

University of Zagreb FACULTY OF SCIENCE

Josip Batur

Development of neutron sensors for finding crude oil, methane hydrates and rare earth elements

DOCTORAL DISSERTATION

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Sveučilište u Zagrebu PRIRODOSLOVNO-MATEMATIČKI FAKULTET

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Razvoj neutronskih senzora za nalaženje sirove nafte, metan hidrata i elemenata rijetkih zemalja

DOKTORSKI RAD

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Dr. Davorin Sudac was born on November 27, 1968, in Karlovac, Croatia. He earned his degree in experimental physics from the Faculty of Science, University of Zagreb in 1997. He completed his MSc in 2003 with a thesis titled "Application of Fast Neutrons for Chemical Composition Analysis of Materials." He obtained his PhD in Nuclear Physics in 2007, defending the dissertation "Development of a System for Detecting Hazardous Materials Using Fast Neutrons."

Dr. Sudac has been employed at the Ruđer Bošković Institute (RBI), Department of Experimental Physics, since 1999. He was promoted to Research Associate in 2008 and Senior Research Associate in 2014. His research focuses on the application of 14 MeV neutrons in the detection of explosives, chemical agents, narcotics, and hazardous materials, as well as on the development of neutron-based sensors for cargo inspection, underwater detection of unexploded ordnance, and industrial applications of neutron techniques.

Currently, dr. Sudac is involved in the EU-funded project UnderSec, working on the development of the Concealed Material Identification Module (CMIM), a neutron-based device for the underwater detection of explosives and narcotics. He also serves as the National Counterpart for the IAEA project RER1023, focusing on radiotracer applications and environmental monitoring.

Dr. Sudac has published 79 scientific papers, with 69 indexed in CC, and has an h-index of 16 (WoS) and 18 (Scopus).

Dr. Ilker Meric was born on July 27, 1982, in Istanbul, Türkiye. He earned his BSc in physics from Yeditepe University and the University of Bergen (UiB), Norway, specializing in experimental physics and instrumentation. He completed his MSc (2008) and PhD (2012) at UiB, focusing on Monte Carlo (MC) modeling and nuclear methods for subsea fluid characterization.

Following his PhD, Dr. Meric held a postdoctoral position at UiB (2012–2016), working on MC modeling for high-speed gamma-ray tomography. In 2016, he was awarded funding from the Trond Mohn Foundation and Western Norway University of Applied Sciences (HVL) to develop a proton Computed Tomography (proton CT) system for improved proton therapy treatment planning. He then joined HVL as a researcher and research group leader.

In 2020, Dr. Meric became an Associate Professor at HVL and secured additional funding from the Research Council of Norway to develop an advanced imaging system for proton therapy range verification. In 2023, his collaborations led to the funding of the NOVO (Next Generation Imaging for Real-time Dose Verification Enabling Adaptive Proton Therapy) project through the European Innovation Council (EIC) Pathfinder Open program. Since March 2024, he has been managing the NOVO project, with HVL as the coordinating institution.

In addition to research, Dr. Meric teaches Control Systems Theory and Instrumentation and supervises BSc students at the Department of Computer Science, Electrical Engineering, and Mathematical Sciences at HVL.

Dr. Meric has published 75 scientific papers, conference proceedings, and reports, and holds a patent for the NOVO imaging system (Norway, Japan, USA). He has an h-index of 13 and an i10-index of 21.

Development of neutron sensors for finding crude oil, methane hydrates and rare earth elements

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This dissertation investigates the development and application of neutron-based sensors for detecting crude oil, methane hydrates, and rare earth elements (REEs) through experimental measurements and Monte Carlo simulations. The study explores the associated alpha particle (AAP) method and pulsed fast-thermal neutron activation (PFTNA) to determine detection limits and optimize background suppression.

A compact neutron probe was developed for C/O logging using AAP, significantly reducing background noise compared to fast neutron activation analysis (FNAA). The probe's spatial and temporal resolutions were determined as 10 cm and 2 ns, respectively, and its functionality was tested under high-temperature conditions. The PFTNA method was employed to determine the minimum detection limits (MDLs) for chlorine and water in crude oil, yielding (62 ± 6) mg/L and (2 ± 2) vol.

Methane hydrate detection was conducted using the AAP method in a submarinebased setup, yielding an MDL of (67 ± 25) vol.%, for one-hour measurements. The detection of REEs focused on gadolinium and lutetium, achieving MDLs of (12 ± 1) ppm and (3.8 ± 0.7) ppm, respectively. Monte Carlo simulations validated experimental results and optimized measurement conditions. The developed methodologies demonstrate the feasibility of neutron-based techniques for remote in-situ elemental detection, with future applications in autonomous underwater vehicles for deep-sea exploration.

(162 pages, 114 references, 103 figures, 16 tables, original in English)

Keywords: Neutron-based detection, Associated alpha particle method (AAP), Pulsed fast-thermal neutron activation (PFTNA), Monte Carlo simulations, Crude oil, Methane hydrate, Rare earth elements

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Metode neutronske analize omogućuju precizno određivanje elementarnog sastava različitih materijala, čime imaju široku primjenu u industriji, geologiji i fundamentalnoj fizici. Ova disertacija istražuje primjenu triju glavnih neutronskih metoda – Fast Neutron Activation Analysis (FNAA), Associated Alpha Particle (AAP) metode i Pulsed Fast-Thermal Neutron Activation (PFTNA) – u svrhu detekcije sirove nafte, metan hidrata i elemenata rijetkih zemalja. Eksperimentalni postavi razvijeni su za specifične scenarije karakterizacije uzoraka korištenjem neutronskog zračenja, dok su Monte Carlo simulacije provedene kako bi se optimizirala geometrija eksperimenta i bolje razumjeli eksperimentalni rezultati. Ova istraživanja predstavljaju doprinos razvoju tehnika zasnovanih na neutronima za daljinsku i in-situ karakterizaciju materijala u industrijskim i prirodnim okruženjima.

Motivacija

Precizna analiza elementarnog sastava materijala ključna je u brojnim znanstvenim i industrijskim primjenama, osobito u energetskom sektoru i rudarstvu. Pronalaženje novih izvora energije i strateških materijala postaje sve važnije zbog rastuće globalne potražnje, dok istovremeno zahtijeva pouzdane i neinvazivne metode analize.

Sirova nafta ostaje jedan od primarnih izvora energije, a njena kvalitativna i kvantitativna analiza igra ključnu ulogu u optimizaciji proizvodnje. Omjer ugljika i kisika (C/O) jedan je od ključnih parametara pri određivanju sastava naftnih ležišta, jer omogućuje diferencijaciju nafte od vode u ležištima. Također, važna stavka istraživanja u naftnim nalazištima je i procjena količine mineralnih soli i vode u sirovoj nafti, spojeva koji uzrokuju pogoršanje kakvoće nafte, začepljenja cijevi i slično. Tradicionalne metode analize često su ograničene složenim geološkim uvjetima i niskom prostornom rezolucijom, zbog čega postoji potreba za razvojem učinkovitijih metoda koje mogu smanjiti nesigurnosti u određivanju sastava ležišta.

Metan hidrat, kristalni spoj u kojem su molekule metana zarobljene unutar kristalne rešetke leda, smatra se jednim od najvećih potencijalnih izvora prirodnog plina na Zemlji. Njegova detekcija i kvantifikacija predstavljaju izazov jer se uglavnom nalazi na velikim oceanskim dubinama, često unutar složenih sedimentnih formacija bogatih raznim spojevima. Učinkovita eksploatacija metan hidrata mogla bi značajno utjecati na globalno energetsko tržište, no prije nego što se razviju održive metode vađenja, nužno je uspostaviti pouzdane tehnike detekcije koje omogućuju precizno određivanje njegove zasićenosti u sedimentima na morskom dnu. Osim energetske važnosti, metan hidrat igra ključnu ulogu u klimatskim procesima, budući da njegovo oslobađanje može pridonijeti globalnom zatopljenju, što dodatno naglašava potrebu za preciznim praćenjem njegovih količina i distribucije.

Elementi rijetkih zemalja (ERZ) ključni su za suvremenu industriju, posebice u proizvodnji elektroničkih uređaja, magnetskih materijala, katalizatora i drugih visokotehnoloških proizvoda. Njihovo iskopavanje i prerada predstavljaju izazov zbog raspršenosti u prirodi i geokemijske sličnosti s drugim elementima, što otežava njihovu selektivnu ekstrakciju. Poseban problem predstavlja detekcija gadolinija i lutecija, budući da njihova koncentracija u rudama na oceanskom dnu izravno korelira s ukupnom količinom ERZ-a u tim naslagama, ali su prisutni u vrlo malim količinama. Razvoj preciznih analitičkih metoda ključno je za bolje razumijevanje njihovog prostornog rasporeda te povećanje učinkovitosti njihovog iskorištavanja.

Sve navedene primjene zahtijevaju napredne analitičke tehnike koje omogućuju brzu, neinvazivnu i preciznu detekciju elemenata u različitim kompleksnim okruženjima. Neutronske metode pokazuju veliki potencijal u tom kontekstu, ali je potrebno dodatno istražiti njihovu učinkovitost, optimizirati eksperimentalne uvjete i smanjiti utjecaj pozadinskog šuma kako bi se osigurala njihova pouzdanost u terenskim uvjetima.

Neutronske metode

Tri glavne neutronske metode korištene u ovom radu su Fast Neutron Activation Analysis (FNAA), Associated Alpha Particle (AAP) metoda i Pulsed Fast-Thermal Neutron Activation (PFTNA). Svaka od ovih metoda koristi interakcije neutrona s atomskim jezgrama za generiranje karakterističnih gama zraka koje omogućuju identifikaciju elemenata u uzorcima.

FNAA metoda, korištena u određivanju C/O omjera, temelji se na interakciji brzih neutrona, proizvedenih u D-T (deuterij-tricij) ili D-D (deuterij-deuterij) fuzijskim reakcijama, s atomskim jezgrama u uzorku. Brzi neutroni se sudaraju s jezgrama putem neelastičnog raspršenja, pri čemu dolazi do pobuđenja jezgre i emisije promptnih gama zraka specifičnih za elemente prisutne u materijalu. Iako je FNAA korisna zbog svoje brzine i preciznosti, metoda pati od visokog pozadinskog šuma zbog složenih gama spektara koji nastaju višestrukim interakcijama neutrona s okolinom. Zato je često potrebna dodatna optimizacija signala i primjena sofisticiranih tehnika analize kako bi se izvukli korisni podaci.

AAP metoda, korištena u određivanju C/O omjera i detekciji metan hidrata, koristi povezane alfa čestice i gama zrake za poboljšanje preciznosti elementarne analize. Ova metoda se oslanja na D-T reakciju, u kojoj fuzija deuterija i tricija proizvodi 14 MeV neutrone i alfa česticu u suprotnom smjeru. Detekcijom alfa čestice moguće je točno kolimirati neutronski snop, čime se značajno smanjuje pozadinski šum i omogućuje selektivna analiza interakcija neutrona s ciljnim metama. Kada se 14 MeV neutroni sudare s atomima u uzorku, nastaju promptne gama zrake specifične za određene elemente, koje se detektiraju gama detektorom. Prednost AAP metode leži u visokoj osjetljivosti i mogućnosti izolacije signala, čime se omogućuje točnija identifikacija elemenata čak i u složenim geološkim uvjetima ili visoko pozadinskim okruženjima.

PFTNA metoda kombinira pulsirajuće izvore brzih neutrona s detekcijom gama zraka nastalih kao rezultat dvaju ključnih procesa: neelastičnog raspršenja i termalnog hvatanja neutrona. Brzi neutroni proizvedeni D-T reakcijom inicijalno uzrokuju emisiju promptnih gama zraka kroz neelastično raspršenje na atomima uzorka, dok se u vremenu između pulseva mjeri emisija odgođenih gama zraka koje nastaju nakon što se neutroni termaliziraju i bivaju uhvaćeni od strane jezgara. Ova tehnika se pokazala korisnom u određivanju koncentracija klora i vode u sirovoj nafti, gdje je mjerenje zaostali gama zraka između neutronskih pulseva omogućilo razdvajanje signala specifičnih za pojedine elemente.

PFTNA metoda je također korištena u detekciji gadolinija, gdje su brzi neutroni termalizirani u uzorku, a zatim uhvaćeni od strane gadolinijevih jezgara, što rezultira emisijom gama zraka specifičnih za ovaj element. Detekcija tih gama zraka između neutronskih pulseva omogućila je kvantifikaciju gadolinija čak i pri niskim koncentracijama, čime se metoda pokazala korisnom za analizu rijetkih zemnih elemenata u sedimentima oceanskog dna.

Eksperimentalni postavi i procedure

U prvoj fazi eksperimenta za detekciju sirove nafte korišten je API-120 D-T generator koji proizvodi 14 MeV neutrone, s ciljem usporedbe FNAA i AAP metoda u analizi omjera ugljika i kisika (C/O). U eksperimentalnom postavu, neutronski snop bio je usmjeren na mete sastavljene od kvarcnog pijeska pomiješanog s različitim udjelima grafita, dok su bočice s dizel uljem korištene kao izvor neželjene pozadine. Detekcija promptnih gama zraka nastalih neelastičnim raspršenjem neutrona provedena je pomoću LaBr₃:Ce detektora, dok je za detekciju alfa čestica korišten YAP:Ce scintilator. Dobiveni gama spektri analizirani su prilagođavanjem modela putem minimizacije χ^2 funkcije, pri čemu je pretpostavljeno da se ukupni spektralni odgovor može prikazati kao linearna kombinacija spektara pojedinih kemijskih elemenata prisutnih u uzorku. Izračunati C/O omjeri prikazani su na kalibracijskim pravcima u odnosu na stvarne vrijednosti korištene u eksperimentu. Na kraju, uspoređeni su kalibracijski pravci dobiveni FNAA i AAP metodom, uz analizu razlike u detekciji između slučajeva s prisutnim izvorom pozadinskog šuma i onih bez njega.

Nakon što je potvrđeno da AAP metoda značajno smanjuje šum u određivanju C/O omjera u usporedbi s FNAA metodom, razvijena je kompaktna neutronska proba, koja se razlikuje od prvotne postave po tome što su gama detektor, alfa detektor, tricijeva meta i pripadni fotomultiplikatori smješteni unutar istog kućišta probe. Kao izvor neutrona korišten je Texas Nuclear Corporation (TNC) neutronski generator, koji omogućuje rad u pulsnom režimu. Nakon što je smanjenje šuma primjenom AAP metode pokazano i s ovom probom, uređaj je testiran u visokotemperaturnim uvjetima sličnim onima koji vladaju u naftnim bušotinama. Visokotemperaturni uvjeti su simulirani omatanjem ISOPAD grijaće vrpce oko kućišta probe na mjestima gdje su smješteni detektori. Pri različitim temperaturama, vremenska rezolucija probe ispitivana je iradijacijom grafitnih blokova postavljenih na dvije različite lokacije, dok je energetska rezolucija analizirana širinom vrha 1.436 MeV gama zrake (raspad ¹³⁸La) pri različitim temperaturama. Nakon konstrukcije neutronske probe, ista je korištena za mjerenje koncentracije klora i vode u sirovoj nafti. Kao mete su korišteni uzorci dizel ulja s paketićima kuhinjske soli različitih masa za simulaciju klora te emulzije dizela i vode u različitim omjerima za ispitivanje sadržaja vode. Prilikom detekcije klora i vode, neutronski izvor radio je pri različitim frekvencijama, dok su gama zrake skupljane u periodima između dva neutronska pulsa. Za identifikaciju klora korištena je promptna gama zraka energije 6,11 MeV, nastala termalnim hvatanjem neutrona na ³⁵Cl, dok je zakašnjela gama zraka energije 6,13 MeV, produkt aktivacijske reakcije ¹⁶O(n,p)¹⁶N, korištena za određivanje prisutnosti vode u dizelu. Za detekciju gama zraka korišten je BaF₂ detektor, dok su neutroni termalizirani pomoću parafinskog moderatora. Dobiveni gama spektri analizirani su χ^2 prilagodbom, nakon čega su konstruirane kalibracijske krivulje koje prikazuju odnos između izmjerene i stvarne koncentracije klora te između izmjerene i stvarne količine vode u uzorcima. Tako dobivene kalibracijske krivulje korištene su za izračunavanje minimalnog detekcijskog limita (MDL) klora i vode u nafti, omogućujući preciznu procjenu osjetljivosti metode.

Prilikom detekcije metan hidrata, korišten je API-120 neutronski generator, koji je, zajedno s pripadajućim detektorima (LaBr₃:Ce i YAP:Ce) te ostalom elektronikom, smješten unutar tipične podmornice kako bi se simulirali realni uvjeti primjene ove metode. Kao uzorci korišteni su mješavine kvarcnog pijeska s različitim volumnim zasićenjima simulantom metan hidrata, pri čemu je simulant izrađen miješanjem vode i šećera saharoze. Mjerenja su provedena AAP tehnikom, gdje je reakcija od interesa bila inelastično raspršenje neutrona na ugljiku ¹²C(n,n')¹²C, prisutnom u suvišku u simulantu metan hidrata, pri čemu kao produkt nastaje promptna gama zraka energije 4.44 MeV. Analiza spektra provedena je usporedbom broja događaja u ugljičnom prozoru gama spektra za različite uzorke zasićenja metan hidratom. Na temelju ovih podataka konstruiran je kalibracijski pravac, koji povezuje neto broj događaja u ugljičnom prozoru sa volumnim zasićenjem metan hidrata u kvarcnom pijesku. Pomoću ovog pravca izračunata je i minimalna detekcijska granica (MDL) za metan hidrat u simuliranim uvjetima.

Prilikom mjerenja gadolinija, kao mete su korišteni mokri i suhi uzorci kvarcnog pijeska s različitim količinama Gd_2O_3 . Budući da gadolinij posjeduje najveći udarni presjek za hvatanje termalnih neutrona, bio je pogodan za analizu PFTNA metodom. Kao generator neutrona korišten je TNC, dok je za detekciju gama zraka korišten BGO detektor. Termalizacija 14 MeV neutrona postignuta je korištenjem blokova parafina. Spektri su analizirani usporedbom broja događaja u tri različita energetska prozora, nakon čega su konstruirane kalibracijske krivulje, koje povezuju neto broj događaja u svakom od tih prozora s količinom Gd₂O₃. Pomoću tih krivulja izračunata je minimalna detekcijska granica (MDL). Lutecij je detektiran pasivnom metodom, koristeći dvije karakteristične gama zrake, pri 202 keV i 306 keV, koje su produkt prirodnog raspada ¹⁷⁶Lu. Mete su se sastojale od kvarcnog pijeska s različitim primjesama Lu₂O₃, dok je kao gama detektor korišten HPGe poluvodički detektor, okružen prethodno dizajniranim olovnim štitom. Spektri su analizirani metodom χ^2 prilagodbe, nakon čega su izrađene kalibracijske krivulje, koje povezuju izmjerenu i stvarnu količinu lutecija, te je na temelju njih izračunata minimalna detekcijska granica (MDL).

Monte Carlo simulacije

Monte Carlo simulacije korištene su u ovom radu za optimizaciju eksperimentalnih postava, procjenu detekcijskih granica te analizu distribucije neutrona i gama zraka unutar sustava. Simulacije su provedene pomoću MCNP6.2 koda, koji omogućuje modeliranje interakcija neutrona i gama zraka s materijalima na temelju stohastičkih metoda. U svim simulacijama provedenim u ovom radu, eksperimentalna geometrija je pojednostavljena, tako da sadrži samo ključne komponente; mete od interesa, detektore, izvor neutrona, te veće izvore pozadinskih smetnji.

U poglavlju o detekciji sirove nafte, Monte Carlo simulacije korištene su za modeliranje interakcija 14 MeV neutrona s metama koje su sadržavale ugljik, kisik, vodu i klor. Simulacije su provedene kako bi se omogućila usporedba AAP i FNAA metoda, pri čemu je za generiranje spektra korištena **f8** opcija, koja prati energiju i broj gama zraka koje talože energiju unutar definiranog volumena, simulirajući tako odgovor detektora.

U simuliranim spektrima, C/O omjer određen je odnosom broja događaja u 4.44 MeV vrhu ugljika i 6.13 MeV vrhu kisika. Simulacije su korištene i pri utvrđivanju vremenske i prostorne rezolucije neutronske probe, gdje je korištena vremenska T kartica u paru sa f8 i f4 karticama, kako bi se simulirao vremenski odziv detektora. Dodatno, pri analizi detekcije klora u sirovoj nafti, modeliran je sustav u kojem je klor homogeno raspoređen unutar dizel ulja, što eksperimentalno nije bilo izvedivo. Simulacije su omogućile

usporedbu slučajeva homogene i nehomogene raspodjele klora, pružajući uvid u utjecaj raspodjele elementa na detekcijsku osjetljivost metode.

U detekciji metan hidrata, simulirana geometrija obuhvaćala je izvor neutrona, metu, željezno postolje, detektor i podmornicu. Točkasti izvor neutrona emitirao je 14 MeV neutrone u stožastom snopu, simulirajući uvjete AAP metode. Simulacija spektra provodila se u dva koraka. U prvom koraku, **f4** opcija korištena je za prikupljanje fluksa gama zraka unutar simuliranog detektora. U drugom koraku, tako dobiveni fluks korišten je kao histogram distribucije izvora fotona, koji su zatim usmjereni prema detektoru, gdje je pomoću **f8** opcije prikupljen pulsni odziv detektora i generiran konačni spektralni odziv. Ovaj postupak korišten je za smanjenje statističkih nepouzdanosti simulacijskih rezultata. Dodatno, primijenjeno je Gaussovo energetsko proširenje (GEB), čiji su parametri određeni iz eksperimentalnih podataka. Ovim postupkom omogućena je bolja usporedba eksperimentalnih i simuliranih spektara.

U poglavlju o detekciji elemenata rijetkih zemalja (ERZ), Monte Carlo simulacije korištene su za optimizaciju zaštite detektora, modeliranjem olovnog štita oko HPGe detektora kako bi se smanjio utjecaj pozadinskih gama zraka tijekom pasivne detekcije lutecija. U simulacijama su testirani olovni štitovi različitih debljina, s ciljem određivanja optimalne konfiguracije zaštite. Kao izvor gama zraka, korišten je eksperimentalno izmjeren spektar cezija (bez štita), koji je u simulacijama poslužio kao histogramska distribucija izvora fotona. Ti fotoni su potom propagirani kroz olovne štitove različitih debljina, kako bi se analizirala njihova učinkovitost u prigušivanju pozadinskog zračenja. Simulirani spektri proizvedeni su korištenjem **f4** opcije, kojom je praćen fluks gama zraka nakon prolaska kroz štit. Za procjenu učinkovitosti zaštite, uspoređivan je broj događaja u 662 keV vrhu cezija između različitih debljina olovnog štita.

Rezultati

U slučaju detekcije sirove nafte, razvijena je kompaktna neutronska proba s integriranim alfa i gama detektorima, što je omogućilo primjenu AAP metode za određivanje C/O omjera. Eksperimentalni rezultati pokazali su da AAP metoda značajno smanjuje pozadinski šum u odnosu na FNAA, omogućujući točniju detekciju ugljika i kisika, što je potvrđeno i MC simulacijama. Daljnja ispitivanja pokazala su da je proba zadržala funkcionalnost čak i u uvjetima visokih temperatura, iako je zabilježeno smanjenje amplitude signala gama detektora za 60% pri 160°C, dok se energetska rezolucija na 1.436 MeV pogoršala s 6,5% na 12%. Utvrđene su vremenska i prostorna rezolucija neutronske probe od 2 ns, te 10 cm, što je potvrđeno i MC simulacijama.

Korištenjem PFTNA metode ispitana je mogućnost određivanja koncentracija klora i vode u sirovoj nafti. Utvrđeno je da je MDL za klor iznosi (62 ± 6) mg/L, što je unutar zahtjeva za izvoz sirove nafte koji propisuju sadržaj klora manji od 50 mg/L. Za vodu je određena MDL vrijednost od (2 ± 2) vol.%, no relativna nesigurnost ovog rezultata bila je visoka zbog teškoća u izradi emulzija s niskim sadržajem vode. MC simulacije sugerirale su da homogena raspodjela klora u sirovoj nafti, kakva se može očekivati u realnim uvjetima, može dovesti do neželjenog povećanja MDL-a. Simulacijski rezultati ukazuju da se ovaj problem može ublažiti optimizacijom raspodjele termalnih neutrona u meti, tako da bude izotropna, umjesto anizotropne raspodjele prisutne u eksperimentalnom postavu.

Kalibracijska krivulja između zasićenja metan hidrata i neto broja događaja u ugljičnom prozoru je uspostavljena, pri čemu je eksperimentalno određen MDL iznosio $(67 \pm 25)\%$. Velika relativna pogreška u rezultatu proizlazi iz malog broja točaka u kalibracijskom pravcu, što ograničava preciznost mjerenja. Povećanjem broja točaka poboljšala bi se točnost rezultata i smanjila nesigurnost. Srednja vrijednost MDL-a upućuje na to da ova metoda nije primjenjiva čak ni na nalazištima s visokim zasićenjem metan hidrata, poput onih na Aljasci, gdje saturacija doseže do 54%. Također, vrijedi napomenuti kako je jedno od ograničenja eksperimentalnog postava bilo to što su mjerenja provedena u zraku, dok bi prisutnost vode u stvarnim uvjetima dovela do termalizacije neutrona, smanjujući broj onih koji sudjeluju u neelastičnom raspršenju na ugljiku. Buduća istraživanja trebala bi se usmjeriti na jače izvore neutrona, koji bi mogli kompenzirati ovaj gubitak i dodatno sniziti MDL, kao i na provođenje eksperimenata u realističnijim uvjetima, koji bolje oponašaju podmorska nalazišta. Monte Carlo simulacije korištene su za usporedbu kalibracijskih pravaca i razvoj simulacijskog modela, koji bi, uz odgovarajuće korekcije, mogao služiti za predviđanje ishoda mjerenja i optimizaciju eksperimentalnih uvjeta. Ovaj model bio bi posebno koristan pri pripremi postava za daljinska in-situ mjerenja na oceanskom dnu. Simulacije su pokazale značajnu razliku u nagibu kalibracijskog pravca u odnosu na eksperimentalne podatke, što se uglavnom pripisuje nemogućnosti da se potpuno precizno simulira sastav materijala i geometrija eksperimentalnog postava.

