Title: CALIUM-252 NEUTRON ACTIVATION FOR TERRESTRIAL, SEA FLOOR AND POSSIBLE PLANETARY SURFACE ANALYSIS

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200-Word Abstract (This abstract will be set in type and printed under the title on the first page of the paper. Do not type abstract on oversized paper provided.)

The high neutron emission rates presently available from $^{252}$Cf sources have dramatically improved the potential applications of both laboratory and in situ neutron activation analyses of minerals. In recent laboratory studies of 200 lb. ore samples, techniques have been developed which permit the very rapid analysis of more than 16 elements at concentrations which are generally well below those of commercial interest. These developments were based on studies conducted with 260 µg and 1.8 mg $^{252}$Cf sources for neutron activation and a 50 cc Ge(Li) diode for the gamma-ray spectrometric analysis. In feasibility studies carried out in several feet of water in an ocean tidal zone, it was demonstrated that elements such as Au, Ag, and Mn could be measured in concentrations as low as a few ounces per ton. This report describes the technology which has been developed for either ground-based or shipboard laboratory mineral analysis, the technology and equipment which is being developed for in situ analysis of the floors of fresh and salt water basins, and the potential applications of this technology for planetary surface analysis.

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INTRODUCTION

In situ elemental analysis is extremely desirable in a large number of applications. Mapping of the mineral composition of terrestrial areas and of the ocean floor could be greatly simplified by rapid in situ elemental analysis, while the surfaces of the planets could be analyzed remotely. In considering possible methods for multielement analysis, one normally considers x-ray, arc or mass spectrometry, and alpha scattering techniques. While these techniques are usually considered as laboratory tools, they can potentially be used for in situ analyses, and indeed, the alpha scattering techniques have received worldwide attention because of their successful implementation in analyzing major elements in the lunar surface. All of these procedures involve rather complex instrumentation and have not been seriously considered for hostile environments such as the ocean floor or for the surface analysis of planets with dense atmospheres.

Two major developments during the past few years have dramatically changed the potential of neutron activation analysis for both the quantitative measurements performed in mineral assay laboratories and for a variety of in situ mineral analyses. These include the production of useful quantities of the isotopic neutron source, $^{252}$Cf, and the development of very efficient, high resolution Ge(Li) gamma-ray detectors for measuring the neutron activation products.

The extremely compact nature of the $^{252}$Cf source permits two different approaches to mineral analysis by neutron activation. When the neutrons are captured by the various elements in the mineral, "prompt gamma-rays" are emitted immediately, and their measurement can be employed to determine the elemental content of the sample. This method has been investigated for the measurement of manganese and gold\(^1\) in simulated ocean floor conditions, and silver in simulated terrestrial deposits\(^2\). In addition, the capture of neutrons by most elements produces radionuclides of the element, and in their subsequent decay "delayed gamma-rays" are emitted which can be measured to determine the elemental content of the sample. The detection of prompt gamma-rays allows the measurement of certain elements such as iron and silicon, which cannot be determined by subsequent radionuclide analysis. However, the necessary physical proximity of the $^{252}$Cf neutron source and detector for the prompt gamma-ray measurements makes a much less sensitive procedure for the nondestructive analysis of many of the elements in minerals. Recent studies in our laboratory have demonstrated that by induced radionuclide analyses the majority of elements of commercial interest can be measured in minerals at concentrations well below those of economic value\(^3\). These measurements also suggest that in situ analysis of terrestrial surfaces and the floors of fresh and salt water basins can be made with comparable sensitivities to those
which we have observed in the laboratory.

A major constraint in the use of $^{252}$Cf sources for in situ analysis has been the relatively high radiation level associated with milligram-size $^{252}$Cf sources which are required for this work. In recent developments at our laboratory, it has been demonstrated that neutron multiplication of 30 to 40 fold can be achieved in a small sub-critical assembly\(^4\). This technology could allow a 30 to 40 fold smaller $^{252}$Cf source to be used for the in situ analysis program. When an actual in situ neutron irradiation was to be made, the 30 to 40 fold multiplication could be obtained by mechanically inserting the source into the multiplier device. The major advantages of this technology in both economy of the $^{252}$Cf source size and the radiation shield problems during shipment and non-use periods are obvious.

