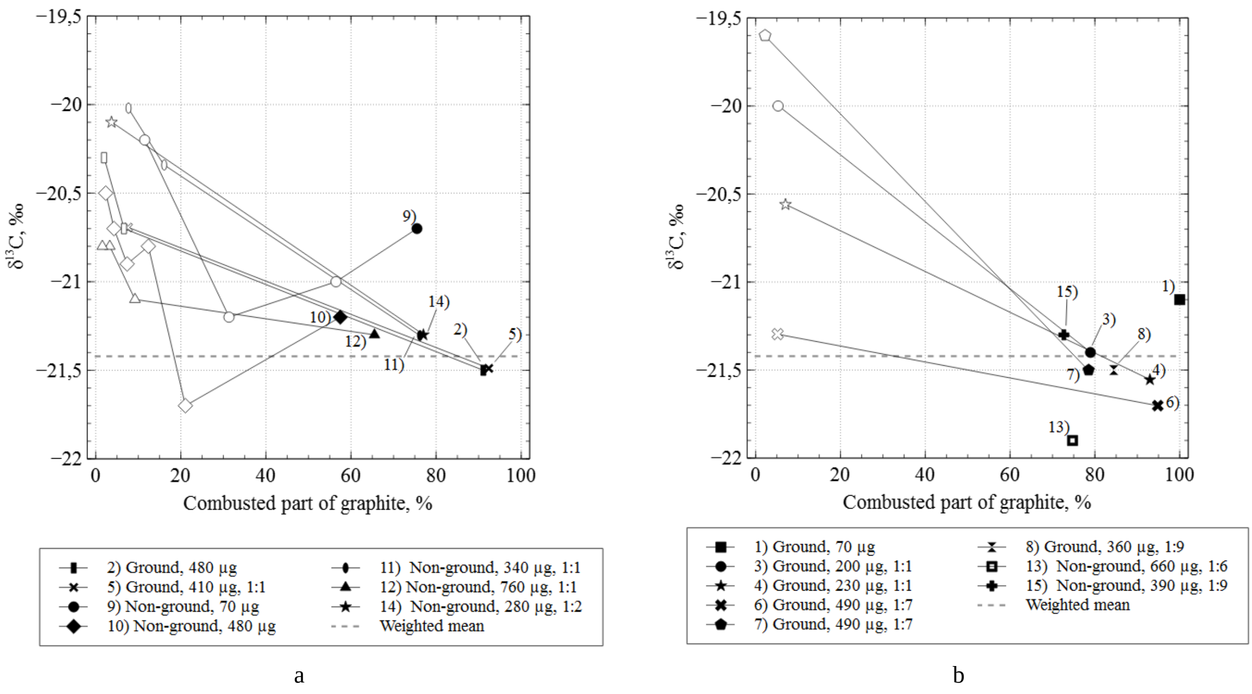
$$\delta^{13}C_M = \frac{\sum\limits_{n=1} \delta^{13}C_n \cdot I_n}{\sum\limits_{n=1} I_n}, \tag{4}$$

where $\delta^{13}C_M$ is the weighted mean; $\delta^{13}C_n$ is the isotope ratio value of *n*th measurement; I_n is the signal intensity of *n*th measurement. In other words, calculating the mass weighed average of all parts of the graphite from single sample we estimated the “true” stable carbon isotope ratio of the sample. We found that for this particular graphite $\delta^{13}C = –21.4$ ‰.

Internally mixed $Mg(ClO_4)_2$ with the sample increases the combustion efficiency especially when it is mixed with graphite in proportion 6:1 or more and allowed to obtain stable carbon isotope ratio close to the true $\delta^{13}C$ value of the graphite (Fig 3). Mixing an oxidant in smaller proportions with the graphite did not give desirable combustion enhancement.

Table 2. The burnt part of graphite and intensity of each measurement

No.	Graphite preparation	Amount of graphite, µg	Amount of $Mg(ClO_4)_2$, µg	Burnt part of Graphite, %					Intensity, mV				
				Initial sample	Residues I	Residues II	Residues III	Residues IV	Initial sample	Residues I	Residues II	Residues III	Residues IV
1	Ground	70	–	n.d.					1193				
2	Ground	480	–	91.1	6.6	1.9			5497	288	69		
3	Ground	200	230	79.0	5.3				1957	83			
4	Ground	230	310	81.3	7.7	1			2207	167			
5	Ground	410	460	75.8	7.6	1			3629	299			
6	Ground	490	2930	73.7	5.7	1.2			4340	237			
7	Ground	490	3430	78.5	2.2				5291	92			
8	Ground	360	3100	84.5					4184				
9	Non-ground	70	–	75.51	56.47	31.32	11.51		526	352	221	91	
10	Non-ground	480	–	57.48	21.08	12.37	7.38	4.28	3152	877	521	297	165
11	Non-ground	340	340	51.3	14.4	7.4			1861	393	188		
12	Non-ground	760	740	65.5	9.2	3.3	1.6		5861	567	186	75	
13	Non-ground	660	4120	74.7					6318				
14	Non-ground	280	560	77.0	3.7				2659	68			
15	Non-ground	390	3560	72.7					3694				
16	USGS24	320							4112				
17	USGS24	210							2574				
18	USGS24	210							2582				



a b

Fig. 3. The δ^{13}C dependence on the burnt part of the graphite. Better graphite combustion is observed when graphite mass ratio with an oxidant is more than 1 : 6 (a) while (b) illustrates poor combustion even adding some amount of an oxidant. Grey marker represent initial measurement of graphite sample and the white ones represent measurements of the graphite residues in the furnace. The legend shows the method of sample preparation, amount of graphite and the mass ratio C : $Mg(ClO_4)_2$

One dissadvantage of the magnesium perchlorate is that it tends to absorb H_2O from the environment and this property complicates the sample preparation and can cause some errors during weighing [10].

Blank measurements without tin capsule produce any appreciable signal intensity, while empty tin capsule or tin capsule with magnesium perchlorate generates about 6 mV peak height.

As mentioned above, stable carbon isotope ratio method can be used as independant physical method to estimate total neutron flux through graphite stack and later use the graphite irradiation history to quantify long live difficult to measure radionuclides, which are present in the graphite in the nuclear reactor. The goal is to achieve best measurement precision, because carbon isotope ratio in the irradiated graphite is sensitive to the neutron flux. In other words, error on estimation of long lived radionuclide concentration in the graphite from nuclear reactor depends on the precision of the carbon isotope ratio differences in pristine and irradiated graphite. Largest deviation from the true carbon isotope value in the graphite is observed when non ground graphite is measured in only one run. Isotope ratio difference between „true“ and measured value can be up to 0.7 ‰. For the estimation of the uncertainty of the neutron flux due to incorrectly measured δ^{13}C value in the real irradiated graphite additional modelling calculation must be performed.

4. CONCLUSIONS

The continuous measurement of original graphite samples does not give proper evaluation of the stable carbon isotope ratio due to memory effect. Up to 0.7 ‰ deviation from true value was observed for the non-ground graphite sample. When the sample preparation (grinding) is not available, the oxidant additive is needed.

The optimal amount of graphite in the sample was from 200 μg to 490 μg and the amount of an oxidant was more than 6 times of the graphite mass in the sample. Our suggested method for the graphite burning enable to measure the true carbon isotope ratio in the sample thus avoiding isotope fractionation during the combustion of the graphite.

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