Rezultati detekcije gadolinija pokazali su da se PFTNA tehnika može pouzdano koristiti za detekciju gadolinija čak i u niskim koncentracijama, pri čemu je eksperimentalno određena minimalna detekcijska granica (MDL) od (12 ± 1) ppm u gama-energetskom rasponu 2.55–3.3 MeV. Ova razina osjetljivosti dovoljna je za identifikaciju koncentracija gadolinija u sedimentima Tihog (68 ± 2 ppm) i Indijskog oceana (39 ± 2 ppm).

Pri detekciji lutecija, Monte Carlo simulacije pokazale su značajno smanjenje pozadinskog gama zračenja u germanijskom detektoru pri debljini olovnog štita od 5cm, što je maksimalna debljina koju smo mogli postići eksperimentalno, pa je aktivni dio HPGe detektora bio okružen s 5 cm olovnog štita. Eksperimentalno je određena MDL vrijednost od $(3.8 \pm 0.7 \text{ ppm})$ nakon 50-satnog mjerenja, što je dovoljno za detekciju lutecija u Tihom oceanu $(6.0 \pm 0.3 \text{ ppm})$, ali više od koncentracija u Indijskom oceanu $(2.55 \pm 0.29 \text{ ppm})$, za koje bi bilo potrebno produžiti vrijeme mjerenja kako bi se postigla ista razina pouzdanosti. Smanjenje vremena mjerenja, a da MDL ostane isti, moglo bi se postići korištenjem većeg broja detektora u eksperimentu. Buduće istraživanje usmjerit će se na razvoj kompaktnog senzora koji bi se mogao integrirati unutar malog daljinski upravljanog vozila, omogućujući in-situ detekciju gadolinija na oceanskom dnu.

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Introduction

The neutron is a chargeless subatomic particle which is, alongside protons, found in the atomic nuclei. It has a mass slightly greater than that of a proton, and it plays a role in a stability of the atom. Neutrons were first discovered in 1932 by British physicist James Chadwick, whose experiments involved bombarding a beryllium target with alpha particles from the radioactive decay of polonium. These experiments resulted in the emission of charge-neutral radiation that was capable of ejecting protons from a paraffin target. By demonstrating that this neutral radiation consisted of uncharged particles with a mass similar to that of a proton, Chadwick identified the neutron and confirmed the existence of a new type of particle. The neutral charge of neutrons allows them to interact directly with atomic nuclei without being influenced by electric fields, making them convenient for elemental analysis of materials. The neutron-based methods have been studied for many years in various industrial applications where the knowledge of the elemental composition is of interest.

In the oil industry, neutron logging is a valuable tool used to measure the content and distribution of hydrocarbons within oil wells. This method involves analyzing the carbon-to-oxygen ratio of the oil field formations [1–3], which provides insights into the levels of crude oil and water saturation. Operators can make informed decisions about drilling, production, and reservoir management by accurately determining these levels. Neutron logging thus plays a crucial role in optimizing extraction processes, reducing operational costs, and increasing the overall efficiency of oil recovery. Further discussion on neutron applications in oil industry will be provided later in the work.

For the coal industry, neutron-based analysis is crucial for assessing the sulfur and moisture content in coal, as well as the unburnt carbon in coal ash [4], which significantly affects the quality and energy output of coal. In security and customs operations, neutron-based methods are employed to detect contraband materials, including explosives and narcotics [5, 6], chemical warfare [7] and nuclear substances [8]. The penetrating power of neutrons enables the inspection of sealed containers and packages without needing to open them, which is essential for maintaining security and operational efficiency at borders and checkpoints. For instance, the ability to detect nitrogen, oxygen, hydrogen, and carbon [9], common elements in majority of explosives, helps in identifying potential threats.

In the medical field, neutron-based techniques provide innovative solutions for analyzing biological tissues and medical samples. Neutron activation analysis is used in assessing the amounts of trace elements in biological samples [10]. This approach can potentially reveal important information about someone's nutritional status, exposure to environmental toxins, and the presence of biomarkers associated with diseases. Neutron imaging is used to determine the internal structure of tissues non-destructively. This application is valuable for diagnostics, research, and treatment planning, and can offer insights into bone structure [11], tumor presence [12], and other critical health parameters. Also, neutrons find applications in the treatment of cancer, e.g. boron neutron capture therapy (BNCT) [13].

Materials science benefits greatly from neutron analysis, which is used to investigate the internal structures and stress distributions in metals and alloys. Neutron diffraction and scattering techniques can reveal details about the crystal structure [14], phase composition [15], and residual stresses [16] within materials. This information is important for understanding material properties, which influences the design and performance of engineering components and structures.

Environmental science leverages neutron methods to study soil composition and pollution levels. Fast neutron activation analysis, for example, is used to measure zinc and copper contamination levels in soil [17], which is important in the prevention of toxic exposure. This application helps in monitoring and protecting natural resources and assessing the impact of human activities on the environment.

1.1 Neutron production

There are several different mechanisms for the production of neutrons. Firstly, there is spontaneous fission of heavy nuclei. Unlike lighter isotopes, heavy transuranic isotopes can overcome large potential barriers and spontaneously decay into two lighter fission fragments, producing several high-energy neutrons in the process. For instance, a widely used radioactive source of neutrons, 252 Cf, with a half-life of 2.65 years produces, on average, 3.77 neutrons per fission event. One μ g of this isotope produces around $2.3 \cdot 10^6$ neutrons per second with an average energy of 2.1 MeV [18].

Considering that many convenient high-energy alpha and gamma emitters are available, another possibility is to mix an alpha or gamma emitter with an appropriate target material. For instance, the mixture of alpha emitter ²⁴¹Am (half-life 458 yrs) and ⁹Be produces neutrons in the $\frac{4}{2}\alpha + \frac{9}{4}$ Be \rightarrow_6^{12} C $+_0^1$ n + 5.71MeV nuclear reaction. Furthermore, mixing some gamma-ray emitters, such as ²²⁶Ra, ¹⁴⁰La and ¹²⁴Sb with ⁹Be and ²H results in the photoneutron nuclear reactions $\frac{9}{4}$ Be $+\gamma \rightarrow_4^8$ Be $+_0^1$ n - 1.666 MeV and $^{2}_{1}$ H + $\gamma \rightarrow_1^1$ H + $^{1}_{0}$ n - 2.226 MeV.

However, there are several downsides to these isotope-based systems. Firstly, the maximum available flux is relatively low. On average, only about 1 alpha particle in 10^4 and 1 gamma-ray in 10^5 or 10^6 interact to produce a neutron [18]. In addition to posing health hazards, purchase prices and disposal costs of such sources are quite high. Moreover, isotope-based sources cannot be pulsed, which deems these sources impractical for pulsed fast neutron activation analysis (PFNAA) or pulsed fast thermal neutron activation analysis (PFTNA) methods.

A good way to bypass these issues is to use neutron generators (small particle accelerators), which produce much smaller amounts of disposable radioactive waste, have a pulse creation capability, and cease to emit radiation when power is switched off. In these generators, accelerated deuterons interact with either deuterium target through D-D reaction ${}_{1}^{2}H + {}_{1}^{2}H \rightarrow {}_{2}^{3}He + {}_{0}^{1}n + 3.26$ MeV or the tritium target through the D-T reaction ${}_{1}^{2}H + {}_{1}^{3}H \rightarrow {}_{2}^{4}He + {}_{0}^{1}n + 17.6$ MeV. The former reaction produces 2.5 MeV neutrons, while the latter, used for neutron production in this work, produces 14 MeV neutrons. Table 1.1 shows the cross-sections for each reaction as a function of the deuteron projectile energy. The cross-section for ${}^{3}H(d,n){}^{4}He$ peaks in the 100-125 keV range. Additionally,

Deuteron energy (keV)	3 H(d,n) ⁴ He (mb)	$^{2}\mathrm{H}(\mathrm{d,p})^{3}\mathrm{H}\ (\mathrm{mb})$	$^{2}\mathrm{H}(\mathrm{d,n})^{3}\mathrm{He}\ \mathrm{(mb)}$	
25	125	0.7	0.707	
50	1400	4.3	4.56	
75	3250	10.1	11.11	
100	4350	16.5	17.8	
125	4650	21.6	23.7	
150	4150	25.6	29.1	
175	3400	29.1	34.0	
200	2725	32.3	38.4	
225	2150	35.2	42.4	

Table 1.1: cross-sections for several nuclear reactions.[19]

D-D reactions produce neutron yields about two orders of magnitude smaller than D-T reactions, making tritium targets more suitable for generating high-flux neutron sources $(>10^{11} \text{ n/s})$. However, as a result of tritium decay (with a half-life of 12.3 years) and the continuous bombardment of deuterons into the tritium target, additional reactions [20] that contaminate alpha flux measurements may occur: ³He(d,p)⁴He, ²H(d,p)³H and ²H(d,n)³He with a Q-values of 18.35 MeV, 4.03 MeV and 3.27 MeV, respectively. Alpha particles produced in the first additional reaction have energies comparable to that of the alphas produced in the initial D-T reaction, so a high-resolution detector is needed to tell them apart.

1.2 Neutron interactions and energy classification

Neutrons, having no charge, interact with matter through physical collisions with target nuclei. When neutrons encounter a nucleus, they can either scatter off the nucleus or combine with it and the likelihood of different types of interactions depends on two primary factors: neutron energy and the identity of target nucleus. A cross-section σ , measured in barns (10^{-24} cm²), is a measure that quantifies the probability of a specific type of reaction occurring. The probability that any type of interaction will take place is called total cross-section and it is equal to the sum of the cross-sections of all the different interactions that can take place:

$$\sigma_{\text{total}} = \sigma_{\text{elastic}} + \sigma_{\text{inelastic}} + \sigma_{\text{capture}} + \sigma_{\text{fission}} + \dots \tag{1.1}$$

The principal interaction between slow neutrons and the target nucleus is elastic scattering (n,n), in which the total kinetic energy of the target nucleus and neutron remains the same before and after the collision. During this scattering process, neutron transfers a part of its energy to the recoiling nucleus, while the internal state of the nucleus remains the same. The maximum energy that the incident neutron of energy E_n transfers to the target nucleus of atomic weight A is given by [21]:

$$E_{\max} = \frac{4A}{(1+A)^2} E_n$$
 (1.2)

This equation shows that neutrons transfer more energy to lighter nuclei, which is why hydrogen-rich compounds, such as water or paraffin wax, are used as moderators (e.g. water or heavy water in nuclear reactors). Through repeated elastic scatterings as it passes through matter, the neutron gradually loses energy and is slowed down, or moderated, until it reaches an energy level corresponding to the thermal energy of its surroundings. At this point, the neutron's speed distribution can be described by the Maxwell-Boltzmann distribution:

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)$$
(1.3)

This distribution indicates that the neutron's speed is now most likely near the most probable speed:

$$v_{\rm mp} = \sqrt{\frac{2k_BT}{m}} \tag{1.4}$$

Plugging T = 293 K into the equation (1.3) and calculating $\frac{mv_{\rm mp}^2}{2}$ yields the most probable neutron energy at the thermal equilibrium $E_{\rm th} \approx 0.025$ eV. Using this value as our starting point, we can classify neutrons according to energy [22] as:

- Thermal (0.025 eV)
- Epithermal (0.025 0.4 eV)
- Cadmium (0.4 0.6 eV)
- Epicadmium (0.6 1.0 eV)
- Slow (1.0 10.0 eV)
- Resonance (10.0 300.0 eV)
- Intermediate (300 eV 1 MeV)
- Fast (1-20 MeV)

Energy range, known as epithermal, is characterized by neutrons with more energy than those in the thermal range. The upper limit of this range, set at 0.4 eV, is determined by the neutron capture reaction involving ¹¹³Cd. This isotope has a high neutron absorption cross-section below approximately 0.5 eV (cadmium cutoff), which decreases sharply as energy rises. The absorption cross-section for ¹¹³Cd reaches a peak of about 55,000 [23] barns at 0.17 eV. At 0.5 eV, it decreases to 1,100 barns. Cadmium is chosen for these measurements over other elements or isotopes due to its widespread use as a selective neutron absorber. Its significant low-energy cross-section, lack of resonances until 18 eV, and rapid decrease in absorption as energy increases make it ideal for separating low-energy neutrons (below 0.5 eV) from higher-energy ones. The energy range between 0.4 and 0.6 eV is termed the cadmium range. Energies up to 1.0 eV are classified as epicadmium. At 1 eV, the absorption cross-section for ¹¹³Cd drops to 120 barns, a decrease of one order of magnitude, despite only a small increase in neutron energy from 0.5 to 1 eV.

In addition to elastic scattering, neutrons with energies below 10 eV undergo neutron capture reactions (n,γ) with nuclei. Generally, the likelihood of a capture reaction is proportional to the time a neutron spends near the nucleus, which is inversely proportional to the relative speed between the neutron and the nucleus. When a neutron is captured by a nucleus, it forms a compound in an excited state, which typically de-excites by emitting one or more characteristic gamma rays. The energies of those gamma rays correspond to the energy differences between excited and deexcited states, with the small correction to account for the recoil of the nucleus. This process is crucial for many neutron techniques discussed in the later section. In this work, it was used for hydrogen, chlorine and gadolinium detection.

Between approximately 10 and 300 eV, many nuclei display numerous resonances, often spaced less than 1 eV apart. Due to this, neutrons within this energy range are known as resonance neutrons. However, nuclear resonances can extend up to several keV, making the upper limit for resonance neutrons somewhat ambiguous. Typically, nuclear resonances from a few eV to a few keV are spaced far enough apart to be individually identified. Beyond a few keV, the spacing between resonances usually decreases, making it difficult or impossible to resolve them, even if they are distinct. The energy range from the beginning of resonances (usually a few eV) to the point where they can no longer be resolved is referred to as the resolved resonance region. The range above this, where resonances are too closely spaced to be distinguished experimentally, leading to an averaged smooth cross-section, is known as the unresolved resonance region. Example can be seen in the neutron capture cross-section for 157 Gd (Figure 1.1)



Figure 1.1: ¹⁵⁷Gd neutron capture cross-section. Resolved resonances appear in the $\approx 10 - 200$ eV region, while the unresolved resonances appear in the $\approx 200 - 400$ ev energy region. Gadolinium has the highest thermal neutron cross-section (about 155000 barns).[23]

Nuclear reactions that produce other particles, like (n,p), (n,α) , (n,pd), and similar reactions, typically have energy thresholds around 1 MeV. When neutron energies fall between the resonance region and the onset of particle production, specifically from approximately 300 eV to 1 MeV, these neutrons are classified as intermediate.

However, the reaction of interest for this work in intermediate and in fast region (above 1 MeV) is inelastic neutron scattering $(n,n'\gamma)$. After this type of collision, the nucleus remains in an excited state and emits a characteristic gamma-ray during de-excitation. This type of reaction is used in this work for carbon and oxygen detection in the targets of interest.

1.3 Neutron-based techniques

1.3.1 Thermal neutron analysis (TNA)

Thermal neutron analysis (TNA) is a technique that involves the capture of thermal neutrons by the nuclei of a sample being analyzed. When a nucleus captures a thermal neutron, it often results in the emission of characteristic gamma rays, which serve as a fingerprint for the elements present in the sample. For instance, when chlorine is present in a sample, the reaction ${}^{35}\text{Cl}(n,\gamma){}^{36}\text{Cl}$ produces a characteristic gamma ray with an energy of 6.1 MeV. Similarly, the presence of hydrogen can be detected through the reaction ${}^{1}\text{H}(n,\gamma){}^{2}\text{H}$, which emits a gamma ray with an energy of 2.223 MeV.

Thermal neutrons are produced by moderating fast neutrons, a process that involves slowing them down to thermal energies.

This is typically achieved using a moderator, which is a material that reduces the kinetic energy of the neutrons through repeated collisions. The moderator can be integrated into the experimental setup or be part of the sample. Common sources of neutrons for TNA include the radioisotope ²⁵²Cf and various nuclear reactions, such as the tritiumdeuterium reaction ${}^{3}\text{H}(d,n){}^{4}\text{He}$, the deuterium-deuterium reaction ${}^{2}\text{H}(d,n){}^{3}\text{He}$, and the beryllium-deuterium reaction ${}^{9}\text{Be}(d,n){}^{10}\text{B}$ [24].

Due to the significantly lower thermal neutron capture cross-sections of carbon and oxygen compared to elements like chlorine and hydrogen (Figure 1.2), TNA is not suitable for applications that require determining the amounts of carbon and oxygen, such as measuring the carbon-to-oxygen ratio in oil wells.

1.3.2 Fast neutron activation analysis (FNAA)

This technique is used to determine the elemental composition of a sample by inducing $(n,n'\gamma)$ inelastic scattering reactions and subsequently analyzing characteristic gammarays. In this method, fast neutrons with energies above 1 MeV are produced using deuterium-deuterium (D-D) or deuterium-tritium (D-T) neutron generators. For the reaction to occur, the neutron energies must exceed a specific threshold for the isotope of interest. While FNAA is effective for determining the concentrations of various elements,



Figure 1.2: Neutron capture cross-sections for 35 Cl (left) and 12 C (right). The cross-section for chlorine neutron capture is 4-5 orders of magnitude higher in the thermal neutron energy region ($\approx 10^{-8}$ MeV).[23]

it has significant practical limitations. One major drawback is its unsuitability for detecting hydrogen, as the inelastic scattering cross-section for high-energy neutrons is quite low, as shown in Figure 1.3.

Furthermore, FNAA suffers from a high intrinsic background noise due to interactions between fast neutrons and the components of the neutron generator as well as the gamma-ray detectors.Additionally, FNAA, like most other neutron-based methods, has the drawback



Figure 1.3: Neutron inelastic scattering cross-sections for ${}^{12}C$ (left) and ${}^{1}H$ (right). The cross-section for hydrogen is below 10^{-4} barns for the neutron energies around 10 MeV. On the contrary, carbon cross-section shows resonancies around 10 MeV.[23]

of generating a significant background signal. In FNAA, neutrons produced in D-D and D-T reactions can interact not only with the intended target material but also with the surrounding materials, leading to additional background contributions, as will be demonstrated later in this work.

1.3.3 Pulsed fast neutron activation analysis (PFNAA)

Pulsed fast neutron activation analysis employs short nanosecond pulses of neutrons, allowing for coincident measurements and a significant reduction of background radiation. The duration of the pulses must be shorter than the time it takes for a fast neutron to traverse the object being examined. By combining the neutron time-of-flight with the vertical and horizontal movement of both the neutron source and gamma detector, the technique enables three-dimensional scanning of the object [25, 26].

A Van de Graaff accelerator serves as the neutron source, accelerating deuterons to an energy of 5-6 MeV [27, 28]. These accelerated deuterons are directed onto a deuterium gas target, where neutrons with an energy of approximately 8 MeV are generated via the ${}^{2}\text{H}(d,n){}^{3}\text{He}$ reaction. The neutron beam is carefully collimated in both vertical and horizontal directions, and this, combined with the neutron time-of-flight, determines the resolution of the imaging pixels for the object being analyzed.

1.3.4 Pulsed fast-thermal neutron activation analysis (PFTNA)

This method enables the simultaneous detection of characteristic gamma rays from both the inelastic scattering of neutrons with the target nucleus and the thermal neutron capture process. PFTNA uses microsecond neutron pulses, during which prompt gamma rays from inelastic scattering are detected. Between pulses, neutrons are slowed down (thermalized), allowing for the detection of prompt gamma rays from thermal neutron captures. After a predetermined number of pulses, the neutron beam is turned off for several milliseconds or longer to detect delayed gamma rays. This method allows the detection of a broader range of isotopes and it was used in water and chlorine detection in crude oil [29].

1.3.5 Associated alpha particle method (AAP)

In the associated alpha particle technique [32, 33], neutrons are generated through the deuterium-tritium (D-T) fusion reaction, where each reaction produces a fast 14 MeV neutron and a 3.5 MeV alpha particle. By conservation of momentum, these particles move in opposite directions from each other within the center-of-mass frame. The alpha particle serves two key purposes: it helps to monitor the number of neutrons produced



Figure 1.4: Time sequence of the nuclear reactions in PFTNA method.[30]



Figure 1.5: PFTNA analysis scheme. Shielding (usually lead) is added to suppress the background from direct interactions of neutrons with the detector.[31]

and enables the electronic collimation ("tagging") of the neutron beam.

The time-of-flight measurement tags the neutron beam by using the detection of the alpha particle as the start signal and the detection of the gamma-ray, produced from inelastic



Figure 1.6: Scheme of the associated alpha particle measurement. The time-of-flight ΔT determines the distance s of the irradiated volume.[34]

neutron scattering $A(n,n'\gamma)A'$, as a stop signal (Figure 1.6). This electronic collimation technique creates a cone of "tagged" neutrons, with its dimensions governed by the size of the alpha detector. A tagged neutron cone, coupled with time-of-flight measurement, facilitates 3D scanning of the target object and allows for elemental composition analysis through gamma spectroscopy. In principle, the neutron generator can be rotated around its axis, thereby rotating the cone of tagged neutrons and enabling a thorough scanning of the entire target area. Compared to the conventional FNAA method, the AAP technique demonstrates a significant noise reduction [35–40], as will be detailed later in this work [1, 2].

1.3.6 Fast neutron scattering analysis (FNSA)

Unlike the activation analysis methods described earlier, which rely on detecting characteristic gamma rays, fast neutron scattering analysis directly measures the energy of the scattered neutrons. For instance, it has been demonstrated that the combined measurement of the time-of-flight and pulse height of forward and backscattered neutrons provides a "scattering signature" for elements such as carbon, oxygen, hydrogen, and nitrogen [41]. These signatures can then be used to assess the elemental concentrations of these elements in unknown samples. Furthermore, it has recently been shown that combining neutron and gamma backscattering could be used to determine pipeline thickness profile, which can indicate possible damages due to the corrosion [42]. In addition, neutron backscattering has been studied in landmine detection [43], where it showed limitations since slight variations in soil moisture could trigger a false positive signal.

1.3.7 Fast neutron resonance transmission radiography (FNRT)

In FNRT method, objects are examined using neutrons with a broad energy spectrum ranging from 1 to 10 MeV. This technique takes advantage of the unique energy-dependent resonance structures in the neutron interaction cross-section of certain elements within the object being analyzed. By doing so, it helps in identifying the materials present, determining their abundance, and mapping their spatial distribution. To achieve this, both the spectral and spatial distribution of neutrons that pass through the object are measured. The resulting neutron spectrum will display distinct dips and peaks at certain energies, depending on the composition of the object being inspected. Because it can simultaneously detect key elements found in explosives, such as carbon, oxygen, and nitrogen [44, 45], the method is effective for identifying most conventional and improvised explosives. More recently, the method has been applied to the quantitative determination of oil and water weight fractions in sandstone and limestone rock formations and the possibility of using FNRT in determining carbon-to-hydrogen ratio in rock formations was shown [46].

1.4 Detection of characteristic gamma rays

In the previous section, we saw that considerable amount of neutron detection methods is not based on detection of neutrons themselves, but rather on the detection of characteristic gamma rays, byproducts of thermal capture reactions and inelastic collisions. In this section we will shortly describe two different types of gamma detectors and their operational principles. The basic idea behind detectors is converting the deposited gamma-ray energy to electrical charge, which can be collected and analyzed with appropriate electronics

There are three different processes that are significant in gamma ray detection. Firstly, for the lower energies of gamma rays (< 100 keV), there is a photoelectric absorption, where an incident gamma ray of energy E_{γ} interacts with one of the bound electrons in an atom. Electron is ejected from its shell carrying energy E_e :

$$E_e = E_\gamma - E_b \tag{1.5}$$

where E_b is the binding energy of the electron in the shell. The atom is left in an excited state with an energy E_b and is de-excited in two different ways. The first form of de-excitation is X-ray fluorescence, the emission of characteristic X-rays from an atom after an inner-shell electron is ejected and replaced by an electron from a higher energy shell. Some X-rays produced in fluorescence are absorbed through subsequent photoelectric interactions, while others may escape the material. The second form of de-excitation is through Auger cascade, which occurs when, instead of emitting an X-ray, the energy from an electron transition to fill the vacancy is transferred to another electron, ejecting it from the atom. This second ejected electron can lead to further vacancies, creating a cascade of electron transitions and ejections. The probability of photoelectric interaction is described with photoelectric cross-section τ , and it is a function of atomic number Z and photon energy:

$$\tau \propto \frac{Z^n}{E_{\gamma}^m} \tag{1.6}$$

where m and n are in the ranges between 3 and 5 [47]. This proportionality suggests that elements with higher atomic number are more likely to absorb gamma rays and therefore make more suitable detector materials. Generally, photoelectric absorption is a process where total absorption of gamma ray is assumed. This is not entirely correct, since photoelectric absorption happening near the detector surface can lead to X-ray escape. However, this aspect is troublesome only for very small detectors and very small gamma energies and are therefore not of concern for this work.

