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THE USE OF FAST-NEUTRON ACTIVATION ANALYSIS
FOR THE DETERMINATION OF
THE SILICON CONTENT IN COAL, FLYASH, AND SOIL

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I. Introduction

Neutron activation analysis is a highly sensitive, non-destructive technique for qualitative analysis and quantitative determination of elemental concentrations. It has been particularly useful for determining complex samples such as minerals, environmental samples, biological and archeological objects, etc., because it provides a simple alternative to other more difficult and destructive techniques. Neutron activation analysis takes advantage of the fact that a nuclide can be uniquely identified by its decay properties, such as the half life, the mode, and the particular energies of radiation emitted from each particular nuclide.

Neutron activation analysis was first used in 1935 by Hevey and Levi (1) as a method of analysis for the determination of the dysprosium content in yttrium. In 1938, Seaborg and Livingood (2) used deuteron bombardment to determine gallium, iron, copper, phosphorus, and sulfur at the parts per million level at the University of California cyclotron. Within a decade, this method of analysis was used frequently by Ledicotte and Reynolds (3) at the Oak Ridge National Laboratory. Since that time, neutron activation analysis has become a popular analytical method.

Interest in fast neutron activation analysis (FNAA) has grown rapidly in recent years, mainly because it offers a rapid, accurate, and non-destructive method of analysis at a low cost. This interest resulted in many publications describing the equipment design and

experimental technique of FNAA. The authors (4,5) concur that fast neutron activation analysis is a superior method for the determination of silicon content.

Fast neutron activation analysis was employed in this investigation because high sensitivity in determining elemental concentrations can be attained. In addition to its high sensitivity, FNAA has other advantages compared to other analytical techniques. The superiority of this method lies in its use of the nuclear interaction that is independent of the chemical and physical state of the sample. Rather, fast neutron activation analysis depends upon such parameters as neutron activation cross section, radio-isotopic half life, and the characteristic energies of the radiation emitted by product isotopes. Therefore, no pretreatment of the sample is needed, and there is little chance of contamination, another advantage of FNAA. These properties make fast neutron activation analysis extremely suitable for samples that need to be retained in their original form (6).

There are some disadvantages of fast neutron activation analysis. One of its limitations for some elements, is an inability to produce a large enough neutron flux to obtain the desired sensitivity. The purpose of this study is to improve the quality of the activation techniques and to develop a practical system for silicon analysis.

The essential aims of this experiment were to obtain the silicon content of various coal, flyash, and soil samples by refining the method of FNAA, and to test the accuracy of the analysis on samples of coal and flyash with known silicon concentrations. The analyses of the samples were performed using 14-MeV neutron activation analysis from a Texas

Nuclear Model 9900 neutron generator. The fast neutron activation analysis system previously developed for oxygen analysis (7) was employed in this work because this system is specifically designed for rapid and precise analysis using half life nuclides. The FNAA system is also designed to minimize errors associated with flux determination, flux attenuation in the samples, non-reproducible geometry, and timing, but the parameters needed to be optimized for silicon.

II. Theory

Activation analysis is a method of elemental analysis in which a sample is first bombarded by a beam of particles, after which the radioactivity is measured. Both qualitative and quantitative information can be obtained from the type and amount of the emitted radiation. Although the bombarding beam may be protons, neutrons, deuterons, etc., neutrons are the most commonly used. By the same token, the emitted radiation could be beta particles, alpha particles, gamma rays, or x-rays. However, gamma rays are the most commonly measured since the energies of the gamma rays offer specific determination of the emitting species. For the above reasons, the following discussion will concentrate on fast neutron activation analysis using gamma-ray spectroscopy.

The theory of neutron activation analysis is based on the nuclear reaction $A(n,x)B \xrightarrow{\lambda} C$. This reaction states that a stable nuclide A absorbs a neutron to become an unstable nuclide B and another reaction product x, where x could be a proton, a neutron of different energy, two neutrons, etc. Then the unstable nuclide B decays to a stable nuclide C where λ is the disintegration constant of the unstable nuclide B.

The net rate of accumulation of nuclide B is determined by the rate of formation $\sigma\phi(N_t - N)$ less the rate of decay λN . This reaction is expressed by the differential equation:

$$dN/dt = \sigma\phi(N_t - N) - \lambda N. \quad (1)$$

where

σ = the reaction cross section (cm^2)

ϕ = the neutron flux ($\text{n/cm}^2\text{-sec}$)

N_t = the number of target nuclei present

N = the number of radioactive nuclei

λ = the decay constant (sec^{-1}).

If, when compared with N_t , the number of radioactive nuclei is insignificant, the equation (1) may be integrated to give the number of radioactive nuclei present at the end of the irradiation time, t_i .