The present work has been concerned with determining the feasibility of seabed and terrestrial mineral analysis and with developing practical methods for implementing these types of measurements. These studies suggest the feasibility of this type of technology for application to planetary surface analysis on planets with both rare and very dense atmospheres.

TECHNOLOGY DESCRIPTION AND EXPERIMENTAL EVALUATION

Californium-252 provides essentially a point source of fission neutrons which require moderation for their most effective use in either laboratory or in situ activation analysis. The spontaneous fission decay mode of $^{252}$Cf involves the emission of $2.34 \times 10^9$ n.mg$^{-1}$.sec$^{-1}$, thus the actual mass of the $^{252}$Cf source is insignificant. In our initial laboratory feasibility studies\(^3\), the $^{252}$Cf source was contained in the center of a 4-inch thick slab of paraffin. A 200 liter drum located directly over this source served as a neutron moderator and contained a 3-inch diameter vertical access port through which mineral samples could be placed within about 2 inches of a 260 microgram $^{252}$Cf source. The characteristic gamma-ray spectra for some 20 minerals, after 2-5 minute irradiation and counting periods, were obtained from this system. This information demonstrated the practicality of this technology for laboratory mineral analysis. To evaluate the potential of in situ neutron activation analysis of terrestrial and ocean floor regions, the experimental arrangement shown in Figure 1 was used. In this arrangement a 210 microgram $^{252}$Cf source was located in the bottom of a 2 foot diameter by 4 foot high polyethylene tank. This container in turn was located in a 6 foot diameter water-filled polyethylene tank which served as a radiation shield. With this arrangement, bulk ore or simulated ore samples which represented an essentially infinite source could be irradiated. After a short irradiation, they could be rapidly removed and placed under a Ge(Li) diode detector for counting as shown in the illustration. The addition of seawater and fresh water around the $^{252}$Cf source-moderator and the Ge(Li) diode detector permitted the simulation of the anticipated irradiation and counting geometries at the floor of ocean and fresh water basins. Without the water present, a terrestrial (earth's surface) analysis could be simulated. The radiation level at the surface of the 6 foot diameter shield was about 0.3 mR per hour. Measurements of the gamma-ray spectra of various types of ore and of simulated ore samples showed excellent photopeak resolution and indicated the feasibility of employing this type of technology for both terrestrial and ocean floor analysis.

An essential step in developing this technology for seabed mineral analysis was an actual in situ feasibility demonstration. This feasibility demonstration was conducted at the Battelle-Northwest Marine Research Laboratory at Sequim, Washington. For this study 200 pound samples of minerals, or simulated mineral samples containing known amounts of various elements, were placed in the tideland ocean floor during the low tide. These samples were contained in cut-off 55 gallon drums which were approximately 10 inches deep and 22 inches in diameter (see Figure 2). At high tide when the measurements were made, these samples were covered with 4-5 feet of seawater. The samples were irradiated with a 210 microgram $^{252}$Cf source which was located about 2 inches from the bottom of a 6 inch diameter by 10 inch high paraffin moderator. This source was positioned directly over the center of the sample. Irradiation times of 120 seconds followed by a 30 to 40 second decay period and an in situ counting time of 200 seconds were employed. The gamma-ray spectrometric measurements were made with a 50 cm$^3$ Ge(Li) diode which was centered directly over the sample. Figure 3 shows the gamma-ray spectrum of a silver bearing dunite sample which was irradiated and counted under these conditions. The silver content of this sample was 0.05%,
while the manganese content was about 0.1%. The concentrations of Mn and Ag, as well as those of Mg, Al and V, were easily measurable from the photopeak areas. There was not a detectable photopeak from $^{24}\text{Na}$ and the photopeak from $^{36}\text{Cl}$ (37 min) was relatively small. This confirmed our laboratory observations that induced $^{24}\text{Na}$ and $^{36}\text{Cl}$ in the ocean floor should not significantly interfere with measurements of the mineral composition. As indicated in Figure 3, several elements can be observed and measured reasonably well from their photopeak areas after a short irradiation with the 210 microgram $^{252}\text{Cf}$ source; however, this source size is not sufficient for the measurement of all of the elements of interest. From consideration of the total acceptable counting rate, it appears that a 5 mg $^{252}\text{Cf}$ source would be about optimum for this type of application; however, radiation shielding and handling considerations dictate a source of 1 mg or less which should be adequate if a large, efficient Ge(Li) diode detector is used for analysis. If a neutron multiplier unit could be used, the needs for both the high flux during usage and the low flux during loading and shipping could be met.