The next important process is Compton scattering, dominant in the intermediate energy range ($\approx 100 \text{ keV} - 100 \text{ MeV}$). A direct interaction of the gamma-ray with an electron results in partial energy transfer from gamma-ray to the recoiling electron, depending on the scattering angle θ between incident and outgoing gamma ray:



Figure 1.7: The linear attenuation coefficient of germanium. Photoelectric effect is dominant in the lower energy region, while Compton scattering and pair production are dominant in the intermediate and high energy regions, respectively. [47]

$$E_e = E_{\gamma} \left\{ 1 - \frac{1}{1 + E_{\gamma} [1 - \cos\theta] / m_0 c^2} \right\}$$
(1.7)

The maximum energy is transferred when the gamma-ray is backscattered ($\theta = \pi$), which is lower than the energy of the incident gamma-ray. When the angle is 0, no energy is being transferred to the electron. The amount of transferred energy is between these two extremes. Therefore, at all scattering angles less than 100% of the gamma-ray energy is absorbed within the detector. The scattered gamma-ray can scatter further within the detector until finally being absorbed via the photoelectric effect, or it can escape the detector entirely, leading to the recognizable Compton continuum in gamma-ray spectra. The Compton scattering absorption cross-section depends on the atomic number of the material and the energy of the gamma-ray: [47]:

$$\sigma \propto \frac{Z}{E_{\gamma}} \tag{1.8}$$

The final important process, dominant in the high-energy region, is pair production. During interaction with the Coulomb field of the nucleus, incident gamma ray converts into an electron-positron pair. For this reaction to occur, gamma-ray threshold energy of 1022 MeV (the rest masses of electron and positron are 511 keV) needs to be achieved. The excess gamma-ray energy is shared between electron and positron equally and they lose it due to the interactions with detector material. However, at thermal energies, the positron is likely to encounter an electron, which leads to annihilation and subsequent release of two 511 keV annihilation photons. These photons can undergo the aforementioned photoelectric and Compton processes, or they can escape out of the detector, leading to the recognizable annihilation peaks with energies $E_{\gamma} - 511$ keV (first escape peak) and $E_{\gamma} - 1022$ keV (second escape peak). The pair production cross κ section is strongly dependent on atomic number Z [47]:

$$\kappa \propto Z^2 f(E_\gamma, Z) \tag{1.9}$$

Finally, we consider total attenuation coefficient μ_{tot} (Figure 1.7), a measure of how easily a material absorbs or scatters radiation, quantifying the reduction in the intensity of a radiation beam as it passes through the material of thickness t:

$$I = I_0 e^{-\mu_{tot}t}$$
(1.10)

It is equal to the sum of the attenuation coefficients for each significant interaction process between gamma-rays and matter:

$$\mu_{tot} = \mu_{pe} + \mu_{cs} + \mu_{pp} + \mu_{el} \tag{1.11}$$

where the last term represents Rayleigh scattering. Total attenuation coefficient can be expressed in terms of cross-sections [47]:

$$\mu_{tot} = [\rho \times N_A/A](\tau + \sigma + \kappa + \sigma_{el}) \tag{1.12}$$

where ρ is density of the material, N_A is Avogadro's constant and A is the mass number. This relation will be significant in the discussion on the design of appropriate shielding for rare earth elements detection.

1.4.1 Semiconductor detectors

In a free atom, electrons are distributed between precisely determined energy levels. Combining multiple free atoms in a solid broadens those energy levels and energy bands are created, separated by forbidden regions. The uppermost occupied band which contains electrons that participate in chemical reactions, is called the valence band. Above this band, separated by the forbidden region, lies the conduction band. If the electrons are in this energy region, they are free to move and form a current inside the solid once that electric field is applied.



Figure 1.8: Electronic band structure of insulators, metals and semiconductors. [47]

In a typical insulator, the band gap between the valence and conduction band is of the order $E_g \approx 10$ eV, much greater than can be obtained by thermal excitations. In a metal, the conduction band is continuous with the valence band, and therefore always populated by electrons at thermal energies. Application of electric field, however small, leads to current. This makes metals impractical as gamma-ray detectors since electric signals produced by incident radiation would tame in comparison to background signals.

On the other hand, semiconductor solids have a band gap of the order $E_g \approx 1$ eV, much smaller than the insulators. This makes them an excellent choice for radiation detectors since this gap can be surpassed much easier than in insulators and the background current from thermal excitations is much smaller than in metals. When an incident gamma-ray strikes the semiconductor detector, it creates, through processes described previously, primary electrons with energies much greater than the band gap E_g . These electrons are excited from deep occupied bands, effectively leaving a positive hole, to levels way above the base of the conduction band. These primary electrons lose energy by exciting secondary electrons in the shallower-occupied bands. This process continues until electrons are at the base of the conduction band and the holes are at the top of the valence band. If no electric field is applied, electrons and holes will eventually recombine. However, upon application of the electric field, electrons and holes migrate through the material and can be picked up to form an electrical signal. The number of electron-hole pairs n is proportional to the gamma-ray energy absorbed E_{abs} :

$$n = \frac{E_{abs}}{\varepsilon} \tag{1.13}$$

where ε is the average energy needed to create a pair. This equation indicates that an effective gamma-ray detector, which maximizes n, should have a low ε . Additionally, the mobility of the generated electrons and holes must be high, requiring the detector material to be of high purity to prevent impurities from trapping charge carriers. Finally, the material must have a large absorption coefficient for gamma rays, necessitating a high atomic number and high density.

The germanium detector is the preferred choice for semiconductor detectors, and it is the one used in this work for a passive rare-earth element detection. Germanium has a relatively high atomic number (A = 32) and a high density ($\rho = 5.32 \text{ g cm}^{-3}$), which makes it a great gamma-ray absorber. It also has low ε of about 2.96 eV and a high electron and hole mobility, orders of magnitude greater than some of the room temperature operating semiconductor detectors [47].

A key advantage of germanium detectors, and semiconductor detectors in general, is their superior energy resolution compared to scintillation detectors. For example, when detecting a gamma-ray with an energy of 1332 keV (from the beta-decay chain of Co-60), a typical 3×3 inch sodium iodide scintillator has a resolution of about 80 keV (full width at half maximum). In contrast, a typical germanium detector achieves a much finer resolution of around 2 keV for the same energy [47]. Due to their superior energy resolution, semiconductor detectors are highly effective at differentiating gamma rays with closely spaced energies, such as the 202 keV and 307 keV gamma-ray emissions from Lu-176, facilitating precise identification and analysis of these specific gamma-ray lines.

However, germanium detectors are unsuitable for detection methods used in oil wells,

methane hydrate detection research, or active detection involving neutron irradiation of rare-earth elements. Firstly, they must be cooled to cryogenic temperatures (typically using liquid nitrogen) to maintain their energy resolution, which is impractical in the field, especially in remote or confined environments like oil wells or submarines. Secondly, due to the small sizes of germanium crystals, germanium detectors tend to have lower counting rates, meaning they detect fewer events per second compared to scintillators, making them less efficient and more time-consuming for practical purposes. Additionally, they are more expensive and fragile than scintillators, which are more rugged, cost-effective, and easier to deploy in harsh conditions. Finally, the size of germanium detectors and the need for constant cooling further limit their use in oil industry applications, where portability and durability are critical.

1.4.2 Inorganic scintillators

Unlike semiconductors, scintillators are insulators with a band gap on the order of 10 eV (Figure 1.8). In the band structure model described earlier, primary electrons excite secondary electrons, potentially enabling them to bridge the band gap. However, in scintillators, the energy transferred to secondary electrons may be insufficient to elevate them from the valence band to the conduction band. Instead, the electrons and holes become electrostatically attractive and form excitons.

When de-excitation occurs, electrons return to the valence band, releasing electromagnetic radiation in the process. If this radiation falls within the optical wavelength range, it can be detected by a photomultiplier, which converts the light into an electrical signal. This is an operational principle of inorganic scintillators.

Since many scintillators have large band gaps, photons emitted by direct de-excitation from conduction to the valence band would fall outside the visible range. Also, the material is likely to re-absorb these photons before they reach the photomultiplier. This is where activators come into play. Activator states are specific energy levels introduced into the scintillator material by doping it with certain elements, such as rare earth elements or transition metals (e.g. LaBr₃ is doped with cerium). These activator ions are chosen because they have energy levels within the band gap of the scintillator material (Figure 1.9). When an electron-hole pair is generated, the hole has the potential to move



Figure 1.9: Band gap structure of a scintillator. Exciton band (below conduction band) and activator states are shown. [47]

towards a nearby activator site. Electrons in both the conduction band and the exciton band are likely to be captured by these excited activator states. Consequently, the energy of photons emitted during the de-excitation of these activator levels will be reduced, resulting in electromagnetic radiation with a longer wavelength, possibly within the visible spectrum. This shift also means that the emission wavelength of the scintillator will differ from its absorption characteristics, leading to a reduction in light loss before the photons are detected by the photomultiplier.

Scintillator	Density	\mathbf{WL}	DCT	\mathbf{RI}	RCE (%)
	(g/cm^3)	(nm)	(ns)		
NaI(Tl)	3.67	415	230	1.85	100
BaF_2	4.88	310	630 + 0.6	1.5	16 + 5
BGO	7.13	480	300 + 60	2.15	15-20
$LaBr_3$ (Ce)	5.29	380	16	1.9	160
YAP (Ce)	5.37	347	28	1.94	40

Table 1.2: Properties of Various Scintillators. Relative conversion efficiency (RCE) is evaluated relative to NaI using bialkali PMT. Wavelength (WV) is of the light photon at maximum emission. DCT = decay time, RI = refractive index. BaF₂ and BGO have two luminescence components with different decay times. [47].

A scintillator suitable for gamma detection must exhibit several properties to ensure effective performance. Firstly, it needs to have a high light yield, meaning it should produce a substantial number of optical photons per unit of absorbed gamma-ray energy. This high light yield enhances the sensitivity and overall detection efficiency of the system. For instance, materials like sodium iodide doped with thallium (NaI(Tl)) generate approximately 38,000 photons per MeV of deposited gamma-ray energy [47], which is desirable for effective detection.

In addition to high light yield, for high count-rate applications, the scintillator should possess a fast decay time. A rapid scintillation decay time enables quick detection of gamma rays and minimizes the likelihood of pulse overlap, thereby improving the timing resolution of the detector.

The energy resolution of the scintillator is also an important factor, although scintillators generally do not match the energy resolution of germanium detectors. Nevertheless, the scintillator should offer reasonably good energy resolution (3%-10% at 662 keV [47]) to distinguish between gamma rays of different energies accurately.

Another important characteristic is transparency to the emitted light. The scintillator material should efficiently transmit the emitted light to a photomultiplier tube. The density of the scintillator plays a role in its effectiveness. A higher-density scintillator absorbs more gamma-ray energy, which enhances its stopping efficiency. Dense materials like BGO, which has a density of 7.1 g/cm^3 , are often preferred for this reason. Moreover, the light emission wavelength of the scintillator should be compatible with the sensitivity range of the photodetector used. For example, if the photodetector is sensitive to blue light, the scintillator should emit light within the blue spectrum to ensure efficient detection.

Some properties of the scintillators used in this study are provided in Table 1.2. The most frequently used scintillator in this study was lanthanum bromide doped with cerium $(LaBr_3)$. This relatively new material has a refractive index similar to conventional sodium iodide detectors, but it offers significantly improved relative efficiency, higher density, and a much shorter decay time. These properties result in better energy and timing resolution, as well as higher peak efficiency. Its beneficial temperature properties and good energy resolution make it an excellent choice for determining the C/O ratio and detecting methane hydrates through the use of the associated alpha particle method, where

precision and temperature stability [48] are crucial in borehole conditions and at the ocean floor. A significant drawback of lanthanum bromide is its intrinsic radioactivity. Specifically, lanthanum contains the naturally occurring radioisotope ¹³⁸La, which decays through both electron capture and β^- emission. During electron capture, ¹³⁸La decays into ¹³⁸Ba, emitting a gamma ray with an energy of 1435.80 keV. In β^- decay, it transforms into ¹³⁸Ce, releasing a gamma ray with an energy of 788.74 keV. These gamma rays are generated within the detector itself, leading to spectral summation, where the gamma rays from the intrinsic radioactivity of the scintillator are detected alongside the gamma rays from the external radiation source.

Barium fluoride (BaF_2) is a scintillator that does not require an activator. Although it has relatively low efficiency and energy resolution, its primary advantage lies in its extremely short decay time of 0.6 ns. This makes it ideal for applications where precise timing is more critical than high-energy resolution. In this study, BaF_2 was used for PFTNA detection of chlorine and water in crude oil.

Bismuth Germanate (BGO) is another scintillator that does not require an activator. While its relative conversion efficiency (RCE) and energy resolution are not exceptional, its high atomic number and density make it highly effective at absorbing high-energy gamma rays. This capability is particularly advantageous for detecting the multiple gamma rays produced during the thermal neutron capture of gadolinium.

One of the newer scintillators, YAP(Ce) (yttrium aluminum perovskite), was used as an alpha particle detector in AAP applications, including C/O determination and methane hydrate detection, due to its favorable performance characteristics. Since YAP powder exhibits a fast rise time and a narrow peak FWHM, it has shown promise as a fast-acting detector for alpha radiation [49].

1.5 Monte Carlo simulations (MCNP 6.2)

Monte Carlo (MC) simulations are a computational technique used to model and analyze systems with inherent randomness or uncertainty by repeated random sampling. In experimental physics, they are used for simulating complex physical processes, such as particle interactions, radiation transport, or detector responses, where analytical solutions may be impractical or impossible. By mimicking real-world stochastic behavior using pseudo-random numbers, Monte Carlo simulations can predict outcomes, estimate uncertainties, optimize experimental setups, and gain deeper insight into experimental results. In this work, MC simulations are employed to confirm certain experimental findings, (e.g. background noise reduction using the AAP method), to provide possible explanations for results like the temporal and spatial resolution of the neutron probe, and to predict the outcomes of measurements that are experimentally difficult to obtain, such as the detection of chlorine homogeneously mixed in crude oil.

MCNP6.2 (Monte Carlo N-Particle Transport Code) is a widely used Monte Carlo simulation code designed for modeling the interaction of particles, such as neutrons, photons, and electrons, with matter [50]. The MCNP series was originally developed at Los Alamos National Laboratory in the 1950s. It started as a simple neutron transport code but evolved over the decades to model the transport of various particles. MCNPX extended its capabilities to include charged particles, while MCNP5 focused primarily on neutrons, photons, electrons, and positrons. MCNP6.2 combines the two, enhancing the code's ability to simulate complex radiation environments.

MCNP6.2 (and Monte Carlo methods in general) uses pseudo-random sampling, the process of drawing random values from probability distributions to simulate physical phenomena, such as particle transport and interactions. Each physical process—whether it's the free path length, particle energy, or scattering angle—has a corresponding probability distribution, and MCNP6.2 uses random numbers and the cumulative distribution function (CDF) to sample from these distributions.

For instance, when a particle moves through a material, the probability that it travels a distance x without interacting decreases exponentially with distance. This is described by the exponential attenuation law:

$$P(x) = e^{-x/\lambda} \tag{1.14}$$

where P(x) is the probability that the particle travels a distance x without interacting and λ is a mean free path. The mean free path λ is related to the macroscopic total cross-section Σ_T (which is a material-specific property) by:

$$\lambda = \frac{1}{\Sigma_T} \tag{1.15}$$

To perform Monte Carlo sampling, we need the cumulative distribution function (CDF) corresponding to the exponential law. The CDF gives the probability that the particle travels a distance less than or equal to x, and is obtained by integrating the probability density function (PDF), which is normalized to 1:

$$F(x) = \int_0^x P(x') \, dx' = \int_0^x e^{-x'/\lambda} \, dx' = 1 - e^{-x/\lambda} \tag{1.16}$$

Monte Carlo sampling involves generating random values from the probability distribution. To do this, MCNP6.2 employs inverse transform sampling, where the program generates a random number ξ uniformly distributed between 0 and 1, sets this random number equal to the CDF and then solves the equation for x, starting with:

$$F(x) = \xi \Rightarrow 1 - (e)^{-x/\lambda} = \xi \tag{1.17}$$

Solving for x:

$$x = -\lambda \ln(1 - \xi) \tag{1.18}$$

Therefore, if the mean free path in the material is $\lambda = 5$ cm, and the code generates a random number $\xi = 0.8$, the free path length would be:

$$x = -5\ln(0.2) \approx 8.05$$
cm (1.19)

The main features of the MCNP6.2 code that have to be defined in the input file are:

- Cells the fundamental building blocks that define the geometry of the simulation. In MCNP6.2, a cell represents a region of space filled with a material where particle transport occurs. Cells are described using:
 - Material: Specifies the material that fills the cell (e.g., air, water, scintillator material). Each material is linked to nuclear cross-section libraries and its density is specified in the code.
 - **Geometry**: Defines the spatial boundaries of the cell using surfaces such as planes, cylinders, and spheres.
 - **Importance**: In regions with higher importance values, particles are more frequently sampled and tracked. This is particularly useful in scenarios where

some parts of the geometry are of greater interest, such as a detector or a specific volume requiring high accuracy.

- 2. **Surfaces** define the boundaries of the cells. Surfaces are used to form shapes like planes, cylinders, and spheres to construct the system's geometry. Surface is specified by:
 - Surface Type: Includes, among others, planes (e.g., PX, PY, PZ), spheres (SO), and cylinders (CX, CY).
 - Location: The coordinates where the surface exists in the geometry.
- 3. **Materials** defined by specifying the atomic composition and density of substances in the simulation. MCNP6.2 uses extensive nuclear data libraries for neutron, photon, and electron interactions. The material cards are defined by:
 - Material ID: Unique identifier for each material.
 - **Isotopic Composition**: The weight or atomic fraction of each isotope within the material.
 - **Density**: The material density (in g/cm³).
- 4. **Source Definition** The source definition specifies the properties of the radiation source in the simulation:
 - Type of Particle: Neutrons, photons, electrons, etc.
 - Energy Spectrum: The energy distribution of the source particles.
 - **Spatial Distribution**: Where the source particles originate within the geometry.
 - Direction: If the particles are emitted isotropically or in a specific direction.
- 5. **Tallies** used to measure quantities of interest, such as flux, dose, or energy deposition, at specific locations in the geometry. Input file for tally cards contains:
 - Tally Type: MCNP6.2 has a wide variety of tallies (e.g., F4 for flux, F6 for energy deposition, F8 for pulse-height spectra).
 - Particle Type: Neutron, photon, etc.
 - **Regions of Interest**: Specifies which cells or surfaces to measure the quantity in.
 - Energy Bins: The energy range over which the tally is calculated, allowing the production of energy spectra.
 - Time Bins: The time range over which the tally is calculated, allowing the

production of time spectra.

- 6. **Physics Models** specification of physics-related settings that influence particle interactions in MCNP6.2:
 - **Cutoffs**: Definition of the minimum energy below which particles are no longer tracked (useful for reducing computation time).
 - Interaction Models: Adjusting the type of models used for certain interactions (e.g., transport of secondary electrons, photon interactions).
- 7. Variance Reduction Techniques MCNP6.2 includes several variance reduction techniques that help make simulations more efficient and simulation results more accurate by focusing the computational effort where it's most needed. More notable ones include the aforementioned importance (IMP) and:
 - Weight Windows: Provides more precise control over how particles are sampled in different regions.
 - Source Biasing: Alters the energy or spatial distribution of the source to focus on regions of interest.
- 8. **Run Parameters** the input file specifies how long the simulation should run or how many particle histories to track. One can also set up the number of batches and how often the code should output results during a run.

MCNP6.2 offers a wide range of features and capabilities beyond those mentioned above [50]. In this work, MCNP6.2 was primarily used to obtain gamma spectra through flux tallies (F4), which track the neutron or photon flux (particles/cm² per source particle) in a defined volume, and pulse height tallies (F8), which record the energy distribution of pulses in a detector. Additionally, MCNP6.2 was employed to determine the temporal and spatial resolution of the neutron probe for C/O logging, generating time spectra for further analysis..

2

Detection of crude oil

2.1 Motivation

Nuclear well logging is a well-established technique used to analyze the materials surrounding exploratory boreholes. A logging tool is lowered into the borehole, equipped with a neutron or gamma-ray source and one or more detectors encased in a metal cylinder [51]. The detectors respond to the radiation that returns from the formation surrounding the borehole. This response is influenced by factors such as the formation's lithology, porosity, and fluid properties. By interpreting the detector responses, it is possible to infer the characteristics of the materials outside the borehole.

Traditionally, radioactive sources are commonly used for nuclear well logging, with Am-Be (Americium-Beryllium) and 252 Cf (Californium-252) being among the most prevalent. The Am-Be source, which has a half-life of 480 years, emits approximately 2.5×10^6 neutrons per second per curie, with an average neutron energy of 4.18 MeV. The 252 Cf source, with a much shorter half-life of 2.7 years, produces around 4.1×10^9 neutrons per second per curie, with an average neutron energy of 2.2 MeV [31].

However, neutron generators, such as those based on d + d (deuterium-deuterium) or d + t (deuterium-tritium) reactions, offer a viable alternative to radioactive sources. Several compelling reasons support the transition to neutron generators. One major advantage is the ability to bypass the complex regulatory requirements involved in obtaining and handling radioactive sources [31]. Additionally, radioactive sources tend to be costly and have long lead times, which neutron generators can avoid. Safety is another crucial factor; the use of neutron generators reduces risks associated with transportation, such as the potential loss of radioactive sources, accidents, or even terrorism threats [52–54].

administrative burden of source transportation is also significant, requiring extensive paperwork, which can be minimized with neutron generators. Moreover, these generators enhance personnel safety by minimizing radiation exposure. Finally, the risk of losing a radioactive source downhole during logging operations is eliminated, making neutron generators a safer and more efficient option overall.

A common application of neutron generators is assessing the hydrocarbon (oil and gas) and water content in the formations outside the borehole casing. These evaluations are crucial for estimating the volume of recoverable resources, which directly influences the financial valuation of the reservoir. The conventional approach in high-salinity oilfields is sigma logging, also known as pulsed neutron capture (PNC) logging. Sigma logging tool typically consists of a pulsed 14 MeV neutron generator, neutron detector, and two gamma detectors [55]. The fundamental principle of sigma logging is based on measuring neutron decay time, which allows for the determination of the formation's macroscopic capture cross-section [56]. This method leverages the fact that different elements in the formation capture neutrons at varying rates. For instance, chlorine, commonly found in sodium chloride, has a significantly higher neutron capture cross-section than elements like carbon and hydrogen, which are abundant in oil and gas. As a result, layers containing saline water exhibit much shorter neutron decay times compared to hydrocarbon-bearing layers. This contrast in decay times enables the identification of fluid types within the formation.



Figure 2.1: Injection oil well scheme, top view. [31]

However, this method is not effective in freshwater oilfields, where the sigma contrast

between water and hydrocarbons is minimal. In such cases, carbon-to-oxygen (C/O) well logging is used instead to differentiate between fluids in the formation [57–59]. Since hydrocarbons are carbon-rich and water contains oxygen, the C/O ratio provides a reliable indicator of the presence of oil or gas. The C/O logging tool works in the inelastic scattering mode, where a gamma-ray spectroscopy tool measures the carbon and oxygen in the formation of interest by analyzing energy spectra of gamma-rays induced by inelastically scattered neutrons. The main disadvantage of conventional C/O logging, based on fast neutron activation analysis, is considerable background signal.



Figure 2.2: Neutron tool for C/O logging uses two gamma-ray detectors to determine the oil saturation (S_0) . The detector positioned closer to the borehole, known as the near detector, is shielded from the formation, while the far detector is exposed to the formation. [2]

Namely, carbon signals can originate not only from the formation fluid of interest but also from the borehole oil, borehole casing, cement behind the casing, and the formation rock (Figure 2.1). One approach to tackling this issue is a neutron probe that contains two gamma detectors, detector near to the neutron source and the one further away from it [60]. Spacing between the detectors enables the near and far detectors (Figure 2.2) to capture varying amounts of signal from the formation and the borehole. By comparing these differences, it is possible to adjust for the presence of oil within the borehole. It was shown that, for a given porosity and lithology, it is possible to determine both the oil saturation (S_0) and the borehole oil fraction (y_0) using a calibrated neutron tool. If the probe is equipped with two gamma-ray detectors, a set of equations can be established, allowing the two unknowns (S_0 and y_0) to be solved uniquely.

Another possible progress, proposed by [61], was described in this chapter. Neutron

probe using the associated alpha particle method as its operating principle showed a significant decrease in background signal compared to the conventional FNAA approach [2]. In principle, the cone of electronically collimated (tagged) neutrons could be pointed towards the formation of interest, thus dramatically decreasing influence from the other parts of the volume. In addition to room temperature comparison between FNAA and AAP methods, gamma-ray and time spectra differences with increasing temperature of the alpha-detector and gamma-ray detector were provided [1]. This step is crucial in assessing the behavior of the gamma-detector and alpha detector in harsh temperature environments of the boreholes, which can reach up to 175°C [62]. High-temperature conditions reduce the number of available technological solutions and increase the costs of safety measures, particularly within geothermal reservoirs [63].

