MEASUREMENT OF SMALL QUANTITIES OF NITROGEN BY NEUTRON ACTIVATION. V.A. Alexeev, A.I. Ivliev, A.K. Lavrukina; V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow, USSR

Determination of nitrogen content in cosmic matter may serve extensive information about the conditions of the formation and evolution of matter of the Solar system. Neutron activation analysis method allows a high-sensitivity determination of total nitrogen, irrespective of its chemical forms in the investigated sample. This method for the determination of nitrogen in iron meteorites and silicate materials has been developed by Indian scientists /1-3/. In this method the reaction $^7\text{Li}(n,p)^7\text{Be}$ is used. Radiocarbon was finally isolated as $\text{BaCO}_3$ and counted against an end-window counter in solid phase. Counting efficiency was only a few percent.

For increasing the sensitivity of the method and diminishing possible contaminations of the isolated $^{14}\text{C}$ by air carbon, we isolated the radiocarbon as carbon dioxide whose radioactivity was measured in a proportional counter (a version of $^{14}\text{C}$ recording, successfully employed in radiocarbon dating). The technique was elaborated on a sample of toleite basalt from the Indian ocean and the standard sample DT-1. The basalt sample was crushed on a ball mill under argon and separated into different grain size fractions (in $\mu$m): less than 50, 63-100, 150-200, 315-400, and 630-1000. The samples were evacuated, sealed under vacuum, covered by the cadmium foil, and exposed to neutron irradiation in a water-water reactor for 528 hours. The integral thermal neutron flux was monitored by the radioactivity of the products of the reactions $^{58}\text{Ni}(n,\gamma)^{60}\text{Co}$; $^{64}\text{Zn}(n,\gamma)^{65}\text{Zn}$ and $^{59}\text{Fe}(n,\gamma)^{60}\text{Fe}$, and was found to be equal to $(1.6\pm0.3)\cdot10^{12}$ m$^{-2}$. The integral fast neutron flux was monitored by the $^{58}\text{Ni}(n,\gamma)^{60}\text{Ni}$ reaction, and was found to be equal to $(2.1\pm0.2)\cdot10^{12}$ m$^{-2}$. Isolation of carbon was carried out in a vacuum system. Basalt samples weighing 20-100 mg were mixed with a flux (Pb$_2$CrO$_4$ and K$_2$CrO$_4$ in the ratio of 1:10) and with a carrier (CaCO$_3$) and placed into a quartz reactor. The reactor was evacuated at 200°C during the night. Decomposition of the basalt samples was carried out in the presence of oxygen purified from CO$_2$ under a pressure of 2.7·10$^4$ Pa during 3 or 6 hours at 1100°C. Gases formed in the process of fusion were pumped through CuO at 500°C and two condensation traps. The first trap, cooled down to -76°C, served for freezing out the moisture; the second trap, cooled with liquid nitrogen, served for freezing out CO$_2$. The gas thus obtained was kept during one month for removing possible admixture of 222Rn from it, after which the gas was transferred to vacuum system for purification. The yield of carbon usually was within the range of (98±1)%.

The activity of $^{14}\text{C}$ was measured by means of cylind-
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rical proportional counters having the working volume of 20 cm$^3$/4/. For reducing the background, active and passive shield were used /5/. The counters were filled with a mixture of CO$_2$ (50%) and propane (50%). The background of the different counters was within the range of 0.15 to 0.18 cpm. The efficiency of recording of the C-14 beta-particles was equal to about 70%.

Completeness of radiocarbon isolation in the process of decomposition was checked on irradiated basalt samples. Four basalt fractions with the particle size from less than 50 μm to 400 μm were fused with the flux during 3 and 6 hours. The values of the measured activities of C-14 in various basalt fractions are given in the table. Statistical errors ($\sigma$) are less than 5% for all values.

Table Specific radioactivity of C-14 (in dpm per mg of basalt), isolated from irradiated basalt samples

<table>
<thead>
<tr>
<th>$t^+$, hours</th>
<th>Particle size, μm</th>
<th>less than 50</th>
<th>63-100</th>
<th>160-200</th>
<th>315-400</th>
<th>5000-7000</th>
<th>less than 50</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td></td>
<td>0.129</td>
<td>0.081</td>
<td>0.053</td>
<td>0.037</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.133</td>
<td>0.128</td>
<td>0.095</td>
<td>0.079</td>
<td>-</td>
<td>0.160</td>
</tr>
<tr>
<td>6+++</td>
<td></td>
<td>-</td>
<td>0.115</td>
<td>0.120</td>
<td>0.122</td>
<td>0.116</td>
<td>-</td>
</tr>
</tbody>
</table>

$^+$ $t$ is duration of fusion.

++ Comminution of basalt before irradiation was carried out in air; in other cases it was carried out under argon.

+++ Before fusion irradiated sample was comminuted to particle size less than 50 μm.

Specific radioactivity of C-14, isolated from irradiated standard sample DTS-1 (content of N is 27 ppm /6/), was $0.362 \pm 0.018$ dpm/mg.

The results of measurements allow to make the following conclusions:

(1) In case of fusion lasting for 3 hours radiocarbon is isolated practically completely only from basalt fractions with the grain size less than 50 μm (fusion prolonged for 6 hours has not increased the yield of radiocarbon);

(2) in case of fusion lasting for 6 hours radiocarbon is isolated practically completely from basalt fractions with the grain size up to 100 μm;
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(3) when the sample is comminuted under argon, the sample is not contaminated with atmospheric nitrogen: the radioactivity of C-14 isolated from the large-grain fraction of 5-7 mm (0.116±0.006) practically coincided with the radioactivity of C-14 isolated from fractions with the grain size of 63-100 µm and less than 50 µm;

(4) the average radioactivity of C-14, found from the numerical values underlined in the table, is 123±7 dpm per mg of basalt; this value corresponds to 9.2±0.9 ppm N in investigated basalt sample, taking into consideration of C-14 specific radioactivity of irradiated standard sample DTS-1;

(5) when the comminution is carried out in air, contamination of the sample with atmospheric nitrogen has been found and this nitrogen could not be removed in the process of subsequent purification in the vacuum system; the radioactivity of C-14 in the sample comminuted in air proved to be (22±6)% higher than the average radioactivity of C-14 in the samples comminuted under argon. This effect should be taken into account when preparing samples, so as to preclude errors in the determination of nitrogen content;

(6) the discussed above version of the method allows effective determination of C-14 from small amounts of nitrogen - about 0.02 µg N or less.

REFERENCES