A detailed study of the sensitivity with which the various elements in mineral samples can be measured with an approximate 2 mg $^{252}\text{Cf}$ irradiation source is being conducted in a laboratory mockup arrangement. The experimental arrangement used for this program is shown in Figure 4. As indicated, the $^{252}\text{Cf}$ source is located near the bottom of a 12 inch diameter by 12 inch high paraffin moderator. This moderator is centered at the bottom of a 6 foot diameter by 7 foot deep polyethylene tank which in turn is contained in a 15 foot diameter by 7 foot deep plastic swimming pool. With this shielding, no gamma or neutron flux could be observed at the edge of the pool or the surface of the water. However, a neutron dose rate of about 10 mR/hr was observed at the sample channel opening. The mineral samples to be analyzed were contained in 10 inch high by 22 inch diameter cylinders as previously described. With the sample channel and sample dolly arrangement shown in Figure 4, the samples could be placed directly under the source for neutron irradiations. The neutron flux at the surface of the sample and at various depths within it was determined by foil irradiation techniques. Figure 5 shows the thermal neutron flux at the surfaces of paraffin and seawater substrates in the irradiation position directly beneath the $^{252}\text{Cf}$ source. The thermal neutron flux is only reduced by about 25% at the surface of seawater relative to paraffin. The neutron fluxes at the surface of paraffin and fresh water substrates are almost identical. In Figure 6 the horizontal thermal flux profiles at the surface of a dry dunite sample, dunite saturated with fresh water, and a dunite sample saturated with seawater are shown. There is very little difference between the thermal flux at the surface of fresh and salt water saturated dunite, however, the neutron flux at the surface of the dry dunite is substantially less.

Saturation of the dunite with fresh water or seawater increases the density from 1.5 to about 1.8. However, water does serve as an excellent moderator and results in the substantially higher thermal neutron flux at the surface of these dunite samples. As shown in Figure 7, the maximum thermal neutron flux at the center of a seawater saturated dunite substrate is about $1.7 \times 10^7$ n.cm$^{-2}$.sec$^{-1}$ and this decreases somewhat faster with depth than with lateral distance from the source. In this substrate the average thermal neutron flux is about 2 fold less than this center value through the volume of a 20 cm diameter hemisphere and about 3 fold lower through a 35 cm hemisphere. In Figure 8 the thermal and epithermal neutron fluxes at the surface of a seawater saturated dunite substrate are presented. It is important to note that the epithermal flux even at the center of the sample is about 25 fold less than the thermal flux. In addition, the epithermal flux drops off much more rapidly than the thermal flux. Thus the neutron flux impinging on the sample is reasonably well moderated.

Major emphasis in this program has been toward determining the sensitivity with which some 30-40 trace elements can be measured in an ocean floor substrate and determining calibration constants which can be used for an actual seabed mineral analysis. Table I summarizes the sensitivities for the measurement of 16 elements based on the use of a 1.8 mg $^{252}\text{Cf}$ source in the irradiation facility shown in Figure 4, and the 50 cm$^3$ Ge(Li) diode detector system shown in Figure 1. These measured sensitivities were all determined for seawater saturated dunite containing known amounts of the elements of interest; however, several actual mineral samples have been measured and indicate sensitivities within the ranges shown in Table I. The sensitivities are based on a 2 minute irradiation followed by
a 30 to 60 second delay and a 2 minute counting period. Such irradiation and counting periods appear adequate for the in situ analysis of most elements. The sensitivities in Table 1 for the simulated in situ condition are similar to those which were observed earlier in our laboratory mineral assay facility. As suggested from the neutron flux curves for fresh-water-saturated dunite, the sensitivity for elemental analysis at the floor of fresh water basins is only slightly better than for the ocean floor. The sensitivities for elemental measurements on terrestrial areas with a given neutron source size are somewhat less than on the ocean floor because of the lower thermal neutron flux near this substrate surface. However, the rather wide range in sensitivities presented in Table 1 certainly cover the sensitivities for all three types of substrates.