Furthermore, the measurements and the Monte-Carlo simulations of the temporal and spatial resolution of the neutron probe for C/O logging were provided. It was determined that this type of neutron probe can, in principle, distinguish between formation elements spaced 10 cm apart. This is significant because conventional logging tools are unable to effectively resolve features as thin as 10 cm [64].

Finally, crude oil generally contains some water, though the amount varies by location. This water often carries mineral salts, with concentrations reaching up to 200,000 ppm [65, 66]. While the exact composition of these salts may differ, sodium chloride typically makes up the largest portion, with smaller contributions from calcium and magnesium chlorides. If crude oil is not properly treated before being transported to refineries, the mineral salts present can cause significant issues, including pipeline corrosion, blockages, and fouling. For crude oil to be suitable for export, it must contain no more than 0.5% water by volume and a salt content below 50 mg/L [67]. Therefore, most of the water and salt must be rapidly and thoroughly removed at the production site to meet these standards. In the last section of this work, a neutron probe working in PFTNA (pulsed-fast thermal neutron activation) mode is described [29], with an aim of simultaneous detection of chlorine and water amounts in crude oil. This is the continuation of the work presented in [68, 69], where the focus was on the detection of chlorine only.

2.2 C/O logging using AAP method: proof of principle

2.2.1 C/O measurements: Experimental setup and procedures

For the room temperature comparison between FNAA and AAP operation methods, described in [2], API-120 neutron generator was used (Figure 2.3). This device, 3 in. in diameter and weighing only 15 kg, produces 14.1 MeV neutrons and 3.5 MeV alpha particles in the D-T reaction. It comes with the built-in YAP:Ce alpha detector, robust and well-suited for harsh temperature and pressure environments, like the ones present in oil wells [70].The main disadvantage of the API-120 is the lack of a pulsing system, which deems it unuseful for PFTNA. The scintillation crystal is coupled with the Hamamatsu Φ 19 mm R1450 photomultiplier tube. A high-temperature gamma detector was designed and built by Saint-Gobain to meet specific performance requirements. The detector utilizes a 3 cm × 7.62 cm LaBr₃ scintillation crystal, chosen for its excellent high-temperature stability, along with a satisfactory efficiency and peak-to-total ratio.



Figure 2.3: API-120 neutron generator [71].

The targets used in the comparison of the FNAA and AAP techniques were rectangular plastic boxes filled with mixtures of quartz sand (SiO₂) and graphite powder, with varying mass percentages of graphite: 0%, 5%, 10%, 15%, and 20%. These simulants were designed to represent the formation outside the well casing, where graphite powder substitutes for a hydrocarbon source. For each target, the C/O ratio is evaluated by dividing the quantity of carbon with the quantity of oxygen. The quantity of carbon is given by:

$$n_C = \frac{m_C}{M_C} = \frac{p \cdot m_T}{M_C} \tag{2.1}$$

where m_C is the graphite powder mass, M_C is the molar mass of carbon (12 g/mol), p represents the mass fraction of graphite powder in the total mixture and m_T is the total mass of the mixture. Similarly, the quantity of oxygen is:

$$n_0 = 2 \cdot n_{\rm SiO_2} = 2 \cdot \frac{m_{\rm SiO_2}}{M_{\rm SiO_2}} = 2 \cdot \frac{(1-p)m_T}{M_{\rm SiO_2}}$$
(2.2)

where the factor of 2 comes from the two molecules of oxygen per molecule of SiO₂ and the molar mass M_{SiO_2} is 60.08 g/mol. Finally, the C/O value is determined by combining the previous expressions:

$$C/O = \frac{n_C}{n_O} = \frac{p}{2(1-p)} \frac{M_{SiO_2}}{M_C}$$
 (2.3)

The C/O values obtained for p = 0, 0.05, 0.1, 0.15, 0.20 are 0.0, 0.13, 0.28, 0.44, 0.625, succesively. The borehole fluid was simulated using three 0.5 L plastic bottles filled with diesel fuel, representing the background noise. Two different scenarios were studied: in the first case, the probe was placed in the center of the well bore, and in the second case, it was positioned near the well wall. Results for each case were compared to the measurements where no borehole fluid is present (Figure 2.4).

For each scenario, different targets were irradiated with 14 MeV neutrons and their gamma spectra were obtained using AAP and FNAA methods. In the first method, neutrons tagged by the detection of associated alpha particles form a cone (Figure 2.6), with its apex at the tritium target of the neutron generator. When a coincidence event is detected, both the neutron time-of-flight (t-o-f) and the characteristic gamma-ray spectra resulting from inelastic scattering between neutrons and nuclei in the sample are measured. The fast anode output from the gamma detector is routed through a constant fraction discriminator (CFD) before being sent to the start input of the time-to-amplitude converter (TAC). The signal from the alpha detector is fed through the CFD and delay (63 ns) to the stop input of the TAC. In this setup, the TAC is configured with a gate width of 200 ns.

This means that only stop signals arriving within this 200 ns window after the detection of the prompt gamma ray are registered. Anything outside this gate is ignored, which ensures that only relevant gamma rays from fast neutron interactions are considered. At the



Figure 2.4: Photos of the experimental setup for FNAA and AAP comparison. The left photo shows representation the neutron probe in the empty borehole and the formation was simulated by the quartz sand and graphite mixtures. The borehole fluid (oil) is simulated by the diesel fuel placed in the vicinity of the gamma ray detector (LaBr₃) on the right (case 1, middle photo) or on the left side (case 2, right photo). The lead bricks shield the gamma detector from unwanted neutron irradiation. [2]



Figure 2.5: AAP electronics scheme.

same time, the fast output from the LaBr₃ is passed through an amplifier to the analogto-digital converter (ADC), previously triggered by a signal formed in TAC, ensuring that both timing and energy information are captured. These informations are recorded in the list mode of the computer, resulting in a file that contains columns corresponding to time and energy. This approach minimizes the influence of background noise or delayed signals, allowing for precise measurement of neutron flight time accompanied with determining the elemental composition using inelastic scattering events that generate gamma rays. The number of detected alphas (neutrons) in each AAP measurement was 8×10^7 . This consistency is important because it normalizes the neutron flux, which directly affects the intensity of the gamma-ray signals detected in the sample.



Figure 2.6: AAP scheme. The cone of tagged neutrons is defined by the geometry of the problem (dimensions of the YAP:Ce and its distance from the center of the nuclear reaction). Gamma rays from the targets placed inside the tagged neutron cone will be detected, while everything outside will be neglected [2].

On the other hand, the FNAA technique relies on the simple collection of gamma rays during measurements, without coinciding with alpha particle detection. In this method, the alpha detector is not used at all, which simplifies the setup but leads to high levels of background signal as it lacks the precision tagging provided by the alpha particles in the AAP method. In the FNAA setup, the total number of emitted alpha particles (and therefore neutrons) was 1.36×10^7 , which is considerably lower than the number of neutrons used in the AAP approach. The reason behind this is lower counting rate of gamma-ray detection in the AAP method.

The absence of alpha tagging means that, unlike in the AAP method, neutrons are not collimated into a narrow beam directed precisely at the sample of interest. Due to the isotropic nature of D-T reaction, this results in a broader neutron field, which interacts more extensively with the borehole environment, leading to increased background noise. Consequently, in FNAA, signals from borehole fluids or surrounding materials such as the casing are more likely to interfere with the desired measurements. Prior to the main measurements, energy and time calibration were performed, along with profiling of the tagged neutrons. Energy calibration was performed using known gamma peaks from the inelastic scattering of 14 MeV neutrons on carbon, silicon, and oxygen. The primary peaks include the 4.44 MeV gamma line for carbon, the 1.78 MeV line for silicon, and the 6.13 MeV line for oxygen, along with escape peaks from carbon and oxygen (Figure 2.10, left). Time calibration was carried out by delaying the signal from TAC by varying time intervals in delay line component (Figure 2.10, right).



Figure 2.7: Scheme of the experimental setup. [2].

Profiling the neutron cone refers to determining the spatial distribution of the tagged neutrons. The gamma-ray detector was placed in several positions 36 cm away from the tritium target, aligned parallel to the deuterium beam. The counts from TAC were plotted as a function of displacement and gaussian was fitted through the points on the graph, yielding full width at half maximum (FWHM) of 7.5 cm.



Figure 2.8: Profile of the tagged neutron cone. [2]

The importance of this procedure is in determination of the optimal placement of the targets of interest within the experiment.

In the data analysis phase, the chi-squared (χ^2) test was employed to fit the measured gamma-ray spectra with the spectra of known pure elements:

$$\chi^{2} = \sum_{i=1}^{m} \frac{\left(\sum_{j=1}^{n} (\alpha_{j} R_{j,i}) - R_{s,i} / \sum_{i=1}^{m} R_{s,i}\right)^{2}}{(m-n) \left(\sqrt{R_{s,i} / \sum_{i=1}^{m} R_{s,i}}\right)^{2}}$$
(2.4)

The parameters α_j represent the fitting coefficients that correspond to the relative contributions of different elements in the gamma-ray spectra. Specifically, in the AAP method, these parameters account for the relative weight fractions of oxygen, carbon, and silicon (Figure 2.9). In the FNAA method, α_j correspond to the contributions from hydrogen,



Figure 2.9: Spectra of pure elements obtained by FNAA and AAP techniques. The main peaks used for energy calibration are denoted on the subfigure (C). [2]

oxygen, carbon, silicon, and background radiation (mainly from iron stand). The carbon spectrum was obtained by irradiating graphite blocks to isolate carbon's characteristic gamma-ray emissions. For silicon, the spectrum was determined by subtracting the oxygen contribution in the AAP method. In the FNAA method, the hydrogen spectrum was obtained by measuring gamma rays from irradiated paraffin wax and subtracting the carbon contribution, while the oxygen spectrum was derived from water with the hydrogen contribution removed. Similarly, silicon was obtained from SiO₂ after subtracting the pure oxygen contribution. The terms $R_{j,i}$ represent the pure elemental gamma-ray spectra, where each $R_{j,i}$ is the number of counts in channel "i" for a given element "j." The measured spectrum is denoted as $R_{s,i}$. Summation is performed from the minimum to the maximum channel, simplified as i = 1...m, which in this experiment covers the energy range of 1.6–7 MeV for all measurements. The spectra $R_{j,i}$ are normalized such that $\sum_{i=1}^{m} R_{j,i} = 1$ for all elements j. In the AAP method, the number of elements nis 3, while in the FNAA method, n is 5. The least-squares fitting procedure is applied by minimizing the chi-squared (χ^2) value. This is done by taking the partial derivatives of χ^2 with respect to α_j and setting them equal to zero, resulting in a series of linear equations from which the fitting parameters can be determined. For instance, for the AAP measurements we have fitting parameters for carbon (α_C), oxygen (α_O) and silicon (α_{Si}):

$$\chi^{2} = \sum_{i=1}^{m} \frac{\left(\alpha_{C}R_{C,i} + \alpha_{O}R_{O,i} + \alpha_{Si}R_{Si,i} - \frac{R_{s,i}}{\sum_{i=1}^{m}R_{s,i}}\right)^{2}}{(m-n)\left(\frac{R_{s,i}}{\sum_{i=1}^{m}R_{s,i}}\right)^{2}}$$
(2.5)

Taking partial derivatives and equaling with zero gives us the system of three linear equations that can be solved using linear algebra:

$$\frac{\partial \chi^2}{\partial \alpha_C} = 2 \sum_{i=1}^m \frac{R_{C,i} \left(\alpha_C R_{C,i} + \alpha_O R_{O,i} + \alpha_{Si} R_{Si,i} - \frac{R_{s,i}}{\sum_{i=1}^m R_{s,i}} \right)}{(m-n) \left(\frac{R_{s,i}}{\sum_{i=1}^m R_{s,i}} \right)^2} = 0,$$

$$\frac{\partial \chi^2}{\partial \alpha_O} = 2 \sum_{i=1}^m \frac{R_{O,i} \left(\alpha_C R_{C,i} + \alpha_O R_{O,i} + \alpha_{Si} R_{Si,i} - \frac{R_{s,i}}{\sum_{i=1}^m R_{s,i}} \right)}{(m-n) \left(\frac{R_{s,i}}{\sum_{i=1}^m R_{s,i}} \right)^2} = 0,$$

$$\frac{\partial \chi^2}{\partial \alpha_{Si}} = 2 \sum_{i=1}^m \frac{R_{Si,i} \left(\alpha_C R_{C,i} + \alpha_O R_{O,i} + \alpha_{Si} R_{Si,i} - \frac{R_{s,i}}{\sum_{i=1}^m R_{s,i}} \right)}{(m-n) \left(\frac{R_{s,i}}{\sum_{i=1}^m R_{s,i}} \right)^2} = 0$$

$$(2.6)$$

This process effectively quantifies the contributions from carbon (α_C) and oxygen (α_O) in the sample and the measured C/O value is determined by dividing the weight parameters:

$$C/O = \frac{\alpha_C}{\alpha_O} \tag{2.7}$$



Figure 2.10: Energy (left) and time (right) calibration lines.

2.2.2 MC simulations

The Monte Carlo simulations of the FNAA and AAP measurements were conducted using MCNP6.2 code, and the model included essential components only: the target, the borehole fluid, the gamma-ray detector, and the lead shielding. Each component within the simulation model, such as the target, detector, and surrounding air, was represented as a separate cell with defined material densities, isotopic compositions and mass fractions of each isotope within the specified material. Both neutrons and photons were tracked within the simulation environment, which used the ENDF/B-VII.1 library for neutrons and the MCNPLIB04 library for photons. For each isotope, there is an input continuousenergy neutron cross-section library that effectively describes how neutrons interact with that isotope.

The default neutron and photon physics settings were applied in all simulations. Although secondary electrons were not tracked, their production by photons was enabled to ensure the accurate generation of bremsstrahlung photons. Neutrons were tracked down to an energy of 0 eV, while the photon energy cutoff was set at 1 keV.

The simulations employed an "f8 tally," known as the pulse-height tally, to obtain prompt gamma-ray energy spectra. The pulse-height tally records the energy or charge deposited in a specified cell by each source particle and its secondary particles, with scoring conducted at the end of each particle history. Without variance reduction, the scoring process



Figure 2.11: The experimental geometry was modeled using MCNP6.2. In this setup, the light blue cuboid represents the target, while the red cuboid simulates diesel fuel, serving as the borehole fluid. A green cylinder denotes the LaBr₃ detector, positioned with a lead brick (dark blue) placed in front of it for shielding.[2]

is straightforward. For example, consider a unit-weight source with an f8 tally applied in a cell that describes the detector. During a given particle history, suppose there are Kentries into the cell and L departures from that same cell. The energy associated with an f8 tally is the kinetic energy of the particle, with an additional 1.022016 MeV added if the particle is a positron. Particles can enter cell either by crossing a boundary into the cell or by originating within the cell as a source event. Particles may be absorbed within the cell or escape by crossing a boundary out of it. Let E_i represent the *i*-th tally energy of a particle entering the cell, and let D_j be *j*-th tally energy of a particle departing from the cell. The total energy deposited in the cell is given by:

$$T = \sum_{i=1}^{K} E_i - \sum_{j=1}^{L} D_j$$
(2.8)

Suppose that five pulse height bins are specified, e.g. $(T_1 T_2 T_3 T_4 T_5)$. Then, if net energy T is between T_3 and T_4 , MCNP6.2 will post a unit tally in the 4^{th} bin (T_4) . Finally, the full f8 tally is written as a two-column set of numbers, where the first column is pulse height in i - th energy bin, and the second column is relative error.

In the FNAA setup, the neutron source is defined as a point source with isotropic emission. In contrast, for the AAP setup, the neutron source is confined within a narrow cone aimed at the target. The cone angle was determined from the measured full width at half maximum (FWHM) of the neutron beam profile (Figure 2.8), which measured 7.5 cm at a distance of 36 cm from the source.


Figure 2.12: The cone angle alpha, distance from the tritium target and FWHM of the neutron profile.

From the Figure 2.12, the cone angle was calculated using the basic trigonometry:

$$\tan\frac{\alpha}{2} = \frac{\text{FWHM}/2}{36} \tag{2.9}$$

MC simulations of the experiment were conducted exclusively for case 2 of the FNAA/AAP comparison, where the gamma-ray detector is positioned between the diesel fuel and the target. The number of particle histories considered in each simulation was 10^9 . The background signal was not included in the simulations because the primary goal was to compare the relative C/O ratio between the FNAA and AAP methods under idealized conditions, isolating the contributions of carbon and oxygen without additional sources of noise. The C/O value was calculated by dividing the number of counts (pulses) in 4.439 MeV carbon peak and 6.13 MeV oxygen peak.

2.2.3 Results and discussion

Figure 2.13 displays a typical time-of-flight spectrum, characterized by a strong peak against a flat random coincidence background. This peak primarily represents the characteristic gamma rays emitted from the target. A 13 ns time window was selected to balance two key factors in the AAP approach: minimizing background noise and ensuring a sufficient number of counts for reliable statistics.

Figure 2.14 displays the AAP and FNAA spectra for the case 1 setup, where the target contains a mixture with 20% graphite powder. The AAP gamma-ray spectrum, when



Figure 2.13: T-o-f spectrum. Gamma-rays selected in the designated time window are mainly from the target of interest. [2]

diesel is present, shows minimal interference from elements like hydrogen. This spectrum is dominated primarily by gamma rays from the target material itself, resulting from inelastic scattering of neutrons.



Figure 2.14: Typical AAP and FNAA gamma-ray spectra. When diesel (borehole fluid) is present, FNAA spectrum shifts upwards and shows hydrogen peak at 2.22 MeV. [2]

In contrast, in the FNAA spectrum, the entire gamma-ray profile, including the regions associated with the target elements, is shifted upward due to the contribution of background gamma rays originating from neutron interactions with the diesel borehole fluid. Diesel, rich in hydrogen and carbon, produces additional gamma-ray emissions upon neutron capture, especially from hydrogen, which appears prominently in the FNAA spectrum. This background interaction adds a layer of gamma counts across the spectrum, effectively raising the baseline and contributing to an elevated count rate. The AAP and FNAA spectra in Figures 2.15 and 2.16 demonstrate the application of chi-squared minimization to determine the fitting coefficients for carbon and oxygen in the setup through a solution of linear equations. This approach involved setting up a system of equations derived from the chi-squared minimization process, which was then solved using a C program, written by dr.sc. Davorin Sudac, to obtain the optimal values of the coefficients corresponding to the relative concentrations of elements. The minimum chi-squared values are somewhat larger for the FNAA cases likely due to the additional background contributions, which the FNAA method cannot easily exclude.



Figure 2.15: AAP spectra fitted using χ^2 minimization.[2]

This additional background makes it more challenging to achieve an ideal fit, as the FNAA spectrum includes both the target signals and these extraneous contributions, leading to higher residuals (equation 2.4) during fitting.

Figure 2.17 shows the relationship between measured (α_C/α_O) and true C/O values for the AAP and FNAA techniques. Both methods reveal a linear correlation between the



(C) 5% graphite - no borehole fluid (D) 5% graphite - with borehole fluid

Figure 2.16: FNAA spectra fitted using χ^2 minimization. [2]

measured and actual C/O ratios, but the FNAA calibration line is shifted due to an additional carbon signal originating from the borehole fluid. This shift varies based on the carbon and oxygen content in the borehole fluid as well as the exact positioning of the probe within the well. In case 1, a slight upward shift remains in the AAP technique results. This is because the borehole fluid is located between the gamma detector and the target, placing it closer to the tagged neutron cone and allowing for some additional background carbon detection. In contrast, in case 2, the borehole fluid is positioned further from the tagged neutron cone, minimizing the detection of additional carbon from the borehole fluid.

Figure 2.18 presents the FNAA and AAP gamma-ray spectra obtained by MC simulations for a sample with a C/O ratio of 5%. Figure 2.19 displays the final results of the simulations, where the simulated C/O value was calculated by taking the ratio of counts in the 4.439 MeV carbon peak to the 6.13 MeV oxygen peak. In the FNAA method, the borehole fluid's presence is detected, resulting in an upward shift in the calibration



Figure 2.17: Calibration lines for C/O values. Conventional FNAA method yields an upward shift in calibration points due to the presence of the borehole fluid. [2]

points. In contrast, the AAP simulation, which uses a narrow neutron cone directed solely at the target material, shows that calibration points with borehole fluid align with those obtained without borehole fluid, thus confirming the experimental results.



Figure 2.18: Gamma spectra obtained using MC simulations. The number of counts in both methods was normalized per source particle. [2]

The spectra obtained from the MC simulations exhibit sharp, needle-like peaks because Gaussian energy broadening was not applied in this part of the study. This approach was chosen to focus on comparing the pure, unbroadened gamma-ray peaks for carbon and oxygen, allowing for a more precise calculation of the simulated C/O ratio. Gaussian energy broadening was applied later in this work, specifically in the simulations related to methane hydrate detection.



Figure 2.19: Calibration points for C/O values obtained using MC simulations. The conventional FNAA method yields an upward shift in calibration points due to the presence of the borehole fluid. [2]

2.3 Construction of a neutron probe for C/O well logging

Encouraged by the results of the previous section, the neutron probe (NP) for C/O nuclear well logging was constructed. It has a steel casing with an external diameter of 43 mm and consists of several key components: an alpha particle detector designed for high-temperature environments (100–200 $^{\circ}$ C), a gamma-ray detector and PMTs also suited for these temperatures, an outer casing equipped with a tritium target holder, and protective shields for both the alpha and gamma detectors.



Figure 2.20: YAP:Ce scintillation detector side view (left) and top view (middle). The photomultiplier attached to the voltage divider is shown on the right [1].

Deuterons pass through a 6 mm diameter metal cavity and interact with the tritium

target housed in the target holder. The ${}^{3}\text{H}(d,n){}^{4}\text{He}$ reaction produces alpha particles, which are detected by a scintillator-based alpha detector connected to a photomultiplier through a light guide. This high-temperature alpha detector uses a 0.5 mm thick YAP crystal, 38 mm in diameter, coated with a 2000 nm opaque aluminum layer, and placed inside a steel casing (Figure 2.21).



Figure 2.21: The simplified diagram of the alpha detector (below) illustrates its placement within the casing depicted above [1].



Figure 2.22: The images depict the tritium target situated within the target holder on the left, the target holder encased within the NP casing in the center, and the beam stopper, that shields the alpha detector from the deuterons, on the right. The gray area in the right image indicates the impact location for the deuteron beam. [1].

The aluminum coating shields the scintillator from elastically scattered deuterons, electrons, and light. The scintillator is optically divided into four equal sections and each section can detect the alpha signal independently of the other sections. Experiments utilize the Hamamatsu Φ 13 mm R4177-01 photomultipliers, where each segment of the scintillator is connected individually [1]. The gamma detector used in this setup is the LaBr₃, described in the previous section. The scintillator crystal is connected to the Hamamatsu Φ 28 mm R6877A-07 photomultiplier, equipped with a voltage divider. This photomultiplier tube is designed for high-temperature environments, capable of stable operation at temperatures up to 175 °C, and it can handle a maximum temperature gradient of 1.5 °C per minute [72]. The tritium target, exhibiting an activity of 29.6 GBq/cm², comprises a thin layer of titanium tritide deposited on a copper substrate that is 0.3 mm thick and 7 mm in diameter (Figure 2.22). This assembly is securely housed within a target holder. Figure 2.23 illustrates all the components of the neutron probe, including the outer steel casing with a diameter of 43 mm.



Figure 2.23: Disassembled neutron probe and its key components [1].

A Texas Nuclear Corporation 300 keV electrostatic accelerator, serves as the neutron generator, and the D-T reaction accomplished with this accelerator yields neutrons with an energy of 14.8 MeV, while the associated alpha particles have an energy of approximately 2.8 MeV. The main disadvantage of such an accelerator is that it is not suitable for practical use, but unlike API-120, it is equipped with a pulsing system. Background reduction using this setup was confirmed in the first part of the following experimental work [1] and AAP technique was successfully used on the geological samples (provided by INA d.d.) taken from Croatian oilfields.

2.4 High-temperature performance of a neutron probe

2.4.1 Experimental setup

In the high-temperature measurements, the neutron probe (NP) was tested to ensure functionality at elevated temperatures, which are common in oil well environments where temperatures often exceed 100°C. To achieve this, the NP was heated using an Isopad S20 heating tape, which was wound around the NP tube. This flexible heating tape consists of a copper-nickel plated braid that serves as a protective conductor and is well-suited for maintaining controlled temperatures around the NP.

The 10-meter heating tape was divided into two sections. One-third of the tape was wrapped in a single layer around the gamma detector's location on the NP, ensuring localized heating at that position. The remaining two-thirds were wrapped in a double layer around the section containing the alpha particle detector.



Figure 2.24: Scheme of a quadrant segmentation of YAP:Ce alpha detector [1].

This arrangement allowed both detectors to reach and sustain high temperatures while minimizing temperature gradients across the NP components. Temperature probes were installed on both sides of the NP: one on the gamma detector side to monitor the temperature and the other on the alpha detector side to actively control the temperature through a REX-C100 thermostat.

