研究論文

302. *Determination of Oxygen by 14 MeV Neutron Activation Analysis Using a New Analytical Instrument*

全自動式放射化分析装置を用いた 14 MeV 中性子による酸素の定量

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A new analytical instrument using a 14 MeV neutron generator for industrial purpose is described. The instrument used is made up of three parts: a 14 MeV neutron generator (10^{10} n/sec), an automatic control system and a system of measurement.

The neutron generator is a Cockcroft-Walton type accelerator and the automatic control system has sample transfer system and a C-R neutron monitoring system which corrects automatically influence of the fluctuation of neutron flux at a bombardment of samples.

The accuracy of the measurement using this analytical instrument is within $\pm 5\%$ at an oxygen level of 10%.

I. INTRODUCTION

Direct determination of oxygen by the 14 MeV neutron activation analysis was reported by Coleman and Perkin⁽¹⁾, Steele and Meinke⁽²⁾ and Veal and Cook⁽³⁾

Coleman and Perkin⁽¹⁾ used 14 MeV neutron to analyze oxygen in metallic beryllium samples. In the method, the beryllium samples were bombarded with 14 MeV neutrons. The 7.4 sec nitrogen activity produced by the reaction of $^{16}\text{O}(n,p)^{16}\text{N}$ was measured. The lowest limit of measurement of the method is 0.01~0.001%.

Steele and Meinke⁽²⁾ used a low-cost Cockcroft-Walton type accelerator as a source of 14 MeV neutrons. Samples containing 10 mg or more of oxygen were analyzed within the error of $\pm 10\%$ with a fast neutron flux of 10^{10} n/sec.

Veal and Cook⁽³⁾ reported that a 14 MeV neutron activation method was applied to the analysis of oxygen in samples which contain neither fluorine nor boron. The nondestructiveness and the fivefold increase in speed over the conventional Unterzäucher method have been shown. A sensitivity of 0.032% oxygen

is obtainable with neutron intensity readily available by Cockcroft-Walton accelerator (10^{10} n/sec). At an oxygen level of 1%, the accuracy of the measurement is $\pm 17\%$.

In the works of above three groups, all counting rate obtained with the scintillation counter or the proportional counter were normalized by calculation for fast neutron flux, for decay of activity and for analyzer dead time, because the normalization is the indispensable procedure to exclude error in the counting rate due to the fluctuation of neutron flux at the bombardment which is practically unavoidable for the activation analysis by using the accelerator neutron.

In this paper, a new analytical instrument which can automatically normalize with a simple electric circuit, and its application to the determination of oxygen are described.

II. APPARATUS

A Cockcroft-Walton type neutron genera-

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tor, Model NT-20, built by Tokyo Shibaura Elect. Co. was used as a source of 14 MeV neutrons. This machine accelerates deuterium ion up to 200 keV. The tritium loaded targets were obtained from Isotope Div., Harwell, England. (Titanium evaporated on silver disc, 2.85 cm diameter, 0.025 cm thickness, producing a titanium layer approximately $200 \mu\text{g}/\text{cm}^2$ thickness, 2.5 ml tritium is absorbed in the titanium layer). The output of neutron of this machine is $10^{10}\text{n}/\text{sec}$.

Automatic control system: The automatic control system is made up of sample transfer system which can drive in pneumatically the rabbit with sample pellet (Fig. 1) and hold at the position of bombardment (target area) by a blower motor, and a C-R neutron monitoring system which corrects automatically influence of the fluctuation of neutron flux at a bombardment of samples.

Fig. 1 Rabbit

1. C-R neutron monitoring system

In the activation analysis using accelerator neutrons, it is necessary to normalize the observed counting rates for each sample, with regard to fast neutron flux and also necessary to decay of activity, because the neutron flux from the accelerator fluctuates during the bombardment of samples and even during that of one sample. However, the procedure of the normalization is generally tedious when a number of samples are analyzed.

