Determination of Sodium, Arsenic, Antimony and Copper in Carbon by Neutron-Activation Analysis

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The neutron activation analysis of graphite with or without the chemical separation of impurities after irradiation has been reported by several workers[1-3]. In general, the method with such chemical separation has been more satisfactory than that without in terms of sensitivity and precision of analysis. However, the method involving the chemical processing of the irradiated sample has some problems in the process of the leaching-out of impurities from the irradiated graphite. They are: (1) The burning method for the destruction of graphite has the possibility of the evaporation of a portion of the impurities. (2) The leaching method with concentrated nitric acid has the possibility of the incomplete leaching-out of the impurities from graphite. (3) The destruction of graphite with a nitric acid-perchloric acid mixture is difficult.

The purpose of this investigation was to decide the most desirable method for the separation of impurities from the irradiated graphite. On the basis of the results, the burning method, combined with the treatment of a burning boat (quartz) with a hydrofluoric acid-nitric acid mixture, was found to be the most desirable. This method was applied to the determination of sodium, arsenic, antimony and copper in carbon. The analytical values obtained were compared with those obtained by the non-destructive method.

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Experimental

Sample.—About 1 g. of the amorphous carbon prepared by the Nihon Carbon Co., Ltd., was weighed into a polyethylene pouch.

Standards.—One-tenth of a milliliter of each standard solution, prepared as follows, was infiltrated into a filter paper 2 cm. in diameter and sealed in a polyethylene pouch.

Sodium.—The reagent-grade sodium carbonate was dissolved in water and diluted to 270 μg. of sodium per ml. of solution.

Arsenic.—The reagent-grade arsenious acid was dissolved in hydrochloric acid and diluted to 499.7 μg. of arsenic per ml. of solution.

Antimony.—The 99.998% antimony metal was dissolved in aqua regia and diluted to 210.6 μg. of antimony per ml. of solution.

Copper.—The 99.99% copper metal was dissolved in dilute nitric acid and diluted to 266 μg. of copper per ml. of solution.

Irradiation Conditions.—For the irradiation, the sample and standards were placed side by side in a polyethylene capsule. All irradiations were made in the No. 16 Hole (pneumatic tube) of the JRR-1 reactor. The neutron flux was approximately 10^{11} n/cm^2/sec. Each irradiation was continued for 2 hr.

Radiochemical Separation.—The irradiated sample was placed in a quartz boat and burned for 30 min. at 700°C in an oxygen atmosphere. The apparatus used is outlined in Fig. 1. The sample was completely burned. The boat was then treated twice with a hydrofluoric acid-nitric acid (1 : 1) mixture solution on a hot plate, and the apparatus used was washed with hot nitric acid. The resulting solutions were added to the catching solution. After the addition of 1 ml. each of carrier solutions for sodium, arsenic, antimony and copper (sodium 27.0 mg.; the other cation, 10 mg.), the whole solution was evaporated repeatedly with hydrochloric acid and adjusted to agree with the dilute hydrochloric acid solution.

From this solution, each element mentioned above was isolated as follows. (The flow system of the separation is shown in Fig. 2.)

Arsenic, antimony and copper were precipitated as sulfides with hydrogen sulfide and then separated from the sodium. The filtrate was concentrated to about 3 ml. and then poured into a polyethylene tube, which was mounted on a 3×3 inches sodium iodide scintillator. The sodium content was determined by γ-ray spectrometry.

The precipitate of sulfide was treated with an ammonium polysulfide solution, arsenic and antimony being dissolved in this solution and separated from the copper precipitate. This residual precipitate was then dissolved in aqua regia and reprecipitated as thiocyanate from the dilute sulfuric acid solution. The cuprous thiocyanate was filtered off, washed, dried and weighed to determine the chemical yield, and it was then put in a polyethylene tube; the copper content was determined by γ-ray spectrometry.