This setup maintained a stable temperature, with the maximum gradient limited to 1.5°C per minute, thus protecting the NP's sensitive electronics from rapid thermal stress. In the actual measurement configuration, a graphite block was placed in the NP's second



(A) The first quadrant



(C) The third quadrant



(B) The second quadrant



(D) The fourth quadrant

Figure 2.25: Carbon brick placed in different quadrants around NP axis. In high-temperature measurements carbon brick was placed in the second quadrant in two positions spaced 10 cm along the neutron probe. [2]

quadrant at two separate positions, each 10 cm apart along the NP axis. The "second quadrant" refers to a specific angular segment around the NP, derived from the segmentation of the YAP detector (Figure 2.24.), which is used to localize alpha particles generated in neutron interactions. This detector segmentation divides the area around the NP into four quadrants (Figure 2.25), each corresponding to a 90-degree section in which measurements can be taken separately, which was shown in [1]. This quadrant-based setup enhances spatial resolution, enabling the probe to better distinguish between gamma-ray signals originating from different regions around the NP. AAP measurements were conducted at different ambient temperatures, near both the gamma-ray (from $(25\pm1)^{\circ}$ C to $(160\pm1)^{\circ}$ C) and alpha (from $(25\pm1)^{\circ}$ C to $(175\pm1)^{\circ}$ C) detectors to thoroughly test the NP's performance under various temperature conditions.

2.4.2 Results and discussion

Figure 2.26 shows the time spectra and gamma-ray spectra for various measurement temperatures.

The position of the carbon gamma-ray peak within the time spectrum varies according to the location of the graphite block. The separation between the peaks for the two



Figure 2.26: Time spectra (left) and gamma-ray spectra from carbon (right) shown as functions of measurement temperature and graphite block position. [1]

different block positions is approximately 20 channels, corresponding to a neutron travel time of 2 ns, which is the time required for a 14 MeV neutron to cover 10 cm. The time resolution, estimated to be around 2 ns (matching the FWHM of the gamma peak in the time-of-flight spectrum), showed slight variation of 20% with temperature (separation between the peaks at 160 °C is 16 channels). However, the gamma-ray spectra exhibited more pronounced changes with temperature adjustments. The gamma spectra shift to the left with increasing temperature is due to the temperature-dependent changes in the detector's gain. Detector relies on the photomultipliers that convert light signals produced by gamma-ray interactions into electrical signals. As temperature increases, the electronic gain of the PMT or the amplifier often decreases, which reduces the signal amplitude corresponding to a given gamma-ray energy. This reduction in gain effectively "compresses" the spectrum, causing gamma peaks to appear at lower channel numbers, resulting in a shift to the left.



Figure 2.27: Gamma-ray background spectrum (left) and alpha spectrum (right) as a function of temperature.[1]

In addition to measurements on the carbon brick, background measurements were conducted on the lanthanum bromide detector, which includes a 1.436 MeV gamma-ray line from the decay of La-138 to Ba-138. This line was measured because the 1.436 MeV peak is more distinct in the spectral background than the carbon peak, allowing for a more precise determination of the pulse height shift. The gamma-ray detector's pulse height (PH) shift (Figure 2.27, left) was measured at 59% at 160°C, which aligns reasonably well with the manufacturer's (Saint-Gobain) specifications (55% at 175°C). The alpha detector also showed some reduction in signal amplitude, though this effect was less pronounced (Figure 2.27, right). In [48], a 44% shift was observed at 160°C (estimated from Fig. 5 in [48]), although this was with a different crystal size and PMT type than those used here.

For comparison with [48], the variation in counting rate over the 0–1.4 MeV spectrum range is shown in Figure 2.28 (left), where data loss fluctuates between 10 and 20% with changes in temperature. Figure 2.28 (right) displays the variation in counts for the 1.436 MeV gamma peak combined with the 32 keV x-ray peak across temperatures. Within the margin of error (assessed as the square root of the number of counts in 1.436 MeV peak),

the count remains stable, though some losses are observed at 160 °C.



Figure 2.28: Count rate for gamma-ray energies in 0-1.4 MeV range (left) and number of counts in 1.436 MeV + 32 keV peak (right) as a function of temperature.[1]

Energy resolution at each temperature was calculated using formula [48]:

$$R = \frac{\Delta E}{E} \times 100\% = \frac{\Delta p}{p} \times 100\%$$
(2.10)

where Δp denotes the full width at half maximum (FWHM) of the distribution spectrum, while p denotes the value at the peak position of the distribution spectrum. Figure 2.29 shows the degradation of the energy resolution as a function of increasing temperature. The energy resolution measured at 1.436 MeV deteriorated from 6.5% at 25 °C to 12% at 160 °C. This is a somewhat less promising result than the one presented in [48], where energy resolution dropped from 6.0% at 25 °C to around 8% at 175 °C. To accurately assess the neutron probe's capabilities in harsh environments, detection efficiency should be tested in real environments where the neutron probe is fully surrounded by various materials. This real-world setup would probably result in a background shift different than the one noticed in the laboratory conditions.



Figure 2.29: Energy resolution as a function of the temperature. [2]

2.5 Temporal and spatial resolution of the neutron probe

2.5.1 Experimental setup

In this section, temporal and spatial resolutions of the designed neutron probe, are presented. Previously estimated in [1], these values were experimentally verified and further supported with Monte Carlo simulations of the measurements.

The experimental setup is illustrated in Figure 2.30. A 0.5 L PET bottle filled with diesel served as the target and was positioned at four different locations, each separated by 10 cm and aligned parallel to the probe axis. The measurements captured both time spectra and gamma-ray spectra using AAP method. A 300 keV electrostatic accelerator from Texas Nuclear Corporation was the fast neutron generator. The TAC was calibrated following the same procedure described in section 2.2.2, and gamma-ray energy calibration was performed using Co-60 and Cs-137 sources.



Figure 2.30: Experimental setup. The PET bottle filled with diesel fuel is placed in one of the four positions for which the time spectra were measured. Instrumentation (scintillators, photomultipliers) is placed inside the metallic cylinder. [73]

2.5.2 MC simulations

Each simulation setup replicated the experimental geometry using fundamental structures in MCNP6.2, with continuous cell volumes defined by well-specified surfaces, as outlined in Table 2.1. The setup was simplified (Figure 2.31) to include only essential components: the neutron source, lead shielding, $LaBr_3$ detector, and diesel target. Materials filling

	px_1	px_2	py_1	py_2	pz_1	pz_2	radius	density
Diesel	-15	-10	-7.5	8.5	31	36	-	0.823
Lead shield	-	-	-	-	16	37.5	2.0	11.4
$LaBr_3$ detector	-	-	-	-	43.0	50.62	1.905	5.06
Air	-	-	-	-	_	-	200	0.001205

Table 2.1: Geometry and density specifications of the materials used in the simulations (the first position). Dimensions are in cm, while density is in g/cm^3 . $px_1...pz_2$ denote planes in the x, y and z axes. PET bottle filled with diesel is approximated with cuboid, while the lead shield and the detector are approximated with cylinders. Air is a sphere centered at the origin. [73]

	Library	Gamma production
C-natural	6000.80c	yes
H-1	1001.80c	yes
Pb-natural	82000.50c	yes
La-139	57139.80c	no
Br-79	35079.80c	no
Br-81	35081.80c	no
N-14	7014.80c	yes
O-16	8016.80c	yes

Table 2.2: Elemental libraries used in the simulations. There were no lanthanum and bromide gamma production data available. Therefore, f8 tally cannot be used for neutron interactions with the detector. [73]

these cell volumes were characterized by their density and elemental mass fractions. Diesel fuel was approximated with an average chemical formula of $C_{12}H_{23}$. The neutron source, modeled as a point source, emitted 14 MeV neutrons within a narrow cone aimed at the diesel target. The directional vector for this neutron cone was (-0.29605, 0.0, 0.95517), with a cosine angle of $\cos \alpha = 0.98874$, assessed from the profile of the neutron cone.

The diesel target was positioned at intervals of 10 cm along the probe axis (Figure 2.31). The most current default libraries, ENDF/B-VII.1 for neutrons and ENDF/B-VI.8 for photons were applied, as shown in Table 2.2. Only neutrons and photons were tracked in the simulations, utilizing the default neutron and photon physics settings. Neutrons were tracked down to 0 keV, while photons were tracked down to 1 keV, with each simulation

consisting of a total of 2×10^9 particle histories. Time-based tally data was generated through the pulse-height tally card (f8), the time bin card (T), and the energy deposition card F6 which produces average energy deposition within a specified cell in MeV/g. The f8 tally card was paired with the T card for time-binned data, using the FT PHL treatment for specialized tallies. The F6 tally, which converts energy deposition to a light equivalent [50], was combined with the FT PHL (pulse-height light) option to subdivide the pulseheight tally. The resulting pulse-height time tallies were divided into 0.1 ns bins. Since the gamma-ray production data was unavailable for isotopes Br-79, Br-81, and La-139 (Table 2.2), a standard f4 flux tally (particles/cm²) was used to provide further detail to the experiment.



Figure 2.31: 2D schematic of the simulated experimental setup. The point neutron source is positioned at the origin, and the arrow shows the movement of the PET bottle filled with diesel from the first position (nearest to the neutron source) to the fourth position (farthest from the source). [73]

2.5.3 Results and discussion

Time spectra and prompt gamma-ray energy spectra were recorded for a 0.5 L plastic bottle filled with diesel fuel positioned at four different distances along the neutron probe axis. The closest position to the source was labeled as the first, and the farthest as the fourth. The time spectra, displayed in Figure 2.32, reveal that the peak in the time window I shift progressively to the left as the target is moved farther from the neutron source. This time window I was defined based on the carbon peak observed in the gamma spectrum, within an energy range of 3.8 to 4.5 MeV (Figure 2.33). Time window II, which also spans 3.8 to 4.5 MeV, lacks significant peaks within this range, as shown in Figure 2.33. Due to the high iron content in the setup (such as in the probe casing), an iron peak appears in the gamma spectrum, but it lies outside the 3.8 to 4.5 MeV range and is therefore not visible in either time window I or II.



Figure 2.32: Time spectra for the diesel bottle at the first (top left), second (top right), third (bottom left), and fourth (bottom right) positions. Time window I aligns with the prompt gamma rays, shifting leftward by approximately 2 ns at each position. Time window II reflects the detection of scattered neutrons in the first and second positions, and prompt gamma rays generated in the air for the third and fourth positions. [73]

The leftward shift of the mean peak in time window I, as the target moves farther from the source, is expected because prompt gamma-rays serve as the starting signal for the TAC. The observed shifts in mean peak position for time window I are: 2.2 ± 0.1 ns between the first and second positions, 1.5 ± 0.1 ns between the second and third positions, and 1.8 ± 0.1 ns between the third and fourth positions. These shifts are measured with a 0.1 ns error margin, based on the 0.1 ns time bins. Using a neutron speed of 5.2 cm/ns for 14 MeV neutrons, the distances between each pair of positions are estimated as 11.4 ± 0.5 cm, 7.8 ± 0.5 cm, and 9.4 ± 0.5 cm, respectively. Given the observed separation of approximately 2 ns in the time spectra, it is inferred that the system's time resolution



Figure 2.33: Prompt gamma-ray energy spectra for the diesel bottle at the first (top left), second (top right), third (bottom left), and fourth (bottom right) positions. The spectra also display an iron peak originating from the probe casing and iron stand, which is visible across all positions. [73]

is at least 2 ns.

Time window II for the first and second positions appears due to source neutrons being scattered by the diesel target, with later arrival times, and the signal is strongest in the first position. For these positions, the peaks in time window II occur approximately 4.5 ns after those in time window I. At the third and fourth positions, time window II is likely influenced by gamma rays generated in the surrounding air, as these signals are absent from the first and second positions, possibly because they overlap with the main peak in time window I.

The Monte Carlo simulation results, utilizing the f8 pulse height tally, are presented in Figure 2.34. Unlike the experimental time spectra, the simulated time peaks are shifted to the right because all source neutrons were initiated at t = 0. The energy of the photons tallied in the spectra ranged from 1 keV (default photon lower energy cutoff) to 100 MeV (default photon higher-energy cutoff) The mean values of the primary time spectra peaks exhibit a shift of (2.0 ± 0.1) ns for each successive position. These peaks correspond to the prompt gamma rays emitted from the diesel target.

Figure 2.34 demonstrates that many pulses are recorded in the 6–11 ns range. These



Figure 2.34: The f8 time spectra generated with MCNP6.2 for different positions of diesel bottle are shown. Main spectral peaks shift to the right by 2 ns with each successive position. [73]

pulses originate from gamma rays generated in the air and are prominently visible at the third and fourth positions. This observation aligns with the experimental time window II for these positions, as no delayed time window II signals are detected there, unlike for the first and the second positions (Figure 2.32). Similar to the experimental data, these pulses are absent in the first and second positions because they overlap with the main peak.

Figure 2.35 presents time spectra derived from the f4 flux tally, showcasing neutron and gamma-ray flux. The gamma-ray flux was scored in the energy range of 3.8–4.5 MeV, while the neutron flux was scored across the broader range of 3.8–14.0 MeV.

The same as with the f8 pulse-height spectra, f4 flux spectra show shifting of the main gamma peak by (2.0 ± 0.1) ns with each successive position, and the prominent flux from gamma-ray production in the air is tallied in the 6-11 ns range.

The main neutron peaks appear later in time compared to the primary gamma-ray peaks. In addition to this expected result, two interesting effects can be noticed. Firstly, a significant neutron flux is detected in the 9–16 ns range, resulting from neutrons scattered by the air. This was validated through MC simulations comparing neutron flux with and



Figure 2.35: The f4 time spectra produced with MCNP6.2 for various diesel bottle positions reveal that the primary gamma-ray peaks shift to the right by 2 ns with each successive position. Similarly, the main neutron peaks also shift with each new position, appearing later in time relative to the gamma-ray peaks.[73]

without the presence of air in the model (Figure 2.36).



Figure 2.36: F4 flux neutron time spectra generated with MCNP6.2 for the fourth position of the diesel bottle. Flux in the 9-16 ns time range disappears when the air is not present in the model (vacuum).[73]

Secondly, on closer look, an additional bump can be seen next to the main peak of the neutron spectra in the first position. Two additional simulations investigate this effect. In the first scenario, the neutron flux over time was measured with hydrogen completely removed from the diesel bottle, while in the second scenario, carbon was completely removed from the diesel bottle (Figure 2.37).



Figure 2.37: F4 flux neutron time spectra for various positions of the diesel bottle. The hydrogen peak is prominent in the first position, decreases in the second position, and disappears entirely in the third and fourth positions. [73]

At the first position, a considerable amount of neutron flux is observed, originating from both hydrogen and carbon scattering. The hydrogen peak appears later than the carbon peak because neutrons lose more energy during elastic scattering with hydrogen. For the later positions, the hydrogen peaks diminish (second position) and eventually disappear entirely (third and fourth positions). In contrast, at the second, third, and fourth positions, the primary neutron peaks from the diesel align perfectly with the carbon peaks. This observation provides insight into the nature of time window II for the first and second positions in the experiment. If we consider that LaBr3 has a higher efficiency for detecting 14 MeV neutrons scattered off hydrogen, the experimental time window II peaks at these positions could be attributed to neutrons elastically scattered by the hydrogen in the diesel. Consistent with the experimental results, the hydrogen-neutron peaks in the simulations appear approximately 4.5 ns later than the main gamma-ray peak. Additionally, the reduction in the hydrogen peak's intensity for the second position in the simulations may explain the observed decrease in the time window II signal for this position in the experiment. The disappearance of the hydrogen peak in the simulations could also account for the absence of time window II signals at later times for the third and fourth positions in the experiment. A detailed understanding of the LaBr₃ response function would be necessary to confirm this hypothesis.

2.6 Determining chlorine and water levels in crude oil

2.6.1 Experimental setups and procedures

This chapter discusses the PFTNA measurements and results for determining water-cut and chlorine levels in crude oil using a pulsing system component of the TNC accelerator. The PFTNA technique identifies chlorine by detecting gamma-rays from thermal neutron capture reactions on ³⁵Cl, which constitutes approximately 75.77% of natural chlorine. When a capture reaction occurs, the resulting ³⁶Cl isotope de-excites, emitting a cascade of prompt gamma-rays, with the 6.11 MeV gamma-ray being the most prominent (Table 2.3).

Sodium, commonly found in mineral salts, has a relatively low thermal neutron capture cross-section of 0.517 barns, whereas chlorine, with a significantly higher cross-section of 43.5 barns [74], dominates the measured spectra. Consequently, the sodium contribution is negligible in practical analysis.

Water in crude oil is detected through the activation reaction ${}^{16}O(n,p){}^{16}N$, where the resulting ${}^{16}N$ isotope de-excites with a half-life of 0.12 minutes [75], emitting a significant characteristic gamma-ray at 6.13 MeV (Table 2.3). Alternatively, water content could also be determined through thermal neutron capture on hydrogen, which has a cross-section of 0.33 barns and produces a prompt gamma-ray at 2.22 MeV [74]. However, this study focuses on the former method for measuring water levels.

Two types of simulants were used in this experiment. The first group, designed for chlorine detection, consisted of 10 liters of diesel fuel (serving as a borehole oil simulant) mixed with small packets of table salt (NaCl). The second group, used for water content measurements, involved an emulsion of oil and water mixed in varying ratios, with a total

Emitted gamma-rays (MeV)	$\begin{array}{c} \textbf{Relative} \\ \textbf{intensity} \\ (I_{\gamma}/I_{\gamma \textbf{max}} \times 100) \end{array}$	Emitted gamma-rays (MeV)
${f during} \ {}^{35}{f Cl}(n_{{f th}},\gamma)^{36}{f Cl} \ {f reaction}$		after ${}^{16}\mathbf{O}(n,p){}^{16}\mathbf{N}$ reaction
6.110	73.96	6.048
7.414	36.92	6.130
7.790	29.85	6.917
6.619	28.40	7.117
5.715	20.40	-

Table 2.3: Gamma-ray energies for ${}^{35}\text{Cl}(n_{\text{th}},\gamma){}^{36}\text{Cl}$ and ${}^{16}\text{O}(n,p){}^{16}\text{N}$ reactions, supplemented with the relative intensities (compared to the most intense line at 1.16 MeV) for the former reaction [74]. Oxygen activation reaction has a cross-section of 42 mb [75].

volume of 10 liters. Both types of simulants were placed in a glass jar with a radius of 24 cm. The jar was positioned atop paraffin wax blocks, near the tritium target. The paraffin wax served to thermalize the 14 MeV neutrons generated by the target, slowing them down to thermal energies to facilitate neutron capture reactions. A barium fluoride (BaF₂) gamma detector was placed opposite the tritium target, close to the glass jar. Borated rubber was used as shielding to minimize thermal neutron flux reaching the detector. It was positioned beneath the gamma detector and between the jar and the detector, as boron effectively absorbs thermal neutrons.

The target setup was exposed to pulses of fast neutrons generated by the pulsing system components of the TNC generator. The system consists of a pair of deflection plates, a slit (20 mm in diameter), and the corresponding electronics. The deflection plates control the deuteron beam by either raising or lowering it, preventing the beam from passing through the slit.

To produce rectangular neutron pulses via the ${}^{3}\text{H}(d,n){}^{4}\text{He}$ reaction, a positive rectangular pulsed voltage (0.5 kV) is applied to the deflection plates. This voltage deflects the deuteron beam, effectively blocking it from passing through the slit and generating the neutron pulses.

The electronics for generating rectangular pulses of arbitrary frequency and duration



Figure 2.38: Scheme (top) and photograph (bottom) of the pulsing system.

consist of both a low-voltage and a high-voltage section. The low-voltage section, located in the control room, is computer-controlled and used to precisely set the timing, frequency, and duration of the pulses applied to the high-voltage section. The high-voltage section is situated near the vacuum tube containing the deflection plates and is responsible for generating the electric field required to deflect the beam.

The pulses generated by the low-voltage section serve as the start signal for the TAC, while the signal from the gamma detector acts as the stop signal. The output from the TAC, along with the output from the gamma detector's amplifier, is sent to the ADC (Analog-to-Digital Converter) and stored in the computer in list mode.

Two distinct pulsing frequencies and pulse durations were examined. The first setup utilized a pulsing frequency of 10 kHz with a pulse duration of 50 μ s, while the second setup employed a pulsing frequency of 0.1 Hz with a pulse duration of 5 seconds. A 10 kHz pulsing frequency has been successfully used in previous studies for chlorine detection [68], whereas the 5-second pulse duration corresponds to the half-life of ¹⁶N, which is produced



Figure 2.39: A schematic representation of the PFTNA electronics.

through the activation of oxygen. Gamma-ray spectra were recorded exclusively between neutron pulses, during periods when the neutron beam was turned off.

The PFTNA spectra were fitted by minimizing χ^2 (equations 2.5–2.6). For the first scenario, the fitting utilized elemental spectra $R_{j,i}$ of chlorine and diesel fuel, whereas, in the second scenario, the spectra of water and diesel fuel were used. Figure 2.40 shows the gamma-ray spectra of NaCl and pure diesel.

Spectra of NaCl was obtained by subtracting the diesel spectra from the spectra of diesel with one kilogram of NaCl submerged in the liquid. Figure 2.41 shows the gamma-ray spectra of pure diesel and water. The energy ranges used in χ^2 minimization were 4.7-10.8 MeV for the first scenario and 1.9-12.2 MeV for the second scenario. Finally, the χ^2 equations used for fitting can be written as:

$$\chi^{2} = \sum_{i=1}^{m} \frac{\left(\alpha_{\text{Cl}}R_{\text{Cl},i} + \alpha_{\text{diesel}}R_{\text{diesel},i} - \frac{R_{s,i}}{\sum_{i=1}^{m}R_{s,i}}\right)^{2}}{(m-n)\left(\frac{R_{s,i}}{\sum_{i=1}^{m}R_{s,i}}\right)^{2}},$$

$$\chi^{2} = \sum_{i=1}^{m} \frac{\left(\alpha_{\text{water}}R_{\text{water},i} + \alpha_{\text{diesel}}R_{\text{diesel},i} - \frac{R_{s,i}}{\sum_{i=1}^{m}R_{s,i}}\right)^{2}}{(m-n)\left(\frac{R_{s,i}}{\sum_{i=1}^{m}R_{s,i}}\right)^{2}}$$
(2.11)

For chlorine detection measurements, the samples were prepared non-homogeneously by



Figure 2.40: Gamma spectra of diesel fuel and NaCl, measured with 10 kHz pulsing frequency. Since the thermal neutron capture cross-section for sodium is negligible, the pure NaCl spectrum (bottom image) is assumed to consist of chlorine contribution only. [29]



Figure 2.41: Gamma spectra of diesel fuel and water, measured with 0.1 Hz pulsing frequency. [29]

immersing plastic packets containing varying masses of NaCl (0 g, 1 g, 3 g, 5 g, and 10 g) into the oil. This approach was chosen because sodium chloride, an ionic compound, readily dissolves in polar solvents like water but not in non-polar substances such as oil. All measurements were normalized to the number of emitted neutrons $(10^6/4\pi s)$ for consistency. Each measurement was then fitted using the first equation in (2.11), assuming the contributions from chlorine and diesel fuel only.



Figure 2.42: Photo and scheme of the experimental setup for chlorine measurement in crude oil. The scheme on the right contains relevant dimensions in the experimental setup. [29]

For the water-cut measurements, the pulsing frequency was set to 0.1 Hz, with a pulse duration of 5 seconds. Since water does not dissolve in crude oil or diesel fuel, various emulsions were prepared by mixing water with diesel. An emulsion is a combination of two liquids that do not naturally mix. These mixtures are inherently unstable and tend to separate back into their original components shortly after mixing. To maintain stability, an emulsifier is required. An emulsifier facilitates the dispersion of one liquid into another by forming tiny droplets, thereby stabilizing the mixture.

In this experiment, Polysorbate 80 (PS80), a compound made of polyoxyethylene ethers (molecular formula $C_{64}H_{124}O_{26}$) was employed as both an emulsifier and an emulsion stabilizer. PS80 is a nonionic surfactant that dissolves in water. A surfactant, or surface-active agent, reduces the surface tension between two immiscible substances, such as oil and water, allowing them to mix more effectively. It works by surrounding the droplets of one liquid and preventing them from coalescing, which would cause the oil-water mixture to separate.

A total of four water-diesel (W/D) emulsions were prepared with volume percentages of water set at 10%, 20%, 30%, and 50%. The emulsions (Figure 2.43) were prepared in



Figure 2.43: Photo of the experimental setup for water measurement in crude oil.[29]

a 10 L glass vessel using a high-speed mixer and a circulation pump for simultaneous mixing. The amount of PS80 added varied depending on the emulsion: 100 ml was used for the 10% and 50% water emulsions, while 140 ml was used for the 20% and 30% mixtures. Emulsions with less than 10 vol.% water could not be successfully prepared; therefore, additional measurements were conducted using water placed in a plastic bottle submerged in 10 L of diesel fuel. Each gamma-ray spectrum obtained was fitted using χ^2 minimization, under the assumption that the spectrum consisted solely of contributions from diesel fuel and water (Figure 2.41).

2.6.2 Results and discussion

Figure 2.44 presents a typical gamma-ray spectrum for chlorine measurements in crude oil, alongside a fitting curve. Compared to pure diesel, a distinct net count is observed in the 4.7–10.8 MeV region when chlorine is present. This is attributed to prompt gamma-rays generated by thermal neutron capture on chlorine. Consequently, the fitting procedure was restricted to this energy range.

Table 2.4 presents the fitting parameters, α_{Cl} , for different chlorine concentrations in crude oil. These concentrations, expressed in mg/L, were calculated by determining the



Figure 2.44: The gamma-ray spectrum for 10 g of NaCl in diesel fuel: the experimental spectrum with the fitted curve (inset) compared to the spectrum of pure diesel fuel. [29]

$\begin{array}{c} {\rm Chlorine\ concentration}\\ {\rm (mg/L)} \end{array}$	$lpha_{ m Cl}$
0	-0.00067 ± 0.01
61	0.03 ± 0.01
182	0.08 ± 0.02
303	0.1215 ± 0.015
607	0.17 ± 0.01

Table 2.4: Chlorine concentration and corresponding $\alpha_{\rm Cl}$ values. The value $\alpha'_{\rm Cl}$, highlighted in red, is used in the calculations of detection limits. [29]

weight of the chlorine packet, dividing it by the oil volume (10 L), and then multiplying the result by the chlorine mass fraction in the NaCl molecule. The fitting parameters are reported as mean values accompanied by their respective errors.