DISCUSSION

While there are numerous parameters affecting analysis of ocean and fresh-water basin floors and of terrestrial surfaces, they are adequately accounted for if the simulated samples very nearly resemble the actual study areas. There are compensating factors and even if one were to apply the detection efficiency factors obtained for sea floor analysis in the analysis of a dry terrestrial surface, the errors would be less than 50%. Where the actual density of the material is reasonably well known it appears that measurements to an accuracy of +10% will be possible. One problem which must be recognized, however, is that the observed sample sizes are somewhat different for each photon energy. For example, the sample size actually observed with $^{198}$Au which emits a 0.41 MeV is much smaller than that from $^{26}$Al which emits 1.779 MeV photons.

TERRESTRIAL MINERAL EXPLORATION

The very small physical sizes of both the $^{252}$Cf source and the Ge(Li) diode detector make their combined use appear very attractive for in situ mineral exploration programs. From our laboratory studies in which massive (200-lb) ore samples were used, sensitivities comparable to those in Table 1 were obtained and these could be achieved in situ terrestrial mineral analysis.

In borehole measurements a "nuclear probe" consisting of a $^{252}$Cf source separated by a specific distance from a Ge(Li) diode could be used in the simultaneous assay of several elements. The practicality of employing such a logging technique for multiple element analysis in wells or boreholes vs. collecting samples for laboratory analysis at the time of drilling would depend on the objectives of the programs.

SEABED MINERAL EXPLORATION

The continental shelf portions of the ocean floor are known to contain vast reserves of several minerals, yet relatively little exploration of these areas has been performed. The technology, described in this report, for rapid nondestructive mineral analysis in our earlier report and in this work would be applicable to a shipboard laboratory and in situ analysis of the ocean floor respectively. Figure 9 shows a conceptual design of a nuclear probe which is being built for performing in situ mineral analysis of the ocean floor at depths of a few hundred feet. The operation will involve first the positioning of the probe on the ocean floor. A sequence will then be initiated which will rotate the $^{252}$Cf source to the irradiation position, hold it there for a preset time of about 2 minutes, then reverse positions of the $^{252}$Cf source and the Ge(Li) diode detector for a 2-minute count. With this procedure, a rather detailed mineral assay could be made in a 5-minute interval at each point of interest. The probe could be operated from a surface vessel using a TV monitor for probe positioning.

SUMMARY AND CONCLUSIONS

This study employing a $^{252}$Cf neutron source for neutron activation, together with one of the best available Ge(Li) diode gammaray detectors, demonstrates the remarkably practical potential of this approach for in situ mineral exploration. Laboratory studies with a $^{252}$Cf source indicated that most of the elements of commercial interest can be directly measured by a 2-minute irradiation and a 2-minute count. A 1-mg $^{252}$Cf source would be adequate for such measurements and a rather detailed quantitative analysis of a substrate sample could be performed in 5 minutes by a trained technician.

The recent demonstration of the practicality of $^{252}$Cf neutron flux multiplication could permit the use of a 50 microgram source for this application and eliminate most of the shielding problems associated with its use.

In situ mineral exploration of the ocean floor, particularly on continental shelf
regions, appears feasible. Compared with any other potential method for in situ analysis, this approach appears extremely attractive. It could provide a rapid and practical approach to establishing the elemental content both of the ocean floors and of the floors of the large fresh water areas of the world.

In situ analysis of terrestrial surfaces and in boreholes or wells also appears feasible and may prove extremely useful. This approach could allow the rapid logging of boreholes for a wide spectrum of elements. It is obvious that a similar approach could be employed on a roving vehicle for unmanned planetary mineral analysis.