The ammonium polysulfide solution of the precipitate sulfide was evaporated with nitric acid and adjusted to agree with the concentrated hydrochloric acid solution. Arsenic was precipitated as sulfide with hydrogen sulfide from the concentrated hydrochloric acid solution and separated from antimony. The precipitate was digested with aqua regia. After the addition of an antimony solution to this solution as the hold-back carrier, the arsenic was reprecipitated as sulfide. The precipitate was filtered off, washed, dried and weighed to determine the chemical yield, and it was then put in a polyethylene tube. The arsenic content was determined by γ-ray spectrometry.

The concentrated hydrochloric acid solution, from which arsenic had been separated, was adjusted to agree with an about 2 N hydrochloric acid solution. Antimony was precipitated as sulfide from this solution. The precipitate was digested with aqua regia. After the addition of an arsenic-carrier solution to this solution, the separation of antimony from arsenic was repeated. The antimony sulfide formed was filtered off, washed, dried and weighed to determine the chemical yield, and it was then put in a polyethylene tube. The antimony content was determined by γ-ray spectrometry.

Counting.—Each isolated element was mounted on 3×3 inch sodium iodide scintillator attached to an RCL-256 channel pulse-height analyzer, and the γ-ray spectrum was measured. The content of each element was determined by comparing the peak height of the photopeak (i. e., at 1.37 MeV. for sodium-24, at 0.56 MeV. for arsenic-76, at 0.57 MeV. for antimony-122, and at 0.51 MeV. for copper-64) with that for the respective standard.

Results

Radiochemical Purity.—From the results of the γ-ray spectra and the decay curves of the photopeaks, it was found that the arsenic, antimony and copper isolated by this method were radiochemically pure.

Although two photopeaks, at 0.82 MeV. and 0.56 MeV., appeared in the γ-ray spectrum of the sodium fraction, the interference of these activities could be disregarded in the determination of sodium by analyzing the decay curve of the sodium-24 photopeak at 1.37 MeV.

Results.—The results obtained are given in Table I.

TABLE I. RESULTS

Element	Content, p. p. m.	Standard deviation
Sodium	170	±11
Copper	35	± 1.3
Arsenic	0.2	± 0.01
Antimony	0.30	± 0.018

Discussion

Leaching-out Methods of Impurities from Irradiated Carbon.—*The Burning Method.*—Irradiated carbon was burned in an oxygen atmosphere at 700°C in the apparatus shown in Fig. 1. After this burning, much activity was found on the quartz-burning boat. This activity could not be completely leached out from the boat by treating it four times with hot aqua regia. It was found, however, that complete leaching is possible when the boat is treated twice with a hydrofluoric acid-nitric acid (1 : 1) mixture solution. The results are shown in Fig. 3.

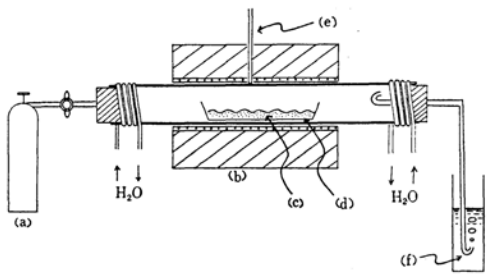

Fig. 1. Apparatus.
(a) O_2 bomb
(b) Heater
(c) Carbon sample
(d) Burning boat
(e) Thermocouple
(f) Catching solution, dil. HNO_3

This solution obtained from the leaching of the quartz boat and from the nitric-acid washing of the apparatus, and the catching solution, together, contained 98~100% of the impurities in carbon.

When a porcelain boat was used, however, the adherring activity could not be leached out from the boat.

The Leaching Method with Concentrated Nitric Acid.—The leaching-out method of impurities from carbon with concentrated nitric acid has