Figure 2.45 shows the calibration curve that connects chlorine concentrations in crude oil with fitting parameters α_{Cl} . The calibration curve is exponential rather than linear. At higher chlorine concentrations, the system begins to saturate because a significant fraction of the thermal neutrons are already captured. The emitted gamma rays cannot increase linearly with concentration because the available neutrons are finite, leading to



Figure 2.45: The values of fitting parameters α_{Cl} for various concentrations of chlorine in crude oil; exponential calibration curve and exponential parameter values are shown.[29]

the exponential saturation observed in the curve.

The calibration equation shown in Figure 2.45 and the α'_{Cl} value for pure diesel (highlighted in red in Table 2.4) are used in minimum detection limit (MDL) calculations. The parameter's negative mean value (-0.00067) at 0 mg/L of chlorine is unphysical and this discrepancy is due to constant calibration shifting. Therefore, in further calculations,



Figure 2.46: Scheme of critical limit L_C and detection limit L_D [47]

value $\alpha'_{\rm Cl} = 0.00 \pm 0.01$ is used. Figure 2.46 illustrates the theoretical normal distribution of the chlorine fitting parameter in two scenarios: the top curve represents the background distribution for pure diesel (0 mg/L of added chlorine), while the bottom curve represents the distribution when the fitting parameter equals the detection limit L_D . In this context, β represents the probability of failing to detect chlorine that is actually present (false negatives), while χ denotes the probability of falsely detecting chlorine when it is not present (false positives).

The critical limit L_C and the detection limit L_D are defined as:

$$L_C = \overline{\alpha'_{Cl}} + k_\chi \sigma_0 \tag{2.12}$$
$$L_D = L_C + k_\beta \sigma_D$$

where α'_{Cl} is the estimated fitting parameter for chlorine in pure diesel (0 mg/L of added salt), while σ_0 and σ_D are standard deviations for samples with concentrations of exactly L_C and L_D , respectively. For a 95% confidence level, the probabilities are set as $\chi = \beta = 0.05$, corresponding to $k_{\chi} = k_{\beta} = 1.645$. Additionally, it is assumed that $\sigma_D = \sigma_0$, which is a reasonable assumption given that Table 2.4 demonstrates similar errors for α_{Cl} . Therefore, it is logical to conclude that the error associated with the detection limit value of the parameter would not differ significantly.

When the value of the fitting parameter equals the critical limit L_C , there is a 50% probability that activity will be detected, and in 50% of measurements, it will be falsely attributed to background noise (false positives). To account for this and reduce the probability of false negatives to 5%, the detection limit L_D is introduced. By setting L_D appropriately, the chance of failing to detect actual chlorine activity is minimized.

Using $\sigma_0 = 0.01$, the detection limit is calculated to be $L_D = 0.0329$ using the above equations.

From the calibration curve shown in Figure 2.45, the minimal detection limit (MDL) for chlorine in diesel fuel was determined to be $(62 \pm 6) \text{ mg/L}$. For a chlorine concentration of 61 mg/L, the measured value of $\alpha_{\text{Cl}} \approx 3\sigma_0$, which is another way to confirm that the MDL is approximately 60 mg/L. This corresponds to the presence of 1 g of NaCl per 10 L of diesel fuel. The MDL can also be defined as the chlorine concentration for which the fitting parameter $\alpha_{\text{Cl}} \approx 3\sigma$, as observed in this case.

Figure 2.47 illustrates the gamma-ray spectrum of an emulsion containing 20 vol.% wa-



Figure 2.47: The gamma-ray spectrum of the emulsion containing 20 vol.% of water. The experimental spectrum with the fitted curve (inset) compared to the spectrum of pure diesel fuel. [29]

ter. The results of the fitting procedure for measuring water content are displayed in Figure 2.48 and Table 2.5. Regardless of sample homogeneity, all data points appear to align along a straight line. Exponential saturation, as observed in the chlorine measurements, is not present in this case because the activation cross-section for oxygen is several orders of magnitude smaller than the thermal neutron capture cross-section for chlorine.



Figure 2.48: The values of fitting parameters $\alpha_{\rm w}$ for various concentrations of water in crude oil together with linear fit are shown. [29]

Water concentration (vol.%)	$lpha_w$
0	0.06 ± 0.03
4.8	0.12 ± 0.03
9	0.235 ± 0.03
10	0.30 ± 0.03
16.7	0.29 ± 0.02
20	0.40 ± 0.03
30	0.49 ± 0.03
50	0.58 ± 0.03
100	1.15 ± 0.03

Table 2.5: Water concentration and corresponding $\alpha_{\rm w}$ values. The value $\alpha'_{\rm w}$, highlighted in red, is used in the calculations of detection limits. [29]

Similar to the chlorine results, an unphysical value resulting from calibration shifting is observed. In these cases, the shift arises from small discrepancies in the reference measurements used to establish the fitting curve, leading to an overestimation (or underestimation) of the parameter in certain conditions. Specifically, for the 100 vol.% water case, this results in a value of 1.15 ± 0.03 , which exceeds the physically meaningful upper limit of 1.00. To account for this, the value is treated as 1.00 ± 0.03 in subsequent calculations. As with the chlorine case, $\alpha'_w = 0.06\pm0.03$ (highlighted in red in Table 2.5) was used in the calculations of L_C and L_D . The L_D value was then applied to the calibration line to determine a minimum detection limit (MDL) for water content of (2 ± 2) vol.%. This MDL has a large relative uncertainty of 100%, indicating poor precision for detecting low water concentrations. Notice, the α_w values closest to the desired industrial limit of 0.5 vol.% exhibit particularly high relative errors, which gradually decrease as the water concentration increases. The primary causes of such large relative MDL error include instability in maintaining consistent calibration and the absence of emulsions for low water

concentrations, which would enable a more uniform inspection of oil and water mixtures.

2.6.3 MC simulations

Since a homogeneous mixture of sodium chloride with diesel fuel could not be achieved experimentally, Monte Carlo (MC) simulations were used to compare results between homogeneous and non-homogeneous targets. The basic components of the experimental setup were simulated: paraffin wax was modeled as a rectangular box with the assumed chemical formula $C_{31}H_{64}$, while the target and BaF_2 detector were approximated as perfect cylinders. The glass jar was disregarded in the simulations, and the target consisted only of diesel fuel ($C_{12}H_{23}$) and sodium chloride. In the non-homogeneous case, sodium chloride was approximated as a sphere placed in the center of the target cylinder, while in the homogeneous case, it was uniformly dispersed within the diesel fuel.





Figure 2.49: 3D representation of the simulation setup. The gamma detector is a green cylinder, while paraffin wax is a blue cuboid. The left image shows a cylindrical subdivision of the target, used for generating weight windows for neutrons within the target. In the right image, subdivision is removed to show a sphere of NaCl in the middle.

The simulations were conducted for 0.5 g, 1 g, 3 g, 5 g, and 10 g of sodium chloride within diesel. Variance reduction techniques were employed to obtain more precise simulation results, including statistical weight windows and source biasing.

Weight windows ensure that neutrons with weights outside a predefined acceptable range are either split (if their weight is too high) into multiple neutrons with lowered weight or undergo Russian Roulette (if their weight is too low), where the neutron is either terminated or saved with its statistical weight increased. This approach focuses computational effort on regions of interest by maintaining balanced neutron contributions, which improves statistical precision. For example, in this simulation, the target cylinder was subdivided into nine concentric cylindrical regions (Figure 2.49). The weight windows (wwn) were created for each cylinder (and for the rest of the cells in the setup) using default weight window parametrization wwp and weight window generator wwg, with neutron importance values set to 2 within the target and 1 outside it, while regions far from the target were set to 0 to terminate particles. After creating the weight window files, they were applied to the simulations, ensuring that neutron tracking prioritized regions where meaningful interactions occur.

Source biasing was applied by directing the point source to preferentially emit neutrons toward the target, reducing the number of particles lost in irrelevant directions. This further increased the efficiency of the simulations by ensuring that most simulated neutrons interacted with the target, contributing to the statistical results.



Figure 2.50: Fast and thermal neutron spatial distributions within the target cylinder. Circles in the middle of the images show the NaCl sphere, centered at (-17, 0, 5) cm. The black points specified by dotted lines show the position of the neutron source (0,0,0) cm. [29]

Figure 2.50 shows the spatial flux distribution for fast neutrons (1-14 MeV) and thermal neutrons $(0-5 \times 10^{-8} \text{ MeV})$ within the target, generated using the coordinate system subdivision defined by the MESH tally. As the paraffin wax neutron moderator was positioned below z = -6 cm, the fast neutrons were predominantly distributed at higher z-values, while thermal neutrons concentrated at lower z-values due to the thermalization process occurring within the paraffin. This behavior is clearly illustrated in parts (b), (c), (e), and (f) of Figure 2.50. Gamma-ray flux of 6.11 MeV gamma-rays, characteristic of the neutron capture reaction by chlorine, was recorded within the BaF₂ detector during the $50 - 100\mu$ s time interval using the **f4** flux tally in combination with the time card **T**.



Figure 2.51: Comparison of 6.11 MeV gamma-ray fluxes between homogeneous and non-homogeneous setups for various NaCl masses. [29]

Figure 2.51 presents a flux comparison between homogeneous and non-homogeneous target setups. As the amount of NaCl in the target increased, the relative errors in the homogeneous case were 16.7%, 11.4%, 7.3%, 5.6%, and 4.1%, respectively. In contrast, the corresponding relative errors in the non-homogeneous case were significantly lower, at 9.6%, 7.6%, 4.9%, 3.9%, and 3.1%. This reduction in error is due to the chlorine being concentrated in the small spherical volume in the non-homogeneous case.

As anticipated, increasing the chlorine content in both configurations resulted in a higher flux of 6.11 MeV gamma rays detected by the BaF₂ detector. However, the flux recorded in the non-homogeneous setup was consistently higher than in the homogeneous one, as illustrated in Figure 2.51. This difference can be attributed to the anisotropic distribution of thermal neutrons within the target, which concentrated more effectively around the centrally located sodium chloride sphere in the non-homogeneous configuration. The average 6.11 MeV gamma-ray flux-reduction ratios between the two setups, corresponding to increasing amounts of NaCl, were 2.17, 1.71, 1.66, 1.62, and 1.23. Given that the average gamma-ray flux was approximately twice as high in the non-homogeneous case when
one gram of NaCl was mixed in diesel fuel, it follows that the corresponding minimum detection limit (MDL) for chlorine content would be approximately twice as large as well.



Figure 2.52: Comparison of 6.11 MeV gamma-ray fluxes between homogeneous and non-homogeneous setups for various NaCl masses. Generated for isotropic thermal neutron source distribution [29]

To explore this effect further, the anisotropy of thermal neutrons was minimized by simulating a thermal neutron source distributed uniformly throughout the entire cylinder and symmetric about the z-axis. Simulations were performed for both non-homogeneous and homogeneous setups containing 1 g and 10 g of NaCl (Figure 2.52). The flux ratio of 6.11 MeV gamma-rays for 1 g of NaCl decreased by approximately 38%, from 1.71 to 1.24, indicating a much closer match between the homogeneous and non-homogeneous cases near the experimentally determined MDL.

To achieve similar results between non-homogeneous and homogeneous cases, the thermal neutron distribution within the sample would need to be symmetrical. This could be accomplished by optimizing various components of the experimental setup. Potential improvements include adjusting the size of the sample containers, implementing alternative neutron reflectors, and incorporating a neutron collimator for the generator to better direct the neutron beam. A more uniform neutron distribution would reduce discrepancies caused by uneven neutron flux within the target material.

3 Detection of methane hydrate

3.1 Motivation

Methane hydrate is a crystalline compound in which methane gas (CH_4) is encapsulated within a water crystal lattice under conditions of high pressure and low temperature, resulting in an ice-like solid [76] with a density of 0.9 g/cm³ [77] and a nominal chemical formula of $C_4H_{62}O_{23}$ [78]. These conditions are typically found in permafrost regions and on the ocean floor at depths of 400 to 1000 meters, where temperatures generally range from 1.5 to 5.0°C [79, 80]. In these environments, methane hydrate structures are commonly formed. On the ocean floor, methane hydrate often occupies the pore spaces between sand particles, as illustrated in Figure 3.1.



Figure 3.1: Sediment containing methane hydrate.[81]

The total carbon content in methane hydrate is approximately twice as high as that in the same volume of crude oil. At 0°C and 1 atm, one cubic meter of methane hydrate dissociates into about 170 m³ of methane gas. Additionally, burning methane generates approximately 32% less CO₂ compared to diesel fuel and nearly 42% less CO₂ than burning coal [82]. Methane hydrate deposits are distributed globally, predominantly in the subduction zones of continental plates, with their total quantity estimated at $(1-5) \times 10^{15}$ m³. These characteristics position methane hydrate deposits as a potential alternative hydrocarbon energy source, offering the dual benefit of reducing carbon dioxide emissions, thereby mitigating climate change, and alleviating the global energy crisis [83].



Figure 3.2: Worldwide distribution of methane hydrate deposits.[84]

Two widely studied methods for methane extraction from methane hydrate deposits on the ocean floor are thermal extraction and depressurization extraction [76]. In thermal extraction, hot water or steam is injected into the hydrate-bearing zone, increasing the temperature and triggering methane hydrate dissociation. The released methane is then collected through production pipes. A variation of this method involves the injection of CO_2 , which can simultaneously replace methane in the hydrate structure while sequestering CO_2 [85]. In the depressurization method, the pressure within the hydrate-bearing formation is lowered by extracting water, destabilizing the hydrate and causing dissociation. In some cases, water is reinjected into the formation to stabilize sediments and prevent subsidence, depending on geological conditions.

However, methane hydrate, and methane gas in general, also present a more concerning aspect. Methane is a highly potent greenhouse gas, approximately 20 times more effective (per molecule) at trapping heat than CO_2 [86]. This creates a significant risk that, if methane is not extracted carefully, it could escape into the atmosphere, accelerating climate change. Such warming could, in turn, elevate ocean temperatures, potentially releasing even more methane and creating a self-reinforcing feedback loop.

Approximately 55 million years ago, during the Paleocene-Eocene Thermal Maximum (PETM), a significant global warming event occurred, marked by a sharp rise in temperatures and drastic changes in Earth's climate. It is widely hypothesized that this event was triggered by the release of approximately 2,500 gigatons (Gt) of methane gas from methane hydrate deposits in subduction zones. This massive release is thought to have been initiated by tectonic activity, such as megathrust earthquakes, which destabilized methane hydrates buried in sediments [87]. Monitoring methane hydrate formations is therefore crucial in the context of modern climate change. Rising ocean temperatures and seismic activity could destabilize existing methane hydrates, potentially releasing large amounts of methane into the atmosphere and accelerating global warming. Studying and monitoring hydrate stability can improve the assessment of risks associated with potential methane releases and support the development of strategies to mitigate their impact on the climate.

Methane hydrate saturation (in volume %) is one of the most important parameters in estimating methane hydrate reservoirs. The values of methane hydrate saturation typically range from 5%–10% up to 30%–40% [88]. For instance, methane hydrate saturations at several sites in the Black Ridge, near the South Carolina shore, were found to be in the 2%–3% range [89]. On the other hand, two locations at Mount Elbert in Alaska exhibited saturation of 50% and 54% [90]. Common techniques used to estimate methane hydrate saturation include resistivity logging, seismic wave testing, and chloride concentration measurements of pore water [88].

In the work presented in [80], the AAP technique was used for the first time in methane hydrate saturation detection measurements. In principle, an AAP-based neutron sensor could be integrated into a remotely operated vehicle (ROV) for deployment on the ocean floor, allowing the inspection of formations of interest [91] without disrupting the rock structure. It was found that 100% methane hydrate saturations could be confidently detected within one hour of AAP measurement. This research builds on previous work [80], with the primary goal of determining the minimum detection limit for in-situ measurements conducted within a one-hour timeframe using the AAP method.

3.2 Experimental setup and procedures

This experiment used the AAP technique to irradiate four samples containing quartz sand (SiO_2) , water, and a methane hydrate simulant. An API-120 neutron generator with a built-in YAP:Ce alpha detector was employed. The gamma detector used was a 7.62 cm × 7.62 cm LaBr₃, with photomultipliers and an electronic scheme identical to those described in subsection 2.2.1. These components, along with their power supplies, were placed in the lower half of a Kevlar submarine [91] with approximate dimensions of 105 cm×112 cm×48 cm (Figure 3.3).



Figure 3.3: Experimental setup, top view.

A rotation device was attached to the neutron generator, allowing it to rotate in 1° increments, thus enabling the tagged neutron cone to rotate. Between the tritium target and the gamma detector, lead shielding in the shape of a truncated cone was placed to shield the detector from gamma rays generated near the tritium target (probe casing).

The gamma detector was mounted on an aluminum plate, which served as a window allowing neutrons to pass through while minimizing the influence of carbon present in the submarine walls. The entire setup was elevated 10 cm above an iron stand using lead bricks. The iron stand served as a base for the placement of the samples (Figure 3.4). Due to the unavailability of real methane hydrate, a simulant was prepared following the

method described in [80]. This involved mixing water and sucrose sugar ($C_{12}H_{22}O_{11}$) in a 3:1 mass ratio. To determine the resulting chemical composition, the contribution of each element was calculated based on the molar masses of water (H₂O) and sucrose. First, the total mass of the mixture was divided into 75% water and 25% sucrose by mass. Then, using the molecular weights of water (18.015 g/mol) and sucrose (342.3 g/mol), the number of moles of each compound in the mixture was determined. Next, the total number of carbon, hydrogen, and oxygen atoms was computed by multiplying the moles of each compound by the number of atoms per molecule. Finally, the atomic ratios were normalized to the smallest whole numbers, yielding the nominal chemical formula $C_4H_{46}O_{23}$. This closely resembles the nominal formula of methane hydrate ($C_4H_{62}O_{23}$). The simulant's density was 1.08 g/cm³, slightly higher than the nominal methane hydrate density of 0.9 g/cm³.

Each sample contained 7.7 kg of quartz sand, uniformly distributed in an inox plate with dimensions $40 \text{cm} \times 30 \text{cm} \times 6 \text{cm}$. The sand granules ranged from 0.1 mm to 1.3 mm in size, with a total pore volume of 2.4 L. This pore volume was measured by saturating the sand with water until a thin layer of water covered the surface, ensuring 100% saturation. The total pore volume represented the combined volume of water and methane hydrate simulant in the samples. The samples varied in the volume percentages of water and simulant added, with the following saturation levels considered: 100%, 80%, 60%, and 0% methane hydrate saturation. The last case, representing 100% water saturation, was used as a "background" reference for detection limit calculations. Evaluation in terms of methane hydrate saturation is standard practice in methane hydrate research (e.g., [88]).

Energy-channel calibration of the gamma spectra was performed using Co-60 (characteristic gamma rays at 1.173 MeV and 1.332 MeV) and Cs-137 (characteristic gamma ray at 0.662 MeV) sources. A Gaussian function was fitted to each of the characteristic peaks (Figure 3.5):



Figure 3.4: Experimental setup, side view.

$$f(x) = A \exp\left(-\frac{(x-C)^2}{2\sigma^2}\right)$$

where x represents the position, A is the amplitude, C is the Gaussian centroid (the position of the peak), and σ is the standard deviation of the function. The full width at half maximum (FWHM) is defined as $2\sqrt{2\ln 2\sigma}$, and its values were calculated as they are essential for Monte Carlo simulations. The values shown in the legends are expressed in channels.

The values of C for each peak were utilized in the energy-channel calibration, as shown in Figure 3.6.

Before conducting the sample measurements, the neutron source angle and the optimal placement of the target were determined. Given the excess carbon present in the methane hydrate simulant, these parameters were optimized by determining the position and source angle at which the characteristic 4.44 MeV gamma-ray of carbon was most prominent in the gamma spectra.

The calibration involved irradiating a $10 \text{ cm} \times 10 \text{ cm} \times 10 \text{ cm}$ carbon brick along the x-axis at 7 equidistant positions, spaced 5 cm apart, with the first position being the furthest from the neutron source (Figure 3.7). At each position, the carbon brick was irradiated at 8 relative source angles, β , ranging from 27° to 34°. The relative angle was measured



Figure 3.5: Gaussian fits for Co-60 peak at 1.173 MeV and Cs-137 peak at 0.662 MeV, with the values of x_c and fwhm in the legends



Figure 3.6: Energy-channel calibration line

with respect to the initial angle, which was determined by comparing the position of the photomultiplier (Figure 3.4) to the z-axis (shown in Figure 3.7). The initial angle was

estimated to be 12° , resulting in total neutron source angles with respect to the z-axis ranging from 39° to 46°



Figure 3.7: Scheme of calibration procedure. Movement of carbon brick and respective positions, rotation of the cone of tagged neutrons by relative angle β , tagged neutron cone angle α and coordinate axis are shown.

The number of detected alpha particles in each calibration measurement was 10^7 . Gammaray spectra for two different x-axis positions with the same relative neutron source angle and for two different angles at the same positions are compared in Figure 3.8.

The number of counts at the 4.44 MeV carbon peak is noticeably lower when the brick is placed furthest from the neutron source (position 1). The counts in the 4.44 MeV peak were summed within a carbon window, shown in each spectrum. For each relative source angle, the number of counts was plotted as a function of the position of the carbon brick along the x-axis, and a Gaussian function was fitted to these data points (Figure 3.9). For each graph, the amplitude values A were compared across different relative source angles, and the angle corresponding to the highest amplitude was chosen as the optimal one. In this case, the optimal relative angle was $\beta = 33^{\circ}$. The Gaussian centroid x_c for this angle was then taken as the optimal x-axis position of the target.

Next, with the relative angle $\beta = 33^{\circ}$ and optimal x-axis position determined, the carbon brick was placed at five different positions along the y-axis. Position 0 corresponds to the initial y-coordinate used during the x-axis optimization.

Using the same procedure, the counts in the carbon window were plotted as a function of the y-axis position (Figure 3.10), and another Gaussian function was fitted to determine



Figure 3.8: Gamma-spectra for two different neutron source relative angles and two different positions of carbon brick.

the optimal y-axis placement, y_c . Finally, the coordinates (x_c, y_c) were identified as the optimal target placement, and the middle of the bottom surface of the inox plate was aligned to these coordinates.

After calibration, four different targets were irradiated for approximately one hour, with



Figure 3.9: Gaussian fits for two different relative angles, with parameter values in the legend. The highest amplitude was obtained for relative angle $\beta = 33^{\circ}$.



Figure 3.10: Gaussia fit for the optimal y-axis placement.

each measurement normalized to $1.2 \cdot 10^7$ detected alpha particles. The irradiation time was limited to avoid potential malfunctions of the API-120, as prolonged measurements

may cause this neutron source to shut down. The spectra were analyzed by comparing the number of counts within the carbon window, and the critical limit, detection limit, and minimum detection limit were subsequently calculated.

3.3 MC simulations

The Monte Carlo simulations conducted in this study were designed to replicate the experimental conditions and compare the calibration line with the experimental one. To achieve this, the geometry of the experiment was simplified, retaining only the essential components of the experimental setup. The neutron probe was approximated as a hollow stainless steel cylinder, while the LaBr₃ detector was modeled as a solid cylinder. The lower half of the submarine vessel was represented as a rectangular open box made of Kevlar, with a nominal chemical formula $C_{14}H_{14}N_2O_4$ assumed [92]. Other structural elements included a truncated conical lead shield, an aluminum plate, and an iron stand, both modeled as rectangular parallelepipeds.

The neutron source was defined as a cone of 14 MeV neutrons, identical to the source used in crude oil detection experiments. The direction of the neutron cone matched that of the experimental setup, maintaining a 45-degree angle with the z-axis. The placement of the sample was optimized to match the conditions observed in the experiment, ensuring accurate positioning on the iron stand. The targets consisted of homogeneous mixtures of SiO₂, water and sugar, combined in the same volume ratios as in the actual experiment. Weight fractions were used to define materials on the material card.

Each measurement was simulated in two steps to improve the statistical accuracy of the results. In the first step, the simulation collected f4 gamma flux tallies divided by energy and time bins. The total flux in a 5 ns time window was selected, with the time window centered around the main peak of the time spectrum. In the second step, the collected f4 pulse was used as a histogram-based H-D (Histogram-Discrete) distribution of photon energies, serving as the source in a subsequent simulation. The H-D distribution allows MCNP to sample photon energies directly from the previously recorded spectrum, preserving the energy distribution of the collected photons. The geometry in this step consisted only of the LaBr₃ detector, with a circular disc source placed directly in front of its base. The source photons were energetically distributed in the same way as the



Figure 3.11: Simulation geometry, top view (left), and side view (right).

collected flux. The source disc area matched the base area of the LaBr₃ detector (45.6 cm^2). The f8 tally was used to record energy deposition in the detector for accurate spectral reconstruction. To account for detector resolution effects, the Gaussian Energy Broadening (GEB) function was applied. This function simulates the finite energy resolution of the detector by introducing statistical broadening to the simulated energy spectra, better replicating real experimental conditions. To calculate the parameters for GEB, the following formula was used [50]:

$$FWHM = a + b\sqrt{E + cE^2}$$

To obtain parameters a, b, and c, least squares fit was performed using experimentally obtained FWHMs for cesium and cobalt peaks (Figure 3.5). These were translated from channels to energy using the energy-channel calibration line (Figure 3.6), and the results are shown in Figure 3.12.