In this paper, a new automatic instrument which can automatically normalize the observed counting rates by means of a simple electric circuit is described. When this instrument is used in the activation analysis by accelerator neutron, it is not necessary to keep the neutron flux in constant condition during the bombardment of samples and even during that of one sample.

The principle of this instrument is as follows:

The change rate of the quantity of the activation product in the sample during the bombardment, dN^*/dt is given by

$$\frac{dN^*}{dt} = N\sigma f(t) - \lambda N^* \quad (1)$$

where, N is the number of the target nuclides whose activation cross section is σ ; λ is the decay constant of radionuclide produced; and $f(t)$, which is generally a function of time, is the neutron flux during the bombardment of the target material.

On the other hand, in the electric circuit shown in Fig. 2, the rate of change of the terminal-voltage V of the capacitor C , dV/dt is given by

Fig. 2 C-R integrating circuit

$$\frac{dV}{dt} = \frac{E(t)}{C \cdot R} - \frac{V}{C \cdot R} \quad (2)$$

where $E(t)$ is the input voltage for this circuit; C and R are the resistance and the capacitance of the circuit, respectively.

Eq. (1) is analogous to Eq. (2). Hence, V in Eq. (2) indicates the quantity proportional to the number of the produced radionuclide with half-life T , if one assumes that:

$$E(t) = k \cdot f(t) \text{ and } C \cdot R = \frac{1}{\lambda} = \frac{T}{0.693}$$

where k is a proportional constant.

In practice, the output voltage of the linear ratemeter as shown in Fig. 3 which is proportional to the instantaneous output of 14 MeV neutron generator during the bombardment of individual sample, was applied to the circuit of C and R in series as shown in Fig. 2. V in Eq. (2), i.e. the terminal voltage of the capacitor C , is measured by the vacuum tube voltmeter.

Fig. 3 Schematic diagram of C-R neutron monitoring system

In this system, the end of the bombardments, the start of blower motor of the

pneumatic system to transfer the rabbit from the target area to the detectors, and the start of the counting of the induced activity were controlled by V in Eq. (2).

The neutron detector in the C-R neutron monitoring system was constructed with the plastic scintillator coupled with the photomultiplier tube (Toshiba 7309).

2. Sample transfer system

A three-channel pneumatic tube which could simultaneously activate three samples

with single bombardment was developed to save the loss of the tritium target and to minimize the cost of analysis per sample. The outline of the automatic control system used is shown in Fig. 4. When the three-channel pneumatic tube is used, three samples do not generally arrive at the counting apparatus simultaneously. To achieve automatically the normalization at any bombardment, the counting of samples must be started immediately when V in Eq. (2) reaches the

Fig. 4 Schematic diagram of the analytical instrument with C-R neutron monitoring system

same preset value.

The authors developed a start pulse generator as shown in Fig. 4, which generates a pulse when a bombarded sample arrives at the head of the scintillation detector of counting apparatus of each channel by using a relay circuit and phototransistors. The counting apparatus can be switched on when the value of V in Eq. (2) reaches a preset value provided that the start pulse generator has been operated beforehand.

System of measurement: The counting apparatus was made up of three single-channel γ -ray spectrometers with the scintillation detector ($1\frac{3}{4}$ in. diameter, 2 in. long sodium iodide crystal activated with thallium and

photomultiplier tube: Toshiba 7309).

III. EXPERIMENTAL

1. Preparation of sample for calibration curve

Sucrose sample, varying 100~1,000 mg, and graphite powder, 4,900~4,000 mg, were measured in weighing bottles, and mixed sufficiently. Then the mixed samples were pressed into pellets by means of pelleting machine and these pellets were sealed up in the polyethylene plastic rabbits shown in Fig. 1.

Pellet weight was determined by difference and sucrose weight was determined by calculation. The samples to be analyzed were

treated by the same method.

