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Detection of sulfur in soil samples using 2.5 MeV neutron activation

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Abstract
Sulfur concentrations in soil samples containing 4.4–13.47 wt% sulphur were measured in neutron inelastic scattering using dc beams of 2.5 MeV neutrons from a DD neutron generator. The measurements were carried out using 2230 keV prompt gamma rays from sulfur using a $CeBr_3$ detector. The minimum detectable concentration (MDC) of sulfur was 0.68 ± 0.21 wt%. The present MDC value is about one-fifth of an earlier reported value of 3.50 wt% for 3.2 MeV neutron beams. This study has shown an improvement in the sulfur MDC achieved using 2.5 MeV neutron beam.

Keywords Sulfur contaminated soil samples · $CeBr_3$ detector · 2.5 MeV neutron activation · Portable neutron generator-based activation setup · Minimum detectable concentration · Measurements of sulfur

Introduction

Advances in science and technology demand steady improvements in the precision of research techniques and tools. This requires continuous enhancements in the detection techniques and methodologies [1]. Neutron activation analysis techniques have been widely used in elemental analysis of samples for scientific and industrial applications [2], In the neutron activation analysis technique, the elemental concentration in the sample is determined through measurement of elemental characteristic prompt gamma rays excited through 14 MeV neutron inelastic scattering (NIS) or excited through capture of thermal neutrons in the sample, i.e. TNC reaction. The highest thermal neutron fluxes are obtained in nuclear reactors resulting in the highest detection sensitivities. Our present discussion is restricted to accelerator-based neutron sources, specifically DD and DT neutron generators. Neutron activation with 14 MeV neutrons has been used for those elements with small capture cross sections, such as carbon and oxygen [3–8], while thermal neutron activation has been successfully used for several medium and light elements [9, 10].

Neutron activation analysis has not been carried out frequently for neutron beam energies other than 14 MeV and thermal neutrons. In the literature, only few studies have been reported for neutron activation analysis using 2.8–3.29 MeV neutron beams [11–13]. Scherrer et al. [13] measured gamma radiation from interactions of 3.2 MeV neutrons with various materials. Later, Jiggins and Habbani [12] measured gamma rays from bulk samples using 3.29 MeV neutrons. The 3.29 MeV neutrons from the D(d,n) reaction were chosen in Ref. [12] because of their low associated background and less complex gamma ray spectra.

Recent developments in the manufacturing of portable neutron generators have led to an improvement in the intensity of 2.5 MeV neutrons. Since the DD neutron generator energy is very close to the neutron energy used in Ref. [12], it was deemed worthwhile to carry out neutron activation analysis using NIS of 2.5 MeV neutrons to investigate the minimum detectable concentrations that can be achieved for this beam energy as compared to 3.29 MeV.

It is important to point out that if an element has comparable cross sections for both TNC and NIS channels, it is expected to achieve better detection limits in the measurements using NIS. This is due to an order of magnitude higher flux of fast neutron beams as compared to thermal neutron beams which are produced via moderation of the same fast neutron beam in a hydrogenous medium. The production cross sections of gamma rays from NIS strongly depend upon and fluctuate with neutron energy [14], while production cross sections of TNC gamma rays are relatively

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insensitive to neutron energies [15]. More specifically the production cross sections of 2230 keV gamma rays in NIS from sulfur for 3.85, 3.50, 3.29 and 2.56 MeV neutrons are 0.440, 0.330, 0.109 and 0.175 barns, respectively [14]. This shows that, for 2.50 MeV neutrons, we expect about 61% improvement in detection efficiency over results reported for 3.29 MeV neutrons, just on the basis of differences in cross sections alone.

A Prompt Gamma Neutron Activation Analysis (PGNAA) setup has recently been build around a portable GENIE 16 DD neutron generator that produces 2.5 MeV neutrons. The setup has been tested for the determination of sulfur concentrations in specially prepared sulfur-contaminated soil samples and the results were compared with earlier reported data. Sulfur was chosen for these test studies because of its importance in industrial applications [16, 17]; as well as its significant role in environmental pollution [18, 19]. In what follows, the study will be described in detail. Prior to experimental details, theoretical calculations of gamma ray count rates from contaminated soil samples will be described first.

Gamma rays count rate calculation from sulfur-contaminated soil samples

The intensities of 2230 keV gamma rays from sulfur excited by 2.5 MeV neutrons in the contaminated soil samples were calculated using the code MCNP4B2 [20] for the setup shown in Fig. 1. The setup consists of a cylindrical sample container with 9 cm diameter and 14 cm height placed upright at mid-level of the neutron generator tube and touching it at the neutron target location.