The primary objective of this two-step simulation procedure was to minimize variance and reduce relative errors in the number of detected pulses in the f8 tally. The first step ensured accurate collection of the neutron-induced photon distribution, while the second step improved the efficiency of photon transport simulations. To ensure high statistical precision, each simulation step was performed with 10^9 particle histories.



Figure 3.12: GEB calibration curve.

3.4 Results and discussion

Figure 3.13 shows a typical time-of-flight signal from the TAC, with time gates set at 200 ns. A strong peak is visible against the background of random coincidences. Unlike the time-of-flight spectrum shown in Subsection 2.2.3, this peak is not primarily associated with gamma rays from the target. In this experiment, neutrons traveling toward the targets of interest interact with various materials in the experimental setup, predominantly the aluminum window, the iron stand, and the submarine itself. For this reason, the selected time window (5 ns wide) was chosen to optimize the visibility of the carbon peaks of interest (4.44 MeV and its first escape peak at 3.93 MeV).



Figure 3.13: Typical t-o-f spectrum. The time window selected is 5 ns wide.

Figure 3.14 shows a zoomed-out gamma spectrum within the designated time window

for a target with 100% methane hydrate saturation. The spectrum is dominated by several iron and aluminum peaks, with iron peaks primarily originating from the iron stand, the inox plate, and the neutron probe steel casing, while aluminum peaks stem from the aluminum window, which lies directly in the path of the source neutrons. The identified peaks include those at 0.84 MeV and 1.24 MeV for iron, resulting from the ${}^{56}\text{Fe}(n,n'){}^{56}\text{Fe}$ reactions, and those at 0.99 MeV and 1.81 MeV for aluminum, produced by the ${}^{27}\text{Al}(n,p){}^{27}\text{Mg}$ and ${}^{27}\text{Al}(n,d){}^{26}\text{Mg}$ reactions, respectively [93].



Figure 3.14: Zoomed-out experimental gamma spectrum for the target with 100% methane hydrate saturation.

The relevant section of the gamma spectrum is shown in the zoomed-in Figure 3.15, which compares samples with 100% and 0% methane hydrate saturation. The figure highlights an additional aluminum peak at 2.21 MeV, resulting from the ${}^{27}\text{Al}(n,n'){}^{27}\text{Al}$ reaction. Several notable oxygen peaks are also present at 2.71 MeV, 3.09 MeV, 3.68 MeV, and 6.13 MeV, with two escape peaks at 5.62 MeV and 5.11 MeV accompanying the 6.13 MeV line. Finally, two distinct peaks are observed at 4.44 MeV and 3.93 MeV. The former arises from the inelastic scattering of 14 MeV neutrons off carbon in the ${}^{12}\text{C}(n,n'){}^{12}\text{C}$ reaction, while the latter corresponds to its first escape peak.

For each spectrum, a distinct energy window (carbon window), shown in Figure 3.15, was selected to contain 4.44 MeV peak, and the net number of counts within this window was calculated relative to the sample with 0% methane hydrate saturation (100% water saturation), with an error assumed to be equal to the square root of the number of counts. It is important to note that the difference between the two spectra within the carbon window (and elsewhere) in Figure 3.15 seems not to be significant to the naked



Figure 3.15: Zoomed-in experimental gamma spectra for the samples with 100% and 0% methane hydrate saturation, with the carbon window (4.04-4.63) MeV where the number of counts was compared.

eye. This is because the additional carbon introduced by the methane hydrate simulant constitutes only a small fraction of the total carbon present in the experiment, which is primarily found in the inox plate and the steel probe casing. The influence of these carbon sources could not be completely eliminated, even with the tagged neutron cone and aluminum window. However, when the net number of counts in the carbon window was calculated, the difference became evident.

MH saturation (%)	$N_C - N_{C0}$
0	0 ± 127
60	360 ± 128
80	447 ± 128
100	685 ± 129

Table 3.1: Measured gamma-ray net counts in the (3.83-4.8) MeV carbon window.

Table 3.1 shows the net gamma-ray counts calculated for different saturations of methane hydrate. The symbol N_C represents number of counts in the designated carbon window for various saturations, while N_{C0} represents the number of counts in that same window for a sample with 0% methane hydrate saturation. The value highlighted in red is used in calculations of critical limit L_C and detection limit L_D . The results from the table are presented in Figure 3.16, which shows the net gamma-ray counts as a function of methane hydrate saturation with a linear calibration fit presented in the form $y = k \cdot x + l$, where y is the net number of counts, and x is the methane hydrate saturation.



Figure 3.16: Experimental calibration line of net gamma-ray counts as a function of methane hydrate saturation.

The linearity observed in the experimental calibration line arises from the fact that both the flux of 14 MeV neutrons and the total amount of carbon in the system remain sufficiently low, preventing any significant saturation effects (like in the case of chlorine detection in crude oil). In this regime, the probability of neutron interactions with carbon nuclei remains proportional to the available carbon content, ensuring a direct relationship between methane hydrate saturation and the number of detected gamma counts.

The minimum detection limit was calculated using the same procedure and assumptions as in Subsection 2.6.2. The difference is that, instead of the α'_{Cl} parameter, the value of $N_C - N_{C0}$ for 0% volume saturation was used in the L_C and L_D calculations. The critical limit L_C obtained in the procedure was 208.9 counts above the background, while the detection limit L_D was 417.8 counts above the background. The value L_D was then plugged into the calibration line equation, and the minimum detection limit (MDL) obtained in this procedure was $(67 \pm 25)\%$ volume saturation. The relative error of the MDL is quite high (about 37%), which stems from the fact that only four data points were used for calibration, resulting in large uncertainties in the line parameters k and l.

As for the MC simulations, Figure 3.17 shows a typical time spectrum of the integrated photon flux f4 and the 5 ns time window used as the input source for the second part of the simulation. The time window has the same value as in the experimental case, but here it fully encompasses the peak in the spectrum. The simulated time peak appears narrower because, in the experimental setup, the cone of tagged neutrons is defined by



Figure 3.17: Time spectra obtained by MC simulation.

the time gate set in the TAC, which selects a subset of neutrons from those emitted in all directions. However, since the neutron generator continuously emits neutrons in all directions, some neutrons undergo scattering off of surrounding materials or arrive at the detector from slightly different angles, leading to additional undesired coincidences and broadening of the time peak.

In contrast, in the MC simulations, the cone of tagged neutrons is predefined, meaning that the neutron source does not emit neutrons outside the cone. This eliminates contributions from scattered neutrons outside the intended trajectory and reduces random coincidences, resulting in a narrower time peak.



Figure 3.18: Comparison of zoomed-out gamma spectra between simulation and experiment for the sample with 100% methane hydrate saturation.

The f8 tally, generated in the second part of the simulation, was multiplied by a constant

 (2.6×10^8) to obtain the final number of counts for each energy. This scaling factor was chosen by the eye to match the experimental and simulated carbon peaks at 4.44 MeV. Full MC gamma spectra in the zoomed-out view for 100% methane hydrate saturation, compared to the experimental case, is shown in Figure 3.18. The zoomed-out view of the simulated spectra reveals the same peaks as those observed in the experiment, though with some differences in intensity. While the intensity of the iron line at 0.84 MeV suggests that the amount of iron simulated was approximately correct, the aluminum peaks indicate that the simulated amount of aluminum was underestimated. This discrepancy arises mostly from the inability to precisely measure the thickness of the aluminum plate, as it was already attached to the bottom of the setup.



Figure 3.19: Comparison of zoomed-in gamma spectra between simulation and experiment for the samples with 100% (left) and 0% (right) methane hydrate saturation.

The zoomed-in spectra, shown in Figure 3.19, illustrate how the carbon peak at 4.44 MeV in the simulations aligns well with the experimentally obtained one. Additionally, it can be observed that the background in the energy region ($\approx 2-3.83$) MeV is considerably higher in the experimental case than in the simulations. This discrepancy is most likely due to the simulations including only the essential components of the experimental setup, while other elements present in the actual experiment, as well as parts of the laboratory, contained oxygen, contributing to this oxygen-dominated region.

The same calibration procedure described in the experimental case was applied here as well. In MCNP, the number of pulses per energy bin is reported with the relative error. Therefore, to obtain the total relative error of the pulses collected in the carbon window, error propagation was applied. The MDL was not calculated in the simulation case since, in principle, simulations can arbitrarily reduce uncertainty—and consequently the MDL

MH saturation (%)	$N_C - N_{C0}$
0	0 ± 79
60	189 ± 79
80	250 ± 79
100	315 ± 79

Table 3.2: Simulated gamma-ray net counts in the (3.83-4.8) MeV carbon window.

— by employing variance reduction methods and by running for a sufficiently long time. Also, the simulations will not consider all experimental effects present, thus, the MDL calculated using simulations will only be achievable in theory.



Figure 3.20: Simulated calibration line of net gamma-ray counts as a function of methane hydrate saturation.

The calibration line obtained from MC simulations is shown in Figure 3.20. The mean slope of this calibration line (k = 3.15) is lower than that of the experimental case (k = 6.49); however, these values agree within 2σ . The most likely reasons for this discrepancy are mismatch between the modelled geometry and the experimental geometry of the measurement and imperfect modelling of prompt gamma-ray production in the surroundings. GEB function used in the simulations is also one of the possible factors. Since the net counts represent the difference between the detected number of counts, any inconsistency in the energy broadening directly affects the subtraction process. The GEB parameters were obtained by fitting only three data points (Figure 3.12), resulting in large uncertainties. Furthermore, a scaling factor was applied to match the simulated and measured spectra at 4.44 MeV, but only approximately. This is because, in energy regions with a low number of counts (such as the carbon energy region), the relative uncertainties

in each channel are large, leading to fluctuations from channel to channel, whereas the GEB peak appears overly smooth.

To conclude, due to the large relative error, it remains inconclusive whether the experimentally obtained MDL of $(67\pm25)\%$ is sufficient even for sites with high methane hydrate saturations, such as those near Mount Elbert in Alaska. Future work should focus on irradiating more samples to obtain additional calibration points, leading to more precise calibration lines and, consequently, a more precise MDL. The mean of the MDL itself (67%) is larger than saturations found near Mount Elbert (50% and 54%). However, the neutron source used in this study, the API-120, has a relatively low flux of $10^6 \text{ n}/4\pi \text{s}$. Modern neutron generators offer significantly higher fluxes, which could lower the MDL for one-hour measurements. For example, consider a neutron generator with a flux that is 10 times larger than that of the API-120. Assuming a linear response of gamma-ray production to neutron flux (i.e., no saturation effects, dead time losses, etc.), the number of counts in the carbon peak would increase by a factor of 10, as would the net counts in that peak. Consequently, the calibration slope k would also increase 10-fold. On the other hand, the uncertainty in the background counts scales as $\sqrt{10}$, leading to an increase in the detection limit L_D by the same factor. Given that l = 0, substituting $y = L_D$ into the calibration equation, y = kx + l, and solving for x, we obtain the expression $MDL = \frac{L_D}{k}$. Since L_D increases by $\sqrt{10}$ while k increases by 10, the mean MDL is reduced by a factor of $\sqrt{10}$, decreasing from 67% to approximately 21%, which would be sufficient for sites with high methane hydrate saturations. To achieve an MDL of 21% within a shorter and more cost-effective timeframe of approximately 5–10 minutes per measurement, the neutron source flux would need to be increased by an additional order of magnitude. On the other hand, it is important to note that these experiments were not conducted underwater. In a submerged environment, water would thermalize many fast neutrons before they reach the formation of interest, thereby reducing the number of neutrons available for inelastic scattering with carbon atoms. The simulations conducted in this work serve as a benchmark for future studies, which will incorporate a more realistic environment, such as simulating a full submarine positioned on the ocean floor. Future research efforts will focus on refining the experimental conditions by using neutron generators with higher flux, irradiating more targets, and submerging the entire setup underwater to achieve more realistic measurements.

Detection of rare earth elements

4.1 Motivation

Rare-earth elements (REEs) refer to chemical elements in the lanthanide series (Z = 57 - 71), often including scandium (Z = 21) and yttrium (Z = 39) due to their similar chemical properties [94, 95]. These elements are commonly found together in the same mineral ores [96]. Based on their atomic numbers, REEs are typically divided into light rare-earth elements (Y, Sc, La, Ce, Pr, Nd, Pm, and Sm) and heavy rare-earth elements (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) [94, 95]. These silver, silvery-white, or gray metals are known for their high luster, though they corrode readily when exposed to air. They exhibit high electrical conductivity, making them valuable in various technological applications. Due to their shared chemical properties, separating individual REEs is challenging, as they display only slight differences in solubility and complex formation [94, 97]. These metals naturally occur together in minerals such as monazite and bastnaesite [97]. In nature, REEs are commonly found combined with non-metals, typically in the 3+ oxidation state.

These elements play an important role in a wide range of technological and industrial applications, with new uses continuously emerging. For example, some REE-based alloys are used to produce powerful magnets like NdFeB, which are essential in electric motors [98, 99], wind turbine generators [100], and mobile phones [95, 101]. Compounds such as Y_2O_3 combined with Eu₂O₃ are used to create phosphors (a substances that luminesce), which are vital in the television industry [94].

In the nuclear industry, REEs with high thermal neutron capture cross-sections, such as gadolinium, europium, and dysprosium, are indispensable components of control rods used for regulating or shutting down reactors [95]. In medicine, gadolinium neutron capture therapy (GdNCT) has shown promising potential for cancer treatment [102]. Furthermore, gadolinium-based compounds are already widely used as contrast agents in magnetic resonance imaging (MRI) [103].

Rare-earth ore deposits are found worldwide, with China emerging as the leading producer. In 2017, the country supplied approximately 80% of the global output [95], a figure that has since risen to 90% [104]. The geostrategic importance of rare-earth elements became evident in 2009 when China imposed export restrictions on these critical resources [97]. In 2024, China imposed even stricter regulations on the mining and production of rare-earth elements [105, 106], heightening concerns about potential price increases for these technologically critical resources. Also, rare-earth deposits are rich in thorium and uranium [107], making their extraction a significant environmental concern.



Figure 4.1: The correlation between Lu (top), Gd (bottom), and the total REE content in deep-sea sediments is shown. Data for the Pacific Ocean are provided in the supplementary materials of [108], while data for the Indian Ocean are sourced from [109]. The total REE content represents the combined concentrations of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

These facts increase the need for new sources of REEs. Reference [108] highlights that

deep-sea mud contains surprisingly high concentrations of REEs, ranging from 1000 to 2230 μ g/g. It is estimated that oceanic reserves of REEs are 1000 times larger than terrestrial deposits. Since oceanic reserves lack uranium and thorium, their extraction is both more cost-effective and environmentally friendly.

Deep-sea exploration for REE deposits poses significant challenges due to the inaccessibility of the ocean floor. Unlike terrestrial exploration, which can rely on various surface investigation methods, underwater exploration is limited to sampling the ocean floor through drilling and core extraction for laboratory analysis. Standard laboratory techniques used for such analyses include X-ray fluorescence, neutron activation analysis, and inductively coupled plasma mass spectrometry (ICP-MS) [94]. Data from [108, 109] reveal a strong linear correlation between surface concentrations of Gd and Lu and the total surface concentration of REEs in sediments from the Pacific and Indian Oceans (Figure 4.1). According to [108], lutetium concentrations of 6.0 ± 0.3 ppm and gadolinium concentrations of 68 ± 2 ppm indicate REE-rich deposits (REE > 1000 ppm) in the Pacific Ocean. Similarly, data from [109] show that lutetium concentrations of 2.55 ± 0.29 ppm and gadolinium concentrations of 39 ± 2 ppm point to REE-rich deposits (REE > 1000 ppm) in the Indian Ocean.

Therefore, in this chapter, two nuclear-based techniques were investigated for in-situ REE deposit exploration. These methods allow for faster and more efficient seafloor surveys, contributing to a better understanding of the global REE distribution. The first method, PFTNA, utilizes the large thermal neutron capture cross-section of gadolinium, while the second relies on passive measurement of natural radioactivity originating from the radioactive isotope ¹⁷⁶Lu.

4.2 Active detection of gadolinium

4.2.1 Experimental setup and procedures

Given that gadolinium has an exceptionally large thermal neutron capture cross-section, neutron-based methods are well-suited for detecting rare-earth elements (REEs). While thermal neutrons are commonly produced in nuclear reactors, they can also be generated by thermalizing fast neutrons with an energy of 14 MeV, which are relatively easy to produce. Active REE detection could, in principle, utilize portable, compact 14 MeV neutron generators that can be deployed aboard submarines. The surrounding water would be an efficient moderator, slowing down fast neutrons to thermal energies. Gadolinium has two isotopes with notably high thermal neutron capture cross-sections: ¹⁵⁷Gd and ¹⁵⁵Gd. The resulting nuclear reactions emit characteristic gamma-rays, as illustrated in Figures 4.2 and 4.3.



Figure 4.2: The gamma-ray spectrum resulting from the nuclear interaction ${}^{157}\text{Gd}(n_{\text{th}},\gamma)$ is shown. The thermal neutron capture cross-section for this reaction is 254000 ± 815 b. The natural abundance of ${}^{157}\text{Gd}$ in gadolinium is 15.65% [110]. Figure taken from [74].

The highest gamma-ray yield occurs below 1 MeV; however, as will be demonstrated, the most suitable detection range in our case is between 2.5 MeV and 3.3 MeV. Interestingly, in this range, the detected isotope is 155 Gd, which has a thermal neutron capture cross-section four times smaller than that of 157 Gd.

Figure 4.4 shows the experimental setup. The neutron source used is a 300 keV Texas Nuclear Corporation accelerator equipped with a pulsed ion beam system. A pulsed neutron beam of 14 MeV is generated via the DT nuclear reaction ${}^{3}\text{H}(\text{d,n})^{4}\text{He}$, Q = 17.6 MeV, by accelerating a deuteron beam with a high voltage (120 kV) toward a tritium target located at the end of the deuteron guide. The active area of the tritium target is 6 mm in diameter and consists of titanium (0.95 mg/cm²) deposited on a copper foil (7 mm in diameter and 0.3 mm thick), with an activity of 29.6 GBq/cm² (0.8 Ci/cm²).

Parrafin blocks placed near the tritium target serve as neutron moderators. Inside the paraffin blocks lies the target material; a 1 L plastic container filled with a mixture of quartz sand (SiO₂) and gadolinium (III) oxide (Gd₂O₃) powder. A total of six different



Figure 4.3: The gamma-ray spectrum resulting from the nuclear interaction 155 Gd(n_{th}, γ) is shown. The thermal neutron capture cross-section for this reaction is 60900 ± 500 b. The natural abundance of 157 Gd in gadolinium is 14.80% [110]. Notice the presence of gamma-rays in the energy range of 2.45–3.27 MeV, unlike 157 Gd, which does not emit gamma-rays in this energy region. Figure taken from [74].



Figure 4.4: Experimental setup for active detection of gadolinium.

targets were prepared, containing 1500 g of SiO₂ and varying amounts of Gd₂O₃: 0 g, 0.025 g, 0.05 g, 0.1 g, 0.25 g, and 0.5 g. Calculated concentrations of Gd₂O₃ in the dry sand mixtures are 0 ppm, 17 ppm, 33,67 ppm, 167 ppm, and 333 ppm, respectively. The quartz sand and Gd₂O₃ powder were thoroughly mixed to ensure a homogeneous distribution of gadolinium within the container. Two types of targets were considered: one with the dry sand and one with the wet sand. Each target was irradiated five times,



and data were collected during the intervals between neutron pulses (Figure 4.5).

Figure 4.5: The time spectrum of neutron pulses is shown, with data collected during the intervals between two pulses. The time between pulses was 50 μ s, while the frequency was 10 kHz.

The neutron beam intensity varied between measurements, averaging approximately 10^6 n/s in 4π . Since all measurements were normalized to the same number of emitted alpha particles, the duration of individual measurements ranged from 53 to 85 minutes, depending on the neutron beam intensity (60 minutes for $I \sim 10^6$ n/s). The alpha detector used was a YAP:Ce scintillator, 1 mm thick and 4 cm in diameter, mounted on a sapphire window attached to a CF63 flange. One side of the scintillator was coated with a silver layer 1 mg/cm² thick. The scintillator was placed 21 cm away from the tritium target at an angle of 53° relative to the incident deuteron beam. The YAP:Ce scintillator was coupled to a Hamamatsu R1450 photomultiplier tube with a 1.9 cm diameter. The YAP:Ce scintillator was used to normalize all measurements to the same number of emitted alpha particles. The gamma detector used was a 3" × 3" BGO crystal, protected from thermal neutrons by a 2 cm thick layer of borated rubber.

The electronics was set in the same manner as in the PFTNA measurement of chlorine and water cut in crude oil (Figure 2.39). Figure 4.6 shows the gamma-ray spectra of dry quartz sand and the background (with the target removed). The spectra are dominated by a gamma-ray with an energy of 2.22 MeV, emitted by hydrogen (from the paraffin wax) following thermal neutron capture. Peaks corresponding to ²⁸Si are also present; silicon emits two intense gamma-rays with energies of 3.5 MeV and 4.9 MeV after capturing



Figure 4.6: The gamma-ray spectra of the background (with the target removed) and pure dry quartz sand are shown.

thermal neutrons. The background gamma-ray spectrum, recorded with the neutron beam turned off, is shown in Figure 4.7. This spectrum is dominated by gamma-rays with energies below 2.5 MeV, a fact that becomes important when determining the minimum detection limit (MDL). It is important to note that during measurements, the gamma detector registers not only gamma-rays produced in the irradiated sample by thermal neutron capture but also natural radioactivity (mainly from the decay chains of ⁴⁰K, ²³⁸U, and ²³²Th [111])) and gamma-rays resulting from the activation of the surroundings. Since the neutron beam intensity fluctuates, the collected background is not constant, as the duration of individual measurements varies.

After collecting the gamma-ray spectra for each concentration of Gd_2O_3 , the net counts were determined by comparing the number of counts in pure quartz sand with those in the mixtures across three distinct energy regions. Subsequently, the minimum detection limits (MDLs) were calculated for each energy region for both dry and wet sand.

4.2.2 Results and discussion

Typical gamma-ray spectra for different concentrations of Gd_2O_3 are shown in Figure 4.9. Due to the energy resolution of the BGO detector used, individual gamma-rays emitted by Gd cannot be resolved; instead, an excess of events is observed in specific regions of the spectrum compared to the sample without Gd. The majority of gamma-rays are emitted



Figure 4.7: The gamma-ray spectra of the background (neutron beam off). Prominent peaks belong to the decay chains of 40 K (1.460 MeV), 238 U (1.76 MeV), and 232 Th (2.61 MeV).



Figure 4.8: The gamma-ray spectra of a sample with the same concentration of Gd_2O_3 (17 ppm) are shown for different measurement times and same number of detected alphas. Note the excess of events in the energy region below 1.6 MeV.

in the region below 2 MeV, but a noticeable difference is also observed above 2.5 MeV. Three distinct energy regions ((1.0-1.2) MeV, (0.6-1.3) MeV, and (2.55-3.3) MeV) of the spectrum were selected, and the net number of counts was calculated relative to the pure SiO_2 sample.

The Tables 4.1-4.3 present the net gamma-ray counts measured for different concentrations of Gd_2O_3 in both wet and dry sand samples across various energy regions. The symbols N_W and N_D represent the measured gamma-ray counts for wet and dry sand samples,



Figure 4.9: The gamma-ray spectra of the samples with a Gd_2O_3 concentrations of 333 ppm (top) and 17 ppm (bottom). Energy regions selected for net calculations of the number of counts are (1.0-1.2) MeV, (0.6-1.3) MeV, and (2.55-3.3) MeV.

respectively, while N_{0W} and N_{0D} correspond to the background counts for wet and dry sand without Gd₂O₃ (0 ppm concentration). The net counts, $N_W - N_{0W}$ and $N_D - N_{0D}$, are obtained by subtracting the background counts from the measured counts. The results are provided for increasing Gd₂O₃ concentrations, ranging from 0 to 333 ppm, and the values highlighted in red are the ones used in L_C and L_D calculations. The results from

Conc. (ppm)	$N_{\rm W} - N_{0{\rm W}}$	$N_{\rm D} - N_{0{\rm D}}$	
0	0 ± 1196	0 ± 1083	
17	1923 ± 1108	3937 ± 1942	
33	6042 ± 1303	5225 ± 1724	
67	8122 ± 971	8443 ± 1727	
167	15602 ± 1205	18004 ± 1202	
333	25378 ± 1316	29831 ± 858	

Table 4.1: Measured gamma-ray net counts in the energy region 1 for different concentrations of Gd_2O_3 .

Table 4.2: Measured gamma-ray net counts in the energy region 2 for different concentrations of Gd_2O_3 .

Conc. (ppm)	$N_{\rm W} - N_{0{\rm W}}$	$N_{\rm D} - N_{0{\rm D}}$
0	0 ± 5375	0 ± 7512
17	5100 ± 4882	14158 ± 10479
33	22330 ± 4533	17623 ± 8909
67	26761 ± 4713	26682 ± 8603
167	53971 ± 6537	59994 ± 7253
333	88402 ± 7203	101479 ± 5670

Table 4.3: Measured gamma-ray net counts in the energy region 3 for different concentrations of Gd_2O_3 .