This integration results in the equation:

$$N = \frac{\sigma\phi N_t}{\lambda}(1 - e^{-\lambda t_i}). \quad (2)$$

The number of radioactive nuclei present at the end of the irradiation time (N_t) can be expressed as a function of the sample weight, the molecular weight of the sample, and the length of time the

sample was irradiated, as follows:

$$N_t = \frac{N_0 I \sigma W}{\lambda M} (1 - e^{-\lambda t_i}) \quad (3)$$

where

N_0 = Avogadro's number (6.023×10^{23} atoms/gm-atom)

I = isotopic abundance of the radioactive nuclei

W = sample weight

M = molecular weight of the sample

t_i = irradiation time.

Before the number of radioactive nuclei can be calculated by the above equation, several factors such as reactor flux and elemental error cross section must be known. Since these factors are difficult to measure accurately, a comparative method is used wherein a standard of known elemental composition is irradiated in the same flux as the unknown. By taking the ratio of the number of radio-nuclei formed in the unknown and the standard, the following is obtained:

$$\frac{N_u}{N_s} = \frac{\frac{N_0 I \sigma \phi_u W}{\lambda M} (1 - e^{-\lambda t_u})}{\frac{N_0 I \sigma \phi_s W}{\lambda M} (1 - e^{-\lambda t_s})} \quad (4)$$

Since the same conditions are applied to the unknown and standard and the values σ , I , and M are assumed to be identical for the same element, cancellation can be made in the above equation. The following expression is then obtained:

$$\frac{N_u}{N_s} = \frac{W_u \phi_u}{W_s \phi_s} \quad (5)$$

In this experiment, the unknown and the standard could not be irradiated simultaneously. Neither could they be counted at the same time. Therefore, an equation is used to correct the above expression. This equation relates the area of the peak to time, as follows:

$$\begin{aligned} A_\gamma &= N_\gamma E g \tau \\ &= \lambda N_0 K g \tau e^{-\lambda} \end{aligned} \quad (6)$$

where

E = detector photopeak efficiency

τ = length of counting interval

g = geometric counting factor

K = number of gammas per decay.

Although the unknown and standard cannot be counted at the same time, they can be counted using the same geometry and equivalent time intervals. By substituting for N in the above equation, the computational equation is obtained as follows:

$$\frac{W_u}{W_s} = \frac{A_u \phi_s e^{-\lambda t_u}}{A_s \phi_u e^{-\lambda t_s}} \quad (7)$$

III. Experimental

A. Procedure

There are three stable isotopes of silicon: Si^{28} , Si^{29} , and Si^{30} . Their respective abundances are 92.21%, 4.70%, and 3.09% (8). $\text{Si}^{28}(\text{n,p})\text{Al}^{28}$ and $\text{Si}^{29}(\text{n,p})\text{Al}^{29}$ are the most promising nuclear reactions of silicon for activation analysis. Al^{29} is not produced by nuclides other than Si^{29} during irradiation with 14 MeV neutrons. However, the main gamma ray photopeak of the 6.6 min Al^{29} nuclide occurs at 1.28 MeV, which is approximately the same energy as the single escape peak of the 17.78 MeV peak of Al^{28} . Since more Al^{28} is produced than Al^{29} when silicon is activated by 14 MeV neutrons, the 1.28 MeV gamma peak of Al^{29} may have an interference. Al^{28} is produced not only by the $\text{Si}^{28}(\text{n,p})\text{Al}^{28}$ reaction, but also by the $\text{Al}^{27}(\text{n},\gamma)\text{Al}^{28}$ reaction. The only different characteristic of these reactions is that the $\text{Si}^{28}(\text{n,p})\text{Al}^{28}$ reaction requires a fast neutron, and the $\text{Al}^{27}(\text{n},\gamma)\text{Al}^{28}$ reaction needs a thermal neutron. Therefore, a mixture of Al_2O_3 and benzoic acid was run prior to the actual experiment in order to test whether carbon atoms would thermalize the neutrons to a point where extensive neutron capture would occur. No trace of Al^{28} was found. Thus, the $\text{Al}^{27}(\text{n},\gamma)\text{Al}^{28}$ reaction will not interfere. Therefore, the $\text{Si}^{28}(\text{n,p})\text{Al}^{28}$ reaction was the best choice for silicon

analysis.