A cylindrical $CeBr_3$ gamma-ray detector, with 76 mm diameter and 76 mm height, has its longitudinal axis aligned with the target plane of the neutron generator and faces the upright sample cylinder. The sample is in physical contact with the neutron generator tube. The center-to-center sample-detector distance is 8.6 cm. Lead shielding was placed around the detector and sample to shield them against unwanted gamma rays and neutrons. Lead shielding consists of eleven rectangular lead brick each of 10 cm × 15 cm × 5 cm (height × length × thickness) dimensions. Four bricks were used to build a shielding wall on either side of the sample-detector arrangement. The remaining three bricks were put on top of the wall as a roof. The whole setup rests on a massive iron table. The major constituent of the dry soil sample was SiO_2 with 88.01 wt% concentration [5]. The calculation procedure is similar to the one used for 14 MeV neutrons activation analysis [4–6]. The neutron energy was chosen to be 2.5 MeV and the sample consisted of sulfur-contaminated soil samples with 0–20.0 wt% sulfur contents. A total of 10^9 neutron source particles were transported from the neutron target to the sample to produce 2230 keV gamma rays from sulfur. These gamma rays were then transported to the detector volume. Gamma ray intensities were counted using the F1 tally with a relative error $R = 0.1$ given by MCNP code. The average neutron flux in the samples was not needed for our calculations and therefore was not included in the MCNP cacu-lations. Figure 2 shows the calculated count rate of sulfur prompt gamma rays for various sulfur concentrations in the soil samples. The uncertainity in the data is smaller than the size of the data symbol. The count rate increases linearly with increasing sulfur concentration. Later, the calculated

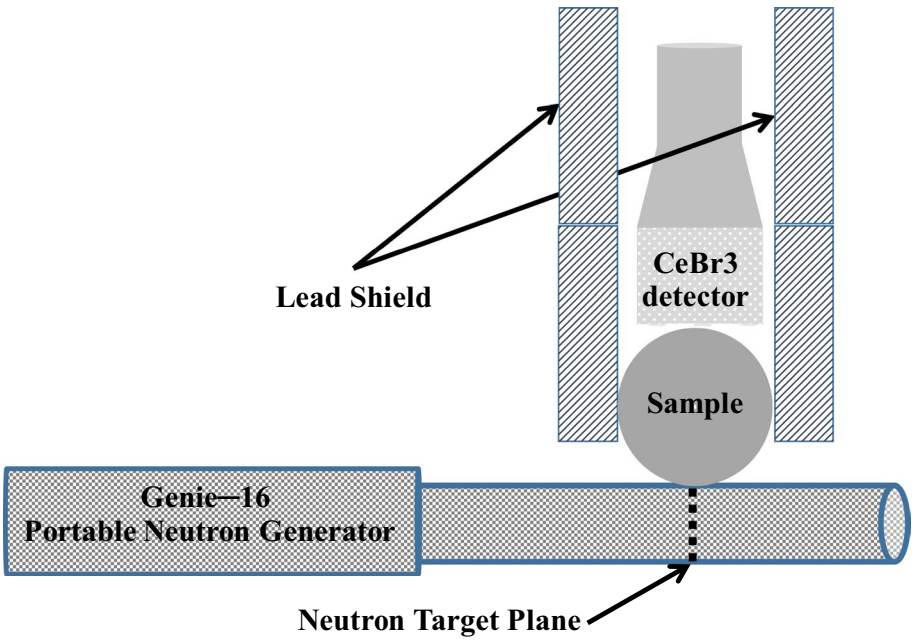

Fig. 1 Schematic representation of the 2.5 MeV neutron inelastic scattering-based prompt gamma ray activation analysis setup built around a Genie 16 portable neutron generator. Figure is not drawn to scale

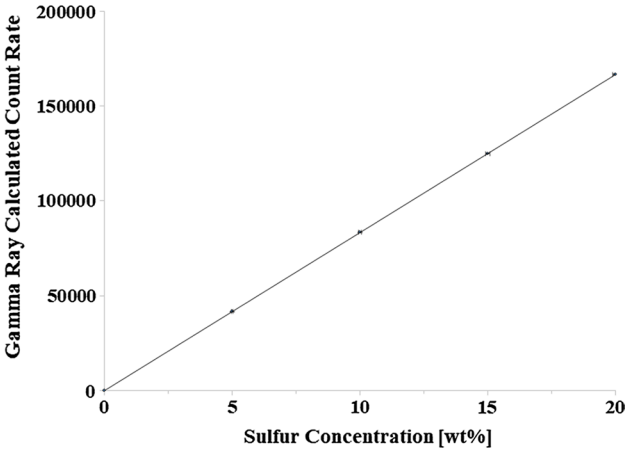

Fig. 2 Calculated ccount rates of 2230 keV gamma rays of sulfur in soil samples with various sulfur concentrations

count rate curve will be compared with the experimentally measured gamma ray count rate.