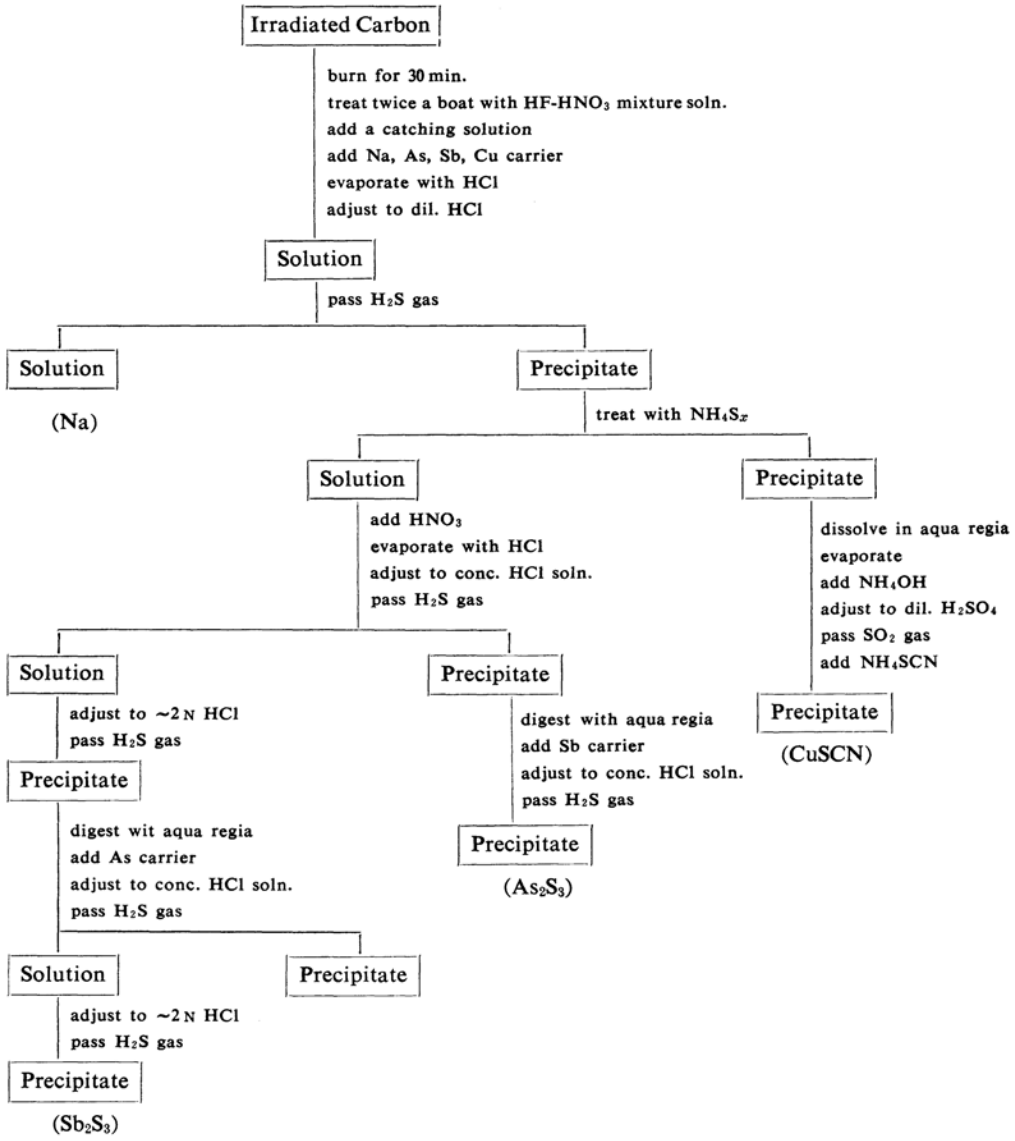

Fig. 2. Flow system of separation.

been reported by several workers[4,5]. However, as it was doubtful that they can be leached out completely by this method, an experiment was made.

About 1 g. of irradiated carbon was treated in a beaker on a hot plate with about 50 ml. of concentrated nitric acid, adding a small volume of nitric acid at some intervals. The γ-ray spectrum of the carbon treated was measured after having been heated for some hours; the results are shown in Fig. 4. The leaching-out of impurities by this method was not complete, however, even when the sample was heated for 7.5 hr. with concentrated nitric acid.