2. Bombardment and measurement

The rabbits containing samples to be analyzed were transferred from the position of the sample charger to target area with three-channel pneumatic tube. When the rabbits arrived at the target area, the bombardment of samples were automatically started by the deuterium ion-beam shutter which was driven by the signals of the arriving indicator for samples shown in Fig. 4. In our experiment, further operations, namely, the stop of bombardment, the transfer of samples to detector, and the start of counting, were performed fully automatically with the automatic control system and the stop of counting was performed with a preset timer. For example, when the value of V reached a preset value (for example, 95) the bombardment of sample was stopped, and at the same time the blower motor was started and the rabbit was driven back from the target area to the counting apparatus. V exponentially decreases after the above operations, and it indicates the discharge of the capacitor C in Fig. 2, namely, the disintegration of the radionuclide produced. Then, the counting apparatus was switched on when the value of V reached 70, provided that the start pulse generator had operated beforehand, and was switched off after a constant time by means of the preset timer (60 sec).

For the determination of oxygen, the values of resistance R and capacitance C of C-R neutron monitoring system were chosen 51 k Ω and 200 μ F respectively which corresponded to the 7.4 sec half-life of ^{16}N , and the counting

time was 60 sec.

Since the counting rates obtained by the above method were already normalized, the observed values can be used without the following normalization procedure for neutron flux and decay. In our experiment, the neutron flux was not kept constant during the bombardment of samples nor during that of one sample and also no notice was taken for the bombardment of time and the cooling time, because the C-R neutron monitoring system does not necessitate to keep them constant.

The background radiations from other radionuclides produced in the sample were eliminated by discriminator level (about 5.5 MeV) of the pulse height analyzer.

IV. RESUTES AND DISCUSSION

The results of a series of standardization are given in Table 1. The calibration curve for oxygen obtained from the data of Table 1 by the least squares method shows good linearity as is shown in Fig. 5.

Table 1 Results of a series of standardization

Standard material :
Sucrose (JIS "Special Grade")
Discriminator level : 5.5 MeV

Amount of sucrose (mg)	Number of measurement	Average of observed counting rates
109	5	1,225
316	5	3,063
581	4	5,289
745	5	6,700
901	5	8,100
$Y = 16.77X + 294$		

Table 2 Results of analyses of pure compounds by 14 MeV neutron activation, (1)

Compound	Calculated oxygen(mg)	Discriminator level (MeV)	Number of determination	Average of found (mg)	Relative standard deviation(%)
Zinc oxide	186.5	2.4	6	186.8	3.0
		5.5	3	175.3	4.7
		2.4	2	258.5	0.8
Benzoic acid	131.0	5.5	3	242.0	4.1
		2.4	7	134.0	2.9
		5.5	2	129.5	4.9
Sodium oxalate	237.2	2.4†	2	358.5	1.0
		5.5	3	241.0	4.1
		2.4†	2	321.5	0.2
Potassium acid phthalate	299.8	5.5	3	309.0	2.0
Sulphamic acid	239.5	2.4	2	243.5	0.8
		5.5	3	231.0	2.1

Fig. 5 Calibration curve for oxygen determination
(C-R neutron monitoring system)

The results of analysis of pure compounds, such as zinc oxide, benzoic acid, sodium oxalate, potassium acid phthalate, and sulphamic acid, are given in Table 2. The results indicate that it is necessary to choose 5.5 MeV as a discriminator level for the analyses of oxygen in sodium oxalate and potassium acid phthalate.

The nickel oxide was used to determine the effect of fluctuation due to the pellet makings and the standard error of the average of the analytical results of the activation method using C-R neutron monitoring system. The results of oxygen determination in nickel oxide are given in Table 3, which show that the difference of 1/100 in oxygen content is distinguished by this method. It was also clear that the fluctuation of pellet making is negligible from the statistical consideration on the data of analytical results.

At an oxygen level 100~300 mg/sample, the relative standard deviation of this method using C-R neutron monitoring system was 3~5%.