Experimental

Samples of pure sulfur and dry soil were first weighed separately and then mixed thoroughly together to prepare four sulfur-contaminated soil samples with 4.4, 7.1, 9.6 and 13.47 wt% sulphur. These contaminated soil samples were first weighed and then filled into cylindrical plastic containers made of PET polymer chain with chemical formula $(C_{10}H_8O_4)_n$. The mass of the empty cylindrical container was 58.0 g. The masses of the four contaminated soil samples varied from 1400 to 1650 g while the mass of the pure soil sample was 1450 g.

The samples were irradiated with dc beams of 2.5 MeV neutrons produced by 70 keV deuterons with 50 μA beam current. The deuteron beam current, gas pressure, and high voltage were continuously monitored and recorded on the neutron generator control panel for later reference. The neutron emission rate delivered by the GENIE 16 DD neutron generator was 4.7×10^7 n/s at the specified beam current and high voltage as recorded by the built-in neutron intensity monitor of Genie-16 neutron generator. The gamma-ray spectra were acquired by a Multi Channel Buffer (MCB)-based data acquisition system coupled to a PC-based workstation. The MCB, supplied by EG&G Ortec-USA, utilizes ScintiVision software for data acquisition and spectrum analysis. The pulse height spectrum of the detector was calibrated using a Bi-207 source with three gamma rays with energies of 570, 1063 and 1770 keV. The spectra from the contaminated soil samples were counted for 3600 to 5000 s preset time.

First, the $CeBr_3$ detector background spectrum was acquired using 2.5 MeV neutrons with an empty plastic sample container and is shown in Fig. 3.

The spectrum shows prompt gamma ray peaks similar to those reported earlier in Ref. [21] due to the inelastic scattering of 2.5 MeV neutrons from Br^{79} and Br^{81} in the $LaCeBr_3$ detector with energies predominantly below 1.6 MeV [21]. We expect a similar background spectrum from Ce and Br elements, common in both detectors, ours and the one used in Ref. [21]. The following gamma rays with energies of 542, 569, 664, 824, 846, 972, 1022, and 1133 keV from bromine as well as the 1347 keV gamma rays from cerium were observed and are shown in Fig. 3. Also shown in Fig. 3 are the background Fe peaks at 1627 keV and 1965 keV from the iron support table [22].

Next, the gamma ray spectrum was recorded for a pure soil sample. Figure 4 shows the pure soil sample spectrum superimposed upon the empty container background spectrum, showing the 1780 keV peak of Si [12] along with the

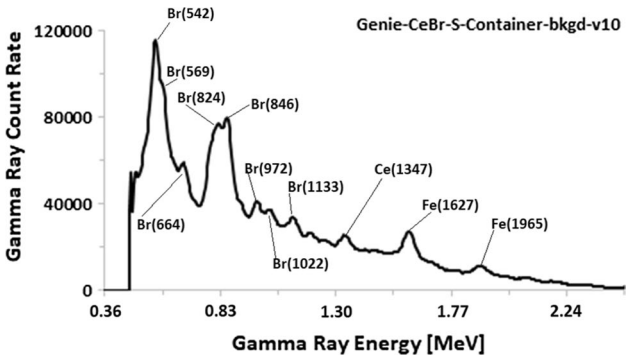

Fig. 3 Prompt gamma-rays pulse height spectrum from an empty sample container and a $CeBr_3$ detector

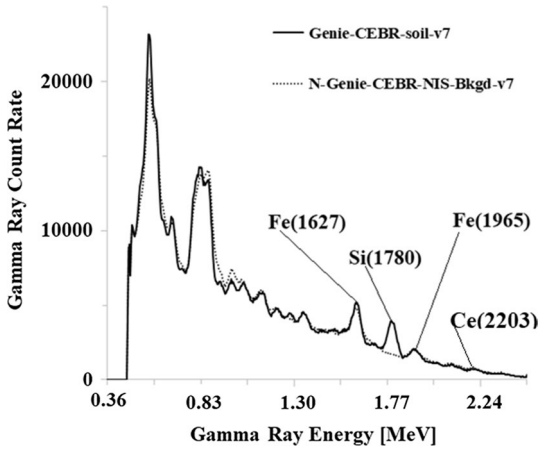

Fig. 4 Prompt gamma-rays pulse height spectrum from a pure soil sample superimposed upon the spectrum from an empty sample container