In this work, the analyses of the samples were performed by 14 MeV neutron activation analysis. A Texas Nuclear Model 9900 neutron generator was employed for producing a neutron flux of approximately $5 \times 10^9 \text{ n/cm}^2\text{-sec}$, an amount typical of most generators (9). The samples analyzed were: terramethylsiane, NBS Standard Reference Material 1632a Trace Elements in Coal, NBS Standard Reference Material 1632 Trace Elements in Coal, NBS Standard Reference Material 1633a Trace Elements in Flyash, Canada Certified Reference Material Project Reference Soil SO-3, and Canada Certified Reference Material Project Reference Soil SO-4.

These samples were packaged and stored in a desiccator (see section B.) until they were to be irradiated. A pneumatic tube transfer system, which consisted of an aluminum sample holder and polyethylene tubing, was employed to transfer the packaged samples into the generator for subsequent irradiation. Each sample was removed from the desiccator and placed in the aluminum sample holder. The sample was propelled into and out of the sample holder by pressurized dry nitrogen gas.

Each sample was irradiated in the 14 MeV neutron flux for 200 seconds. During the irradiation, the sample was automatically rotated about its longitudinal axis by a sample spinner. The sample was returned and immediately placed in a fixed position relative to a lithium-drifted germanium detector. The sample was allowed to delay for 60 seconds and then counted for 200 seconds. The short delay period was used to allow the short-lived N^{16} activity to decay away.

Despite the delay time, a sufficient number of counts were collected

by a multichannel analyzer (MCA) to permit silicon content analysis. The irradiation, delay, and counting time were each controlled by a sequencer with three separate digital timers. This sequencer was constructed by Dr. D. J. Alpert for the purpose of automatic sample transfer, irradiation, delay, rotation, and counting time. Dr. Alpert based this sequencer on the system reported by Morgan and Ehmann (10).

In addition to the lithium-drifted germanium detector, a BF_3 proportional counter was employed to indicate the neutron output of the generator during the irradiation period. The sequencer signaled the MCA to receive and record the number of pulses from the BF_3 proportional counter. After the 60 second delay period, the MCA was then switched to the lithium-drifted germanium detector where the sample activity was counted for a 200 second period. In this way, the neutron production, delay time, and sample activity were all recorded on the same spectrum.

A cassette tape recorder was used to record all the output. Five separate spectra per sample were obtained for all samples analyzed in this study for further data analysis.

B. Sample Preparation and Handling

Each sample was prepared in a laminar flow clean hood for the purpose of minimizing contamination by atmospheric particles. Each sample was sealed in a precleaned 2/5-dram polyethylene vial. All these vials were soaked in concentrated HNO_3 for a day and rinsed with

deionized distilled water and electronic grade acetone. Prior to sample packaging, all these polyethylene vials were baked at approximately 90°-100°C for at least 12-16 hours. Plastic gloves were worn at all times when handling the samples. Additionally, all samples were kept in a desiccator when not in use.

C. Instrumentation

1. Neutron Generator

In this project, a 150 kV D. C. particle accelerator was employed to produce 14-MeV neutrons. Generally, fast neutrons are produced by the following two reactions:

However, the deuterium-tritium (D-T) reaction is commonly used by neutron generators for the production of intense fluxes of 14-MeV

neutrons. The D-T reaction releases 17.86 MeV of kinetic energy allotted between the neutron and the alpha particle. The neutron receives an average of 14 MeV and the alpha particle gains the remainder (11).

The operation of a neutron generator usually depends on the production, extraction, and acceleration of ions. After acceleration, the ions are allowed to strike a suitable target material to produce neutrons.

The principle components of a neutron generator are a high voltage source, an ion source, an accelerating system, a target system, and a vacuum system. Positive ions are produced in a radio-frequency type ion source. These ions are extracted by applying a potential across the ion source bottle. The ions are focused by a gap lens directly behind the exit canal of the ion source base. The ions leave the gap lens and enter the field of the accelerating tube where they are accelerated through a drift tube (potential free region) until they strike the target. A vacuum is maintained in the entire system to minimize scattering of the ion beam (12). This is only a brief description of how a neutron generator works. Nargolwalla and Przybylowicz (9) have provided detailed descriptions of these components.

2. Multichannel Analyzer

The multichannel analyzer, an instrument which takes an analog signal proportional to the energy of the gamma ray and converts it to a digital signal, was used in this work. The conversion is accomplished by incrementing a location in memory which is proportional to the energy of the incident gamma ray. As a result of the different emitted activities of the standards and unknowns, errors may occur due to the loss of different relative counts. The lost counts occur when a second pulse arrives while the multichannel analyzer is operating on the first one. The multichannel analyzer will then ignore the second pulse and that count is lost. The time during which the analyzer ignores any pulses following the one it is converting is known as the dead time (DT). The time when the multichannel analyzer can accept a pulse is called live time (LT). The actual time (AT) can be expressed as the sum of dead time and live time, as follows:

$$AT = DT + LT$$

To approximate the dead time, a reference pulser peak is used. The correction for the dead time is made by the comparison of the area of the sample reference pulser and the standard reference pulser peak. This ratio of the pulser areas is applied to the various samples and standard peak areas to correct for the count losses.

