The Radioactivation Analysis of Graphite for Nitrogen by the $^{14}N(p, \alpha)^{11}C$ Reaction

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(Received August 22, 1964)

A successful method for analyzing graphite for an ultra-trace quantity of nitrogen will be presented. All the methods ever previously reported for determing trace nitrogen (the vacuum-fusion technique, the Kjeldahl method, emission and mass spectroscopy, radioactivation analysis by ^{14}N(n, 2n)^{13}N or ^{14}N(γ, n)^{13}N,[1] etc.) are either inapplicable to graphite or are of limited sensitivity. Further, any surface once exposed to air is contaminated with nitrogen. Making use of radioactivation analysis by means of a ^{14}N(p, α)^{11}C reaction, we succeeded in determining as small an amount as several tens p. p. b. of nitrogen in pyro-graphite. Recently, pyro-graphite prepared by the thermal decomposition of pyridine was found to have very interesting semiconductor characteristics, which would be due to the presence of a trace of nitrogen.

The excitation function for ^{14}N(p, α)^{11}C up to 15 MeV. was measured by the stacked-foil method, each foil being a nylon film about 22 mg./cm^2 thick. The results showed that 1 p. p. m. of nitrogen in carbon gave 5.3×10^3 d. p. s. ^{11}C as the thick-target saturation-activity for 15 MeV.-1 μamp. protons. The mean recoil range of the ^{11}C for the 14.2 MeV. proton was also measured by inserting a recoil-catcher in the stack; it was found to be 0.36 mg./cm^2. With a ^{16}O(α, pn)^{18}F reaction, we previously showed that the surface layer, of a thickness about five times the recoil range of ^{18}F, should be removed in order to eliminate the effect of surface oxygen.[3] Therefore, the surface layer about 1.8 mg./cm^2 thick is removed in the present case. Since the irradiated graphite also contained ^{13}N (formed by ^{13}C(p, n)^{13}N)[4] and longer-lived nuclides (from impurities), chemical treatment was necessary for a reliable measurement of the ^{11}C. Oxidation in strong phosphoric acid developed by Kiba et al.[5] proved useful in decomposing the sample. The graphite itself was the carrier of ^{11}C.

A plate of pyro-graphite (30×10×2 mm.) was placed on a water-cooled target-holder and irradiate with protons (15 MeV., 5 μamp., 10 min.). After the surface layer had been uniformly removed by mechanical grinding, the sample was finely pulverized. It was then added into a flask containing strong phosphoric acid (50 ml.), sulfuric acid (30 ml.) and potassium iodate (25 g.) heated to 160～170°C. Gentle heating was continued, and the carbon dioxide formed was introduced into another flask containing sodium hydroxide (2 N, 200 ml.). To make the absorption of carbon dioxide in a closed system smooth and easy, the air in both the flasks had been replaced with nitrogen oxides (from sodium nitrite and sulfuric acid), and the contents of the absorption flask were separated from atmospheric air by a movable layer of carbon tetrachloride. The nitrogen oxides worked also as a hold-back carrier of ^{13}N. When the oxidation became less vigorous, even at 240°C, perchloric acid (65%, a few milliliters) was carefully dripped in to complete the reaction. When all the graphite had been oxidized, nitrogen oxides were passed through to carry all the carbon dioxide into the sodium hydroxide solution. After the solution had been treated with hydrazine hydrate (1 g.), barium carbonate was precipitated and filtered off. The process after the irradiation required 40 to 50 min. The recovery was almost quantitative, but so large a quantity of barium carbonate was formed that only a part of it was taken for the activity measurement. The annihilation radiation was measured by a scintillation counter of a known efficiency. The decay curve and the γ-ray spectrum were satisfying for a reliable determination of ^{11}C. The nitrogen content was calculated from the disintegration-rate by the absolute method, the only possible source of interference being ^{11}B(p, n)^{11}C under our conditions.

Pyro-graphites made from pyridine contained 1 to several p. p. m. of nitrogen, while those made from propane had less than a few hundred p. p. b. This method appears to be

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[1] E. g. R. C. Koch, "Activation Analysis Handbook," Academic Rress, New York and London (1960), p. 38.

[2] K. Takeya and K. Yazawa, Symposium on Carbon, Tokyo 1964.

[3] K. Saitô et al., *Intern. J. Appl. Rad. & Isotopes*, **14**, 358 (1963).

[4] A. B. Whitehead, *Can. J. Phys.* **36**, 1283 (1958).

[5] T. Kiba, *Chem. and. Chem. Ind. (Chem. Soc. Japan)*, **11**, 730 (1958).

[6] M. Furukawa et al., *J. Phys. Soc. Japan*, **15**, 2168 (1960).

by far the most sensitive method for nitrogen, the detection limit being several p. p. b. A detailed paper will be submitted for publication in the near future.

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