1627 keV and 1965 keV Fe peaks, as well the 2203 keV Ce peak. The peak at 2203 keV is due to cerium activation in the detector. There is no measurable difference in the superimposed spectra in Fig. 4 beyond the 1780 keV silicon peak. This excludes any measurable contribution from the 2020 keV gamma rays from Si-29 and 2200 keV gamma rays from Si-30 in the spectrum. This is due to their small natural abundances as well as small cross sections at 2.5 MeV neutron beam energy [23]. The pure soil spectrum is used for background subtraction from the sulfur-contaminated soil spectra.

All gamma rays detected in this study are listed in Table 1. The capture gamma ray intensities are given in terms of their partial elemental capture cross-sections taken from Ref. [22]. The bromine gamma rays due to NIS are taken from Ref. [20] which reports only relative intensities in arbitray units. The peak energies were identified from the Monte carlo-generated spectrum of Ref. [20]. The NIS cross sections for silicon and sulfur are given within parenthesis and are taken from Ref. [23] and Ref. [14], respectively. The intrinsic activity is mainly due to radioactive impurities from Actinium present in the raw materials of the $CeBr_3$ detector. The intensities of the intrinsic gamma rays depend on the detector size and the amount of actinium contamination.

Figure 5 shows the 2230 keV peak of sulfur from the contaminated soil sample containing 13.47 wt% sulfur. Also shown in Fig. 5 is the 1780 keV Si peak from the contaminated as well as pure soil samples. Since the masses of silicon in both pure soil and contaminated soil samples are almost equal, the silicon peaks in the two spectra overlap.

Table 1 List of gamma rays detected in the present study

Element	E_γ (keV)	$\sigma^Z_{E_\gamma}$ (*b*)
Br	542	0.114
	569	NIS
	664	NIS
	824	NIS
	846	0.0257
	972	NIS
	1022	0.0167
	1133	0.0110
Ce	1347	0.0028
	2203	0.0039
$CeBr_3$	1995	Intrinsic
	2100	Intrinsic
	2360	Intrinsic
Fe	1627	0.0100
	1965	0.0078
	2129	0.0206
Si	1780	NIS (0.400)
S	2230	NIS (0.175)

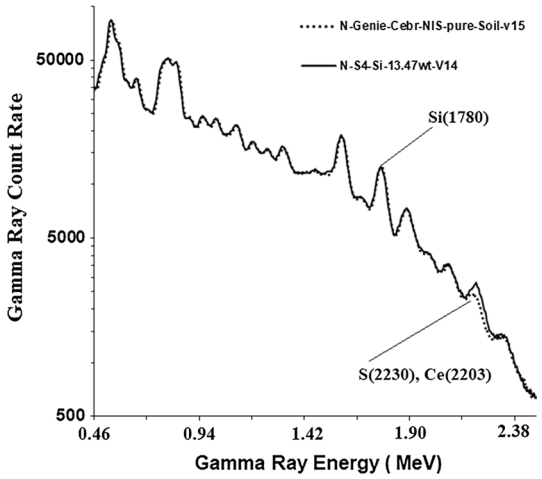

Fig. 5 Prompt gamma-rays pulse height spectrum of a soil sample contaminated with 13.47 wt% sulfur superimposed upon the pure soil background spectrum

The effect of sulfur contamination is quite prominent as can be seen from the difference between the sulfur peaks from pure soil background and sulfur-contaminated soil spectrum.