Another form of count loss is pulse pile-up. Pulse pile-up takes place during the time the system is returning to zero voltage after an

event, resulting in a tailing effect. If a count arrives during the time the system is re-setting to zero, it will not be incremented in the appropriate channel. This effect will result in a large full width at the point corresponding to one half of its height. A large FWHM will affect the accuracy of the result. A pulse pile-up rejector can be used to allow the system to eliminate counts caused by pulses that occur within too short a time interval after an initial pulse.

3. Semiconductor Detector

A semiconductor detector (lithium-drifted germanium detector) was employed in this study for counting the emitted gamma rays. The applications of this instrument include detection, counting of ionizing particles, and accurate determination of their energies. The detector is a block of solid semiconductor material (Ge) which is doped with lithium. When exposed to radiations consisting of charged particles or photons, the electrical conductivity of the semiconductor may be increased. In this respect, the semiconductor detector operates on the same principle as a gas ionization detector (13), although the mechanism of the process is different.

In this detector, a thin layer of lithium is drifted into one surface of the germanium crystal and a reverse bias is applied, forming a depleted zone (13). The gamma rays interact with the matter through

three types of reactions - photoelectric, Compton scatter, and pair production - producing free electrons. The flow of these electrons creates current pulses, and the charge carriers give an output signal proportional to the energy of the gamma rays absorbed. The energy of the gamma rays is proportional to the number of electron pairs formed in the depletion zone, and is also proportional to the current pulses.

D. Sources of Error

1. Systematic Errors

Several sources of systematic error are present in fast neutron activation analysis which will affect the accuracy of the resulting data. Systematic error can result from incidental thermalization and absorption. Variation in irradiation and counting geometry between samples and standards are some of the examples of systematic errors. Also, systematic error can result from samples possessing elements with large neutron capture cross section.

2. Controllable Errors

There are several sources of controllable error present in fast neutron activation analysis which will affect the results. Time variation of neutron flux, irreproducibility of sample position during irradiation and counting, counting statistics, electronic instabilities, and sample handling are the major sources of accidental error.

IV. Discussion

The systematic and controlled errors mentioned in the previous section must be minimized in order to obtain a better result. For the systematic errors, it is necessary that both the standards and the samples possess similar macroscopic densities, physical states, mean atomic numbers, and contents of low mass neutron thermalizing nuclei (14). Furthermore, the concentrations of the standards and the samples should be similar in order to prevent large differences between the standard and sample activities. Careful selection of the standard is important for reducing the extent of systematic errors. In addition, good sample packaging techniques and the use of a sample spinner during the irradiation time can minimize the error resulting from geometric dissimilarity.

For the controllable errors, effective methods have been developed and were used to reduce the error caused by the time variation of the neutron flux. For the most part, considerable care during sample packaging can minimize accidental errors effectively. Additionally, a blank determination is an effective test for the technique.

V. Results and Conclusions

The values of the silicon content and the associated precisions obtained for the samples analyzed in this study are listed in Table I. It was the purpose of this study to employ fast neutron activation analysis for the determination of silicon content in coal, flyash, and soil. The silicon content of coal, flyash, and soil samples have been obtained with accuracies and precisions in good agreement with the accuracies and precisions reported by other researchers performing similar analyses. Terramethylsilane was found to be a suitable standard for this study. Finally, careful sample packaging and handling techniques were found to be crucial for obtaining accurate and precise results. It can be concluded that fast neutron activation analysis using the system at the University of Illinois can be used successfully to determine silicon content.

Table I

Silicon Content

Sample ID	Reported Value(a)	Present Value(b)
Reference Soil SO-3	15.86 ± 0.19	15.4 ± 0.7 15.2 ± 0.7
Reference Soil SO-4	32.0	31.4 ± 1.7 30.7 ± 1.5
1632a Trace Elements in Coal	5.8 ± 0.1	5.65 ± 0.21 5.61 ± 0.30
1632 Trace Elements in Coal	$3.2(c)$ $2.8 \pm 0.6(15)$	3.18 ± 0.30 2.96 ± 0.10
1632a Trace Elements in Flyash	22.8 ± 0.8	22.9 ± 0.8 23.8 ± 0.8

- a). NBS certified values unless otherwise stated.
b). Two separate identical samples for each sample.
c). NBS information value.

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