By using C-R neutron monitoring system,

Table 3 Results of analyses of pure compounds
by 14 MeV neutron activation, (2)

Sample : Nickel oxide (JIS "Special Grade")
Discriminator level : 5.5 MeV

Nickel oxide in pellet (g)	Number of determination	Average of found O (%)
0.9941	5	19.83
0.9629	5	20.44
0.9764	5	20.79
0.9563	5	20.28
1.0020	10	20.39

Average : 20.34%

Standard deviation : 0.62%

Standard error of the average : 0.29%

Oxygen in the sample : $20.34 \pm 0.29\%$

the counting rates of ^{16}N obtained from the same quantity of sucrose must be constant. To ensure it, 1 g of sucrose was bombarded by 14 MeV neutron with the C-R neutron monitoring system and the activity of the radionuclide produced (^{16}N) was measured. Detailed results of counting rates obtained by the above experiment are given in Table 4. These data show that the observed counting

rates are constant without normalizing calculations, and that the standard deviation of observed counting rates is 1.6%.

Table 4 Fluctuation of observed counting rates using C-R neutron monitoring system

Sample : Sucrose (JIS "Special Grade")
1.0115 g $\cong$ 520.1 mg of O
Discriminator level : 200 keV
Number of bombardment : 46
Average of observed counting rates : 24,101
Standard deviation : 394
Relative standard deviation : 1.6%

For any variation in the flux during the bombardment of samples, the observed counting rates of a definite quantity of oxygen must be constant in the activation analysis using C-R neutron monitoring system. One gram of sucrose was bombarded by the 14 MeV neutron with C-R neutron monitoring system under the various different fluxes as shown in the Fig. 6, and the produced activities of sucrose samples were measured. The results are given in Table 5. The experiment reveals that the counting rates obtained under the

Fig. 6 The output of 14 MeV neutron and of C-R monitor vs. time

Table 5 Counting rates obtained under the different neutron flux using C-R neutron monitoring system

Bombardment No.	Observed counting rate
1	22,343
2	22,161
3	22,112
4	22,167

above condition are automatically normalized in agreement with the theoretical consideration which has been mentioned in Chap. II "Apparatus"

The sensitivity for oxygen in our method, which is the nondestructive activation analysis is affected by the other elements in the sample, because the base line voltage of pulse height analyzer in the counting system must be increased to eliminate the interference of the other radionuclides which emit the γ photon or the Bremsstrahlung radiation of high energy. For example, in the determination of oxygen in sodium oxalates, the activities of ^{16}N were measured under the condition that the Bremsstrahlung radiation of β -particle emitted from ^{20}F in the sample

was eliminated by discriminator level 5.5 MeV, because ^{20}F produced by the reaction of $^{23}\text{Na}(n, \alpha)^{20}\text{F}$ emits the 5.4 MeV β -particle. The sensitivities for oxygen in sucrose and sodium oxalate under the above consideration were about 200 count/mg and about 30 count/mg, respectively.

V. CONCLUSION

The above method has been established as a rapid, fully automatic and nondestructive method for the direct determination of oxygen in the industrial product materials such as metal, coal and organic materials, etc.

The analyses of three samples are normally made in a 1.5 min.

The difference of 1/100 in oxygen content can be distinguished by this method.

At an oxygen level of 100~300 mg/sample,

the relative standard deviation of the method using C-R neutron monitoring system is about 3~5%.

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研究論文

303. Reprocessing of UO_2 -dispersed Graphite Fuels, (II)

The behavior of non-gaseous fission products in nitric-acid-leach process

二酸化ウラン分散-黒鉛系燃料の再処理, (II)

硝酸浸出プロセスにおける非揮発性核分裂生成物の挙動

By Kazumi IWAMOTO*, Fumiaki KOBAYASHI* and Junichi SHIMOKAWA*

Experiments were done to investigate the behavior of non-gaseous fission products in nitric-acid-leach process in which the conditions of the leaching and postirradiation heating were changed for the irradiated graphite-base fuel element that most of the fission products had been introduced into the graphite matrix by fission recoil process.

The temperature and time of the postirradiation heating were found to be most effective to drive off the fission products from the graphite. A fast and a slow migration step were observed for the migration of the fission products through the graphite crystal. The former was thought to represent the transfer process of all the fission products that may migrate through the graphite crystal in the temperature region below the heating temperature, and the latter the one of the

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