The Carbon-Destruction Method with a Nitric Acid-Perchloric Acid (1:1) Mixture Solution.— The destruction method using a mineral acid-oxidizing agent mixture solution has been reported by some workers[6]; however, the destruction of carbon by this method was not complete. Fifty milliliters of a nitric acid-perchloric acid (1 : 1) mixture solution was added to about 1 g. of the irradiated carbon; the resultant solution was heated on a hot

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5) T. Sasaki, F. Ichikawa, H. Imai and S. Uruno, 1961 National Nuclear Congress, Tokyo, Japan, Report No. D62 (1961).
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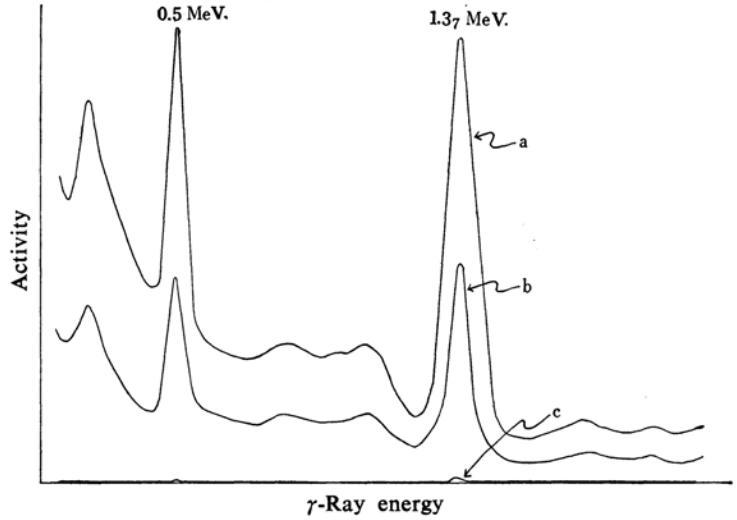

Fig. 3. γ-Ray spectra of adherring activity on the burning quartz boat.
(a) Non-treatment
(b) Treating 4 times with aqua regia
(c) Treating twice with HF-HNO_3 (1 : 1) mixture solution

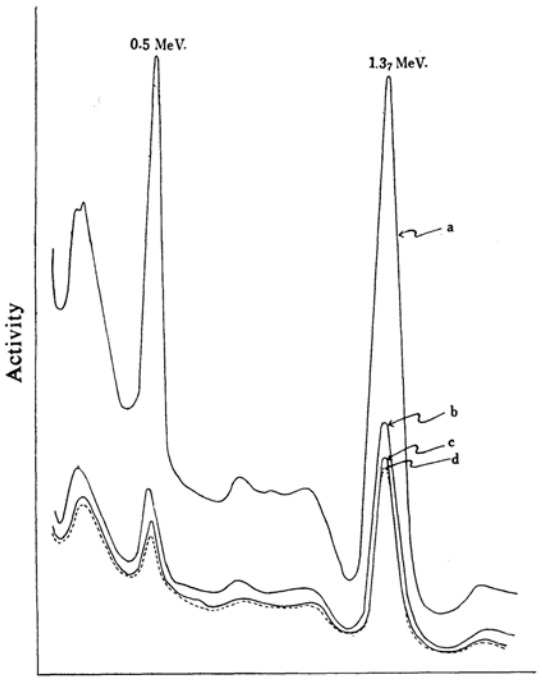

Fig. 4. γ-Ray spectra of carbon after heating for some hours with concn. HNO_3.
(a) Non-treatment
(b) Heating for 2.5 hr.
(c) Heating for 4.5 hr.
(d) Heating for 7.5 hr.

plate for some hours, with a small volume of the same mixture solution being added at some intervals. The γ-ray spectrum of the treated

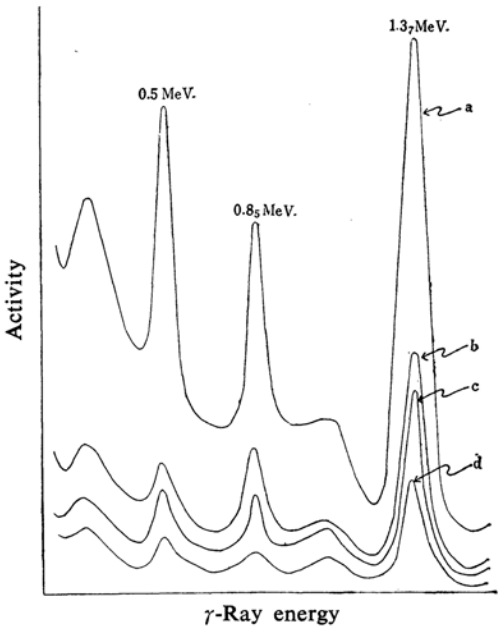

Fig. 5. γ-Ray spectra of carbon after heating for some hours with HNO_3-$HClO_4$ mixture solution.
(a) Non-treatment
(b) Heating for 1.5 hr.
(c) Heating for 2.5 hr.
(d) Heating for 5 hr.