Results and discussion

Figure 6 shows normalized pulse height spectra from sulfur-contaminated soil samples containing 4.4, 7.1, 9.6 and 13.47 wt% sulfur superimposed upon the pure soil spectrum. The spectra were normalized to the same counting time and the same neutron flux using the beam current monitor of the neutron generator. As expected, the height of the 2230 keV

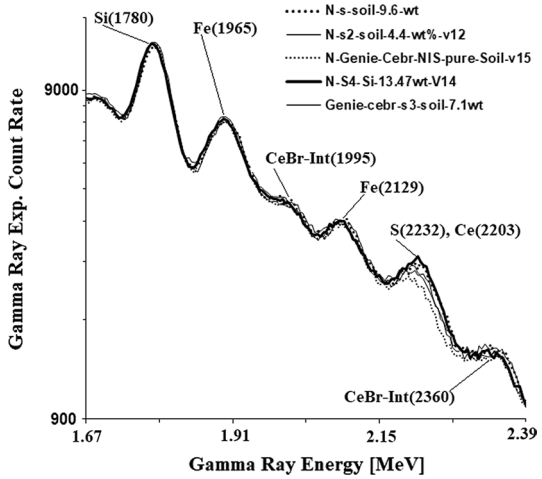

Fig. 6 Prompt gamma-rays pulse height spectra of soil samples contaminated with 4.4, 7.1, 9.6 and 13.47 wt% sulfur superimposed upon pure soil background spectrum

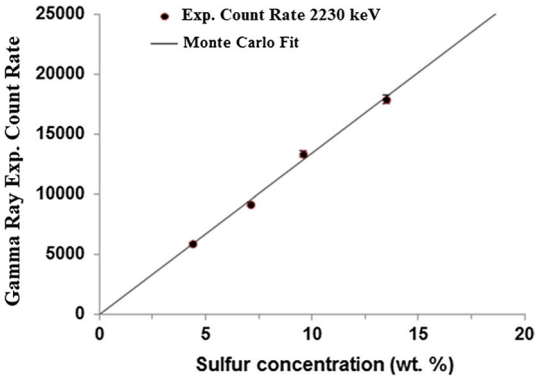

Fig. 7 Normalized net experimental count rate of 2230 keV prompt gamma rays from sulfur measured as a function of sulfur concentration in the contaminated soil samples. The solid line shows data from Monte Carlo calculations

peak from sulfur increases with sulfur concentration in the soil samples. Also shown in Fig. 6 are the 1780 keV Si peak, the 1965 keV and 2129 keV Fe peaks, as well as the 1995 keV and 2360 keV peaks due to the intrinsic activity of the the $CeBr_3$ detector.

The integrated count rates under the 2230 keV sulfur peak were then calculated by integrating the counts under the 2230 keV peaks for each of the five spectra shown in Fig. 6, including the pure soil background spectrum. Figures 7 shows the normalized net count rates from the four spectra of sulfur-contaminated soil samples as a function of sulfur elemental concentration after background subtraction. In Fig. 7 the net counts from the four contaminated samples are superimposed upon the calculated count rate derived from Monte Carlo calculations discussed earlier. There is an excellent agreement between the experimental and the calculated results.

Minimum detection limit of sulfur in soil samples

The minimum detectable concentration (MDC) of sulfur in sulfur-contaminated soil, and its standard deviation σ_{MDC}, were calculated for our setup using the equations [24]

$$\mathrm{MDC} = 4.653 \times [C/N] \times \sqrt{B} \quad \text{and} \quad \sigma_{\mathrm{MDC}} = [C/N] \times \sqrt{(2B)}$$

where C, concentration (wt%); N, net counts under peak, and B, background counts. The values of the concentration per unit counts (C/N) and background (B) were obtained from the data of Fig. 6. The $\mathrm{MDC} \pm \sigma_{\mathrm{MDC}}$ for the S(2230) peak using the $CeBr_3$ detector was 0.68 ± 0.21 wt%. The present MDC value is about one-fifth of the earlier reported value of 3.50 wt% using 3.2 MeV neutrons [12]. This difference might be partially accounted for by the 60% larger gamma ray production cross section for 2.5 MeV neutrons as compared to 3.29 MeV neutrons [14]. The remaining difference might be due to a higher 2.5 MeV neutron flux used in this study. The prompt gamma ray analysis technique using NIS of 2.5 MeV neutrons can also be extended to other elements of interest.

Conclusion

A PGNAA setup build around a GENIE 16 DD neutron generator was used for the determination of sulfur concentrations in specially prepared sulfur-contaminated soil samples using Neutron Inelastic Scattering of 2.5 MeV neutrons. The 2230 keV prompt gamma rays from sulfur were detected in a suitably shielded 76 cm × 76 cm cylindrical $CeBr_3$ detector. The sulfur concentrations ranged from 4.4 to 13.47 wt% and the $\mathrm{MDC} \pm \sigma_{\mathrm{MDC}}$ for sulfur was 0.68 ± 0.21 wt%. This represents a significant improvement upon the previously reported value of 3.5 wt% for 3.29 MeV neutrons.

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