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REFERENCES


SENSITIVITIES FOR THE MEASUREMENT OF TRACE ELEMENTS IN A SIMULATED OCEAN FLOOR MATRIX*

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotope</th>
<th>Half Life</th>
<th>Detectable Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>116mIn</td>
<td>54 min</td>
<td>1-10 ppm</td>
</tr>
<tr>
<td>Selenium</td>
<td>77mSe</td>
<td>18 sec</td>
<td>10-100 ppm</td>
</tr>
<tr>
<td>Silver</td>
<td>108Ag</td>
<td>2.4 min</td>
<td>10-100 ppm</td>
</tr>
<tr>
<td>Titanium</td>
<td>51Ti</td>
<td>5.8 min</td>
<td>10-100 ppm</td>
</tr>
<tr>
<td>Vanadium</td>
<td>52V</td>
<td>3.77 min</td>
<td>10-100 ppm</td>
</tr>
<tr>
<td>Gold</td>
<td>198Au</td>
<td>64.8 hr</td>
<td>10-100 ppm</td>
</tr>
<tr>
<td>Manganese</td>
<td>56Mn</td>
<td>2.5 hr</td>
<td>10-100 ppm</td>
</tr>
<tr>
<td>Aluminum</td>
<td>28Al</td>
<td>2.3 min</td>
<td>1-10%</td>
</tr>
<tr>
<td>Arsenic</td>
<td>76As</td>
<td>26.5 hr</td>
<td>0.1-1%</td>
</tr>
<tr>
<td>Cobalt</td>
<td>60Co</td>
<td>10.5 min</td>
<td>0.1-1%</td>
</tr>
<tr>
<td>Copper</td>
<td>65Cu</td>
<td>5.1 min</td>
<td>0.1-1%</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>101Mo</td>
<td>14.6 min</td>
<td>0.1-1%</td>
</tr>
<tr>
<td>Antimony</td>
<td>122Sb</td>
<td>2.8 day</td>
<td>1-10%</td>
</tr>
<tr>
<td>Cadmium</td>
<td>111mCd</td>
<td>49 min</td>
<td>1-10%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>27Mg</td>
<td>9.5 min</td>
<td>1-10%</td>
</tr>
<tr>
<td>Nickel</td>
<td>65Ni</td>
<td>2.5 hr</td>
<td>1-10%</td>
</tr>
</tbody>
</table>

* Two minute irradiation
Two minute count

This paper is based on work performed under U. S. Atomic Energy Commission Contract No. AT(45-1)-1830.
$^{252}$Cf Neutron Irradiation Facility (Laboratory Prototype for in situ Seabed Mineral Analysis).

Figure 1
Mineral Samples Contained in Cut off 55-gallon Drums

Figure 2
GAMMA-RAY SPECTRUM OF SILVER BEARING DUNITE ON THE OCEAN FLOOR

252
Cf SOURCE: 210 ug
SAMPLE SIZE: 58 cm DIAMETER,
25 cm THICK
IRRADIATION TIME: 120 SEC
DECAY TIME: 36 SEC
COUNTING TIME: 200 SEC
SILVER CONTENT: 0.05%
MANGANESE CONTENT: 0.1%

Detector System: GE(Li) 50 cm³

Radionuclides Observed:

- 108 Ag
- 110 Ag
- 28 Al
- 51 Mn
- 56 Mn
- 27 Mg
- 1013
- 28 Al
- 52 V
- 633
- 658
- 27 Mg
- 56 Mn
- 847
- 1268
- 1434
- 1779
- 1810
- 2110

Channel Number

Counts per Channel

Figure 3
$^{252}\text{CF IRRADIATION FACILITY}$

SIMULATION SYSTEM FOR SEA BED MINERAL ANALYSIS

FRESH WATER

FRESH OR SALT WATER

PLASTIC TANK 6' DIAMETER

SWIMMING POOL 15' DIAMETER

SAMPLE DOLLY

SAMPLE CHANNEL

SOURCE MANIPULATOR

MODERATOR (12" DIAMETER x 12" HIGH)

SOURCE HOLDER

$^{252}\text{CF SOURCE (2 MG)}$

PLASTIC (1/2" THICK)

ALUMINUM PLATE (1/2" THICK)

SAMPLE

Figure 4
HORIZONTAL FLUX PROFILE AT THE SURFACE OF PARAFFIN AND SEA WATER SUBSTRATE BENEATH A $^{252}$Cf SOURCE

Figure 5
HORIZONTAL FLUX PROFILES AT THE SURFACE OF DUNITE SUBSTRATES BENEATH A $^{252}$Cf SOURCE

Figure 6
HORIZONTAL FLUX PROFILE AS A FUNCTION OF DEPTH IN DUNITE SATURATED WITH SEA WATER

Figure 7
HORIZONTAL NEUTRON FLUX PROFILE AT THE SURFACE OF SEA WATER SATURATED DUNITE

Figure 8
Seabed Mineral Exploration Probe Using a $^{252}\text{Cf}$ Neutron Source and a Ge(Li) Gamma-Ray Detector System

![Diagram of the Seabed Mineral Exploration Probe]

Figure 9