carbon was measured and is shown in Fig. 5. It may be seen from Fig. 5 that some portion of the impurities remained in the carbon even when it had been treated for 5 hr., so this method is not desirable.

TABLE II. COMPARISON OF THE RESULTS OF THE DESTRUCTIVE AND NON-DESTRUCTIVE METHODS

Element	Destructive method		Non-destructive method	
	Content p. p. m.	Standard deviation	Content p. p. m.	Standard deviation
Sodium	170	±11	230, 220, 180	—
Copper	35	± 1.3	46, 47	—
Arsenic	0.20	± 0.01	2, 3	—
Antimony	0.30	± 0.018	0.4	—
Manganese	—	—	2.2	—

The Sodium Hydroxide-Fusion Method.—About 0.5 g. of irradiated carbon was added to about 3 g. of sodium hydroxide in a nickel crucible. After they had been fused for one or two hours, the melt was leached with water and dilute hydrochloric acid and the carbon which remained undissolved was filtered off.

The activity of the residual carbon was measured with a γ-ray scintillator. The results obtained, which are shown in Fig. 6, indicate that the fusing method did not provide a complete leaching-out of impurities from carbon, even when the fusing lasted for two hours.

Consequently, it was found that the burning method is most satisfactory.

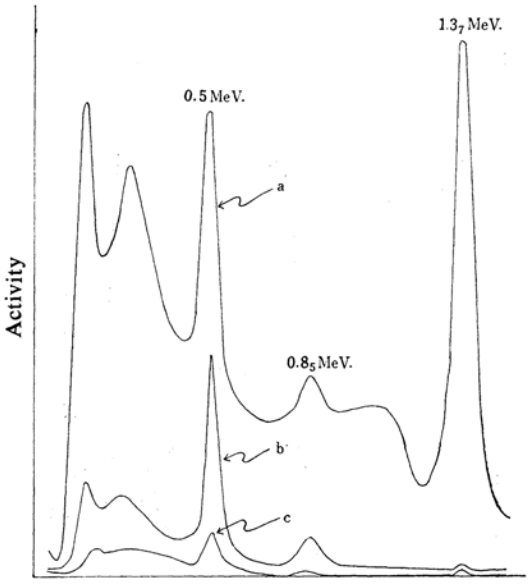

Fig. 6. γ-Ray spectra of carbon after fusing for some hours with NaOH.
(a) Non-treatment
(b) Fusing for 1 hr.
(c) Fusing for 2 hr.

Comparison of the Proposed Method with the Non-destructive One.—Table II compares the results of the destructive and non-destructive methods, which have previously been reported on[7,8].

Not much difference was observed between the results of the two methods, except in the case of arsenic; however, the analytical value of each element in the former was smaller than in the latter. This might be due to the fact that some photopeaks were apparently higher in the latter case, affected by the other peaks near them; this was pointed out in our previous report[9], "Determination of Chlorine and Manganese in Bismuth Metal by Neutron Activation."

The difference between the analytical values of arsenic in the two methods was too large to explain by the effect just mentioned. This large difference may be due to the fact that, in the non-destructive method, the analysis of the decay curve of the photopeak at about 0.5 MeV. into the decay curves of copper-64 (half life: 12.8 hr.), arsenic-76 (half life; 26.8 hr.), and antimony-122 (half life: 2.8 days) was not correct.

The identification of the decay curve for arsenic was difficult in the non-destructive method because its activity was much lower than those of copper and antimony.

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9) Y. Kamemoto and S. Yamagishi, ibid., 83, 463 (1962).