Conc. (ppm)	$N_{\rm W} - N_{0{\rm W}}$	$N_{\rm D} - N_{0{\rm D}}$
0	0 ± 470	0 ± 512
17	1839 ± 590	1811 ± 695
33	4912 ± 449	4885 ± 580
67	7911 ± 707	8689 ± 493
167	15608 ± 866	17855 ± 513
333	23419 ± 1198	28349 ± 628

the tables are presented in Figure 4.10, which shows the net gamma-ray counts as a function of Gd_2O_3 concentrations for wet and dry samples across different energy regions.



(C) Energy region 3.

Figure 4.10: Calibration curves of net gamma-ray counts as a function of Gd_2O_3 concentration for wet and dry sand samples.

The data are fitted using the calibration function $a(1 - \exp(-b \cdot x))$, where a and b are fitting parameters, and x represents the Gd concentration. In all three graphs, the gammaray counts increase with increasing Gd concentration, reflecting the enhanced neutron capture by gadolinium. However, the curves exhibit a clear saturation effect at higher concentrations, where the increase in gamma-ray counts slows down.

Similar to the case of chlorine detection in crude oil (Figure 2.45), this saturation occurs because the probability of neutron capture by gadolinium becomes limited by the finite number of available thermal neutrons. At low concentrations, the relationship between counts and concentration is approximately linear, as neutron capture events are sparse and unaffected by competing absorption processes. As the Gd concentration increases, the neutron flux is progressively reduced due to self-shielding, where gadolinium nuclei increasingly absorb the neutrons, leaving fewer available for further capture events. This effect is more pronounced in wet sand samples, where the gamma-ray counts are systematically higher than in wet sand. The difference arises because water in wet sand attenuates neutrons (absorption by hydrogen), reducing the overall neutron flux available for interaction with gadolinium.

The minimum detection limits were calculated using the same procedure as in Section 2.6.2. However, instead of the α'_{Cl} parameter, the values of $N_{\rm W} - N_{0\rm W}$ and $N_{\rm D} - N_{0\rm D}$ for 0 ppm concentration (highlighted in red in Tables 4.1–4.3) were used in the L_C and L_D calculations. Finally, calculated detection limits L_D were plugged into the calibration curves shown in Figure 4.10 to obtain the MDLs for Gd₂O₃, shown in Table 4.4.

Energy region	MDL_W (ppm)		$\mathrm{MDL}_{\mathrm{D}}$	(ppm)
	$\mathbf{Gd}_2\mathbf{O}_3$	Gd	$\mathbf{Gd}_2\mathbf{O}_3$	Gd
1	31 ± 9	27 ± 8	26 ± 7	27 ± 6
2	41 ± 14	36 ± 12	57 ± 21	49 ± 18
3	12 ± 1	10 ± 1	12 ± 1	10 ± 1

Table 4.4: Minimum detection limits (MDL) for Gd_2O_3 and Gd in wet and dry conditions across different energy regions.

To determine the MDLs for gadolinium from the MDLs of Gd_2O_3 , a simple proportional conversion is used based on the relative molar masses of Gd and Gd_2O_3 :

$$\mathrm{MDL}_{\mathrm{Gd}} = \mathrm{MDL}_{\mathrm{Gd}_2\mathrm{O}_3} \times \frac{2\,M_{\mathrm{Gd}}}{M_{\mathrm{Gd}_2\mathrm{O}_3}} \tag{4.1}$$

where M_{Gd} and $M_{\text{Gd}_2\text{O}_3}$ are molar masses of gadolinium (157.25 g/mol) and gadolinium (III) oxide (362.5 g/mol), respectively.

The results in the tables show that the MDL is consistently smallest in the third energy region compared to the first two regions. This can be attributed to the influence of natural background radiation in the lower energy regions, which increases the noise in the measurements.

In the first two energy regions, natural gamma-ray background, originating primarily from the decay of ⁴⁰K, ²³⁸U, and ²³²Th, interferes with the signal. These background sources emit gamma-rays predominantly in the energy range below 2.5 MeV, overlapping with the measured signal from gadolinium (notably ¹⁵⁷Gd). As a result, the net signal-tobackground ratio is lower in these regions, which increases the uncertainty and raises the MDL. In contrast, the third energy region lies above the significant background contribution. With less interference from natural sources, the signal from gadolinium becomes more distinct and thus lowers the MDL.

Given that gadolinium concentrations of 68 ± 2 ppm in the Pacific Ocean and 39 ± 2 ppm in the Indian Ocean indicate REE-rich deposits (REE > 1000 ppm) [108, 109], we conclude that such concentrations can be detected using the active method by analyzing energy region 3 [(2.55-3.3) MeV]. Although the required measurement time is relatively long, approximately 60 minutes, this is primarily due to the low intensity of the neutron beam used in the experiment, around 10^6 n/s. Modern portable neutron generators can easily reach intensities of 10^8 n/s, or even 10^{10} n/s, significantly reducing the required measurement time in real-world applications.

4.3 Shielding for passive detection of lutetium

In the study presented in [96], it was demonstrated that lutetium can be detected through passive measurement of its natural radiation. However, the required measurement times were significantly long, which highlighted the need for improvements to reduce the overall duration of the detection process. To address this challenge, a shielding system was designed to minimize background radiation and thus shorten the measurement times.
For this purpose, lead was selected as the shielding material due to its high attenuation capability for gamma-rays. The available lead sheets varied in thickness, necessitating an investigation into the optimal thickness that would provide sufficient attenuation while avoiding unnecessary material usage and excess weight.



Figure 4.11: Experimentally obtained 137 Cs spectrum (no lead shielding present) used as an input source for MCNP6.2 simulations.

To evaluate the effect of different lead thicknesses, Monte Carlo (MC) simulations were performed using MCNP6.2 to simulate gamma-ray spectra from a cesium source at various shielding configurations. Cesium-137 was chosen as the reference source because its gamma-ray energy (662 keV) is comparable to that of lutetium's natural radiation gammapeaks (201.8 keV and 306.8 keV) and falls within the same order of magnitude. The input source for the MC simulations was defined using a histogram H-D distribution obtained from experimental measurements of cesium with a germanium detector in an unshielded configuration (Figure 4.11). The source was modeled not as a point source, but rather as a circular disc source with a diameter of 7.62 cm. The spectra were collected using an F8 tally to record the energy deposition within the simulated germanium detector (used in the experiment).

The simulated geometry consisted of a cesium source placed 6 cm away from the germanium crystal, which was modeled as a cylindrical volume with dimensions of 7.62 cm in diameter and 7.62 centimeters in height, composed of natural germanium. Source particles were pointed perpendicular to the base of the germanium cylinder. The lead shielding was positioned between the source and the detector, with varying thicknesses of 0.8 cm, 1.2 cm, 3 cm, and 5 cm. Evaluating multiple thicknesses is essential for determining the optimal balance between gamma-ray attenuation and the practicality of constructing the shield. Insufficient shielding may fail to significantly reduce the background noise, while excessive shielding can introduce practical challenges such as increased weight and spatial constraints.

The attenuation of gamma-ray intensity as it passes through a shielding material can be described by the following exponential attenuation formula:

$$I = I_0 e^{-\mu x}$$

where I represents the intensity of the gamma-rays after passing through the shielding material, I_0 is the initial intensity (with no shielding), μ is the linear attenuation coefficient (in units of cm⁻¹), and x is the thickness of the shielding material (in cm). Since the measured number of counts N in the gamma-ray peak region is proportional to the intensity of the gamma-rays, the formula can be rewritten in terms of the normalized number of counts:

$$\frac{N}{N_0} = y = e^{-\mu x}$$

where N_0 represents the number of counts in the peak when no shielding is present, and N represents the number of counts after the gamma-ray has passed through a shielding layer of thickness x. The left-hand side of the equation is the **normalized count rate**, which can be used as a direct proxy for the relative intensity. After obtaining the MC spectra for different shielding thicknesses (Figure 4.12), a Gaussian function was fitted to the gamma-ray peak in the spectrum without shielding to accurately determine the peak position and the spread of the peak. The Gaussian function is defined as:

$$f(E) = A \exp\left(-\frac{(E - E_0)^2}{2\sigma^2}\right)$$

where f(E) represents the count rate as a function of energy E, A is the amplitude of the peak, E_0 is the centroid of the peak (in this case, 662 keV, corresponding to the characteristic energy of cesium-137), and σ is the standard deviation of the distribution,



Figure 4.12: The cesium peak obtained from MC simulations for different lead shielding thicknesses was analyzed by normalizing the counts within the defined peak window. This peak window was determined based on the Gaussian fit of the spectrum in the "no shield" case.

which defines the width of the peak. In this analysis, the Gaussian fit yielded a centroid $E_0 = 662$ keV and a standard deviation $\sigma = 3$ keV. Based on this fit, a peak window was constructed, centered around 662 keV, with bounds chosen to capture the peak area within 1σ interval from the centroid. The number of counts within this peak window was evaluated for each shielding thickness and normalized relative to the number of counts for the unshielded case (Table 4.5).

Lead Thickness (cm)	Normalized Counts	
0	1 ± 0.003	
0.8	0.392 ± 0.001	
1.2	0.246 ± 0.001	
3	0.0299 ± 0.0003	
5	0.0023 ± 0.0001	

Table 4.5: Normalized counts for different lead thicknesses-simulations.

Figure 4.13 shows the exponential fit of the data presented in Table 4.5, with a linear attenuation coefficient of 1.170 cm^{-1} . The results indicate that for 5 cm of lead, the



Figure 4.13: Attenuation of the 662 keV gamma-ray with different lead thickness with exponential fit-simulations.

662 keV gamma-ray is attenuated by approximately 99.77%. This lead thickness was the maximum that could be achieved experimentally in the laboratory and demonstrates significant attenuation of the 662 keV gamma-ray. Gamma-rays with lower energies, such as those emitted by natural lutetium, were expected to undergo even greater attenuation, as lower-energy gamma-rays are more effectively attenuated [112].

To experimentally verify how different lead thicknesses attenuate the 662 keV gamma-ray, lead sheets and bricks of varying thickness were placed in front of the detector's end cap, where the active germanium crystal is positioned near the cap. A cesium source was then placed in front of the lead sheets, and 4-minute measurements were conducted for each configuration (Figure 4.14).

The gamma spectra for different lead shielding thicknesses are presented in Figure 4.15. The procedure for peak analysis was identical to that used in the simulations, and the corresponding results are shown in Table 4.6 and Figure 4.16. The linear attenuation coefficient obtained from the experimental measurements was slightly lower than that from the simulations ($\mu = 0.975 \text{ cm}^{-1}$). This discrepancy is attributed to the inconsistency in the lead sheets, which were folded to achieve the desired thickness, leading to approximate rather than precise thicknesses, particularly for the thinner sheets (Figure 4.14). However,





(A) No lead shielding

(B) 0.8 cm lead shielding

Figure 4.14: Cesium source placed near the end cap of the detector, with and without lead sheets.

the attenuation observed for the 5 cm lead brick was consistent with the simulation results, showing a reduction of 99.59%.



Figure 4.15: The cesium peak obtained from the experiments for different lead shielding thicknesses was analyzed by normalizing the counts within the defined peak window, consistent with the one used in the simulations.

Therefore, lead shielding was designed to enclose the detector capsule with 5 cm of lead on all sides (Figure 4.17). For this purpose, a hollow lead cylinder with a 5 cm wall thickness

Lead Thickness (cm)	Normalized Counts	
0	1 ± 0.003	
0.8	0.659 ± 0.002	
1.2	0.359 ± 0.001	
3	0.0310 ± 0.0004	
5	0.0041 ± 0.0001	

Table 4.6: Normalized counts for different lead thicknesses-experiment.



Figure 4.16: Attenuation of the 662 keV gamma-ray with different lead thickness with exponential fit-experiments.

was constructed to enclose the detector capsule along its symmetry axis. Additional 5 cm thick lead bricks were placed in front of the detector's end cap . The entire assembly was mounted on 0.5 cm thick iron sheets to provide additional shielding from gamma-rays originating from the ground.

Alternatively, iron and concrete could be considered as background shielding in practical applications. Their primary advantage over lead is their non-toxicity. However, as demonstrated in [113], their linear attenuation coefficients are significantly lower than that of lead. In practice, this would result in a substantial increase in the required shielding volume to achieve the same level of attenuation.



Figure 4.17: Gamma spectra used in least-squares fitting.

4.4 Passive detection of lutetium

4.4.1 Experimental setup and procedures

Figure 4.18 shows the front view of the experimental setup used for gamma-ray detection. The gamma-ray detector employed was a Standard Electrode Coaxial Germanium (Ge) detector with an efficiency of 20% at 1.33 MeV (relative to 3 in. by 3 in. NaI) [114] and an outer cap diameter of 76 mm. This type of detector was chosen due to its superior energy resolution, which allows for precisely identifying closely spaced gamma-rays from the lutetium. To minimize the influence of background radiation, the detector was placed inside a shield composed of 5 cm thick lead and iron plates placed on the stand. This shielding configuration significantly reduced the detector's count rate to below 2 Hz, demonstrating a substantial decrease in the background radiation level, which is crucial for detecting weak signals associated with rare isotopes.

The gamma-ray background spectrum is presented in Figure 4.19 and reveals characteristic peaks corresponding to isotopes from the uranium and thorium decay chains, as well as K_x lines originating from the lead in the shield. The presence of uranium (²³⁸U) and thorium (²³²Th) decay products indicates natural environmental radioactivity, which is a common source of interference in such measurements. The lead X-ray lines result from the interaction of gamma-rays with the shielding material, contributing additional peaks



Figure 4.18: Gamma spectra of natural lute tium (from $\rm Lu_2O_3),$ uranium-238 (from $\rm U_3O_8),$ thorium-232 (from $\rm ThO_2)$

and background.

to the background spectrum.

In addition to the background spectrum, Figure 4.19 also shows the gamma-ray spectra of natural lutetium (from Lu₂O₃), uranium-238 (from U₃O₈), and thorium-232 (from ThO₂). Natural lutetium consists predominantly of the stable isotope ¹⁷⁵Lu, which accounts for 97.41% of its natural abundance, and the radioactive isotope ¹⁷⁶Lu, which represents 2.59%. The isotope ¹⁷⁶Lu undergoes β^- decay with an exceptionally long half-life of 3.73×10^{10} years, decaying into ¹⁷⁶Hf. The newly formed ¹⁷⁶Hf is initially in an excited state and subsequently relaxes to its ground state by emitting characteristic gamma-rays. The two most intense gamma-ray lines observed during this process occur at energies of 201.8 keV and 306.8 keV. These prominent lines serve as a signature of the presence of ¹⁷⁶Lu.

A total of eight measurements were conducted for eight different lutetium concentrations in the sample. The samples (Figure 4.20) were prepared using 160 g of quartz sand and varying amounts of Lu_2O_3 powder, mixed in a small plastic container. The components were thoroughly mixed to ensure a homogeneous distribution of lutetium throughout the sample. Each gamma-ray spectrum was fitted under the assumption that it consists of four distinct contributions: background radiation, lutetium, uranium, and thorium. The fitting was performed using:



Figure 4.19: Experimental setup (front view) for passive measurement of lutetium. Image shows the target holder, placed in front of the end cap of the detector. After the target was placed, an additional 5 cm thick lead brick was placed in front.



Figure 4.20: Samples of Lu₂O₃ mixed with quartz sand from the Adriatic Sea.

$$\chi^{2} = \sum_{i=1}^{m} \frac{\left(\alpha_{\mathrm{Lu}} R_{\mathrm{Lu},i} + \alpha_{\mathrm{U}} R_{\mathrm{U},i} + \alpha_{\mathrm{Th}} R_{\mathrm{Th},i} + \alpha_{\mathrm{bac}} R_{\mathrm{bac},i} - \frac{R_{s,i}}{\sum_{i=1}^{m} R_{s,i}}\right)^{2}}{(m-n) \left(\frac{R_{s,i}}{\sum_{i=1}^{m} R_{s,i}}\right)^{2}}$$
(4.2)

where the parameters α_{Lu} , α_{Th} , α_{U} , and α_{bac} correspond to the respective contributions. Summation was done from the minimum to the maximum channel. These parameters were determined using the χ^2 minimization method to achieve the best fit to the experimental data, and the lutetium parameter α_{Lu} was used for MDL calculation.

4.4.2 Results and discussion

Figure 4.21 presents the gamma-ray spectra along with the corresponding fitting curves for two different lutetium concentrations in the sample. To compare the results and measurement times with [96], the measurements were performed for a duration sufficient to achieve a 3σ confidence level for lutetium detection. The characteristic lutetium peaks at 201.8 keV and 306.8 keV are clearly visible at higher lutetium concentrations, while these peaks are indistinguishable from background at lower concentrations. Nevertheless, even for low concentrations, the presence of lutetium was successfully detected (Table 4.7). Table 4.7 also lists the measurement times required to achieve at least 3σ precision in lutetium detection. Compared to [96], a significant reduction in measurement time is evident. For example, in [96], 131 hours were necessary to detect 2.56 ppm of lutetium in the sample. In contrast, in this experiment, only about 69 hours were sufficient to detect a smaller concentration of 1.71 ppm. This improvement is attributed to the optimized shielding design used in this study, which more effectively blocks background radiation and reduces noise.

Lu_2O_3 Mass / Lu Concentration (mg/ppm)	$lpha_{ m Lu}$	Measuring Time (h)
0/0	0.0007 ± 0.00044	49.87
$0.3 \ / \ 1.71$	0.0020 ± 0.0004	69.49
$0.6 \ / \ 3.48$	0.00194 ± 0.000455	45.83
1.0 / 5.43	0.0031 ± 0.0004	48.48
3.18 / 17.15	0.0064 ± 0.0007	21.92
$5.43 \ / \ 29.09$	0.0088 ± 0.0007	23.38
7.12 / 38.44	0.0128 ± 0.0008	24.04
20.68 / 112.03	0.0350 ± 0.0009	24.14

Table 4.7: Values of lutetium fitting parameters for different concentrations of lutetium. Measurement times were provided in hours.

Lutetium parameters α_{Lu} are presented as a function of lutetium concentrations in Figure 4.22, along with the corresponding linear fit. Unlike the gadolinium measurements, no saturation is observed here, as the sample activities are low and the lutetium concentrations are minimal.



Figure 4.21: The gamma-ray spectra of the samples with a Lu concentration of 112 ppm (top) and 1.7 ppm (bottom), accompanied with χ^2 minimization fitting curves.

Finally, the MDL for lutetium was determined for a 50-hour measurement (the measurement time for the 0 ppm case) using the procedure described in Section 2.6.2. The value of α'_{Lu} , used in the calculations of L_C and L_D , is highlighted in red in Table 4.7. The MDL for lutetium was determined to be (3.8 ± 0.7) ppm. Given that the lutetium concentration of 6.0 ± 0.3 ppm corresponds to rich rare earth element deposits (ERZ > 1000



Figure 4.22: Samples of Lu₂O₃ mixed with quartz sand from the Adriatic Sea.

ppm) in the Pacific Ocean, while the concentration of 2.55 ± 0.29 ppm is typical for deposits in the Indian Ocean, we conclude that these concentrations can be detected using the passive method in the case of the Pacific inside 50 hours. However, in the case of the Indian Ocean, the method would not produce the desired 95% confidence for a 50-hour measurement, and for concentrations lower than that, a longer measurement time would be needed.

There is an additional positive aspect to consider in these results. It is important to note that the passive lutetium measurements described here were performed in a laboratory surrounded by solid ground, which likely contributed to an increase in background radiation levels. If laboratory testing were to be performed at sea, the MDL could be further reduced, as the background radiation in the ocean environment is typically lower than in the lab where these experiments were conducted.

5 Conclusion and future work

This dissertation presents the development and application of neutron-based detection methods for detection of crude oil, methane hydrate and rare-earth elements. The main goal was to investigate how interactions of 14 MeV neutrons with matter and gamma-ray spectroscopy could be used in detection of valuable resources - crude oil, methane hydrate and rare-earth elements.

A major focus of this work was the Associated Alpha Particle (AAP) method, which was demonstrated as a powerful tool for elemental analysis, particularly in environments where traditional neutron activation methods suffer from excessive background noise. The AAP method allows for electronic collimation of the neutron beam, significantly improving signal-to-noise ratios in elemental detection applications.

In the case of crude oil detection, this study successfully demonstrated that AAP-based Carbon-to-Oxygen (C/O) logging sensor can improve the accuracy of hydrocarbon identification in borehole environments [2]. Unlike conventional Fast Neutron Activation Analysis (FNAA), which struggles with background signals from borehole fluids and surrounding rock formations, the AAP-based approach provided a significant reduction in background radiation. The experimental results presented in this work demonstrated that by tagging neutrons in the 14 MeV D-T reaction, it was possible to selectively enhance signals from the target formation. This allows, in principle, for more precise determination of oil saturation levels, even in freshwater oil fields, where traditional sigma logging methods are ineffective.

A neutron probe was designed to compactify the AAP experimental apparatus, integrating key components—including a LaBr₃:Ce gamma detector, a YAP:Ce alpha detector, and their respective photomultipliers—inside a single shielded probe casing [1]. The primary motivation for constructing this probe was to create a field-deployable system while ensuring that all detectors and electronics could operate reliably in high-temperature environments, such as boreholes and deep-sea methane hydrate formations.

To assess the probe's performance under high-temperature conditions, controlled laboratory tests were conducted by gradually increasing the ambient temperature while monitoring detector stability, gain shifts, and signal integrity. Measurements at high temperatures revealed a significant reduction in signal amplitude from the gamma-ray detector, with a nearly 60% decrease observed at 160°C. Additionally, the energy resolution at 1.436 MeV deteriorated from 6.5% at 25°C to 12% at 160°C, indicating a substantial decline in spectral performance. While a similar degradation in signal amplitude was also observed in the alpha detector, the effect was less pronounced. Furthermore, the time resolution exhibited a decline of approximately 20% at elevated temperatures, indicating the deterioration of the probe's spatial resolution. Furthermore, the temporal and spatial resolution of the neutron probe was assessed through both experiment and Monte Carlo simulations, demonstrating a spatial resolution of approximately 10 cm [73], a significant improvement over conventional logging techniques, which can rarely resolve formations thinner than half a meter [64].

The neutron probe was equipped with a pulsing system, allowing for Pulsed Fast-Thermal Neutron Activation analysis (PFTNA), which was employed in this study to detect chlorine and water content in crude oil [29]. By measuring gamma-rays in the intervals between neutron pulses with BaF₂ detector, it was possible to determine the minimum detection limits (MDL) for these key components. The results indicate that the MDL for chlorine content was found to be (62 ± 6) ppm, while for water content, the detection limit was (2 ± 2) vol.%. Given that crude oil intended for export must contain less than 50 mg/L of salt and no more than 0.5 vol.% of water [67], the results demonstrate that the neutron probe can accurately detect chlorine concentrations near this threshold. However, the MDL for water content remains inconclusive due to the large relative error, which arose from the inability to produce stable emulsions with low water content during the experiments. Additionally, it is important to note that chlorine was not homogeneously dispersed in the oil, which could affect detection accuracy. Monte Carlo simulations indicate that such homogeneous distribution could negatively impact the chlorine MDL in this setup. To mitigate this effect, a more isotropic thermal neutron source would be required to ensure uniform neutron interaction throughout the sample.

Future research should focus on refining AAP-based methodologies to achieve higher spatial resolution while also emphasizing field testing of the neutron probe under real-world conditions. Additionally, efforts should be directed toward further reducing the size of the probe by replacing the large TNC accelerator with a more compact neutron generator as the source. Implementing a variable pulsing system would further enhance the probe's functionality, enabling the simultaneous detection of chlorine and water content by adjusting pulsing frequencies within a single measurement.

An AAP-based sensor, with API-120 as a neutron source, was applied to methane hydrate detection, a topic of increasing relevance in energy resource exploration and climate change mitigation. Methane hydrates represent a vast but largely untapped energy source, found on the ocean floors and in the permafrost [77, 80], and their accurate quantification is essential for both resource assessment and environmental monitoring [86, 88]. The experimental results demonstrated that inelastic neutron scattering on carbon atoms present in the methane hydrate provides a reliable signature for methane hydrate presence.

The calibration line between methane hydrate saturation and the net number of counts in the carbon window was established, with an experimentally obtained minimum detection limit (MDL) of $(67 \pm 25)\%$. Relative error of the MDL is large, and the main value suggests that this level of detection is insufficient even for high-saturation methane hydrate formations, such as those found off the coast of Alaska [89]. Relative error could be reduced by irradiating more samples, and consequently obtaining more precise calibration lines. Future research will focus on using a higher-flux neutron generator to further reduce the mean of the MDL, as well as conducting experiments under more realistic conditions. Monte Carlo simulations were utilized to compare calibration lines and develop a simulation model that, with appropriate corrections, can be used in future studies to predict measurement outcomes and optimize experimental conditions. This model could prove particularly valuable in refining the setup before deploying a remotely operated vehicle (ROV) to the ocean floor for in-situ measurements. The simulations showed a discrepancy in calibration slope compared to experimental data, largely due to the imperfections in the geometry and material definitions and future work should aim to refine these parameters. The last major focus of this work was the detection of technologically valuable rare earth elements (REEs) [98, 101], particularly gadolinium and lutetium, using both active (gadolinium) and passive (lutetium) methods. The concentrations of these elements have been shown to serve as reliable indicators of the total concentration of rare earth elements on the ocean floor in the Indian and Pacific Oceans [108, 109].

For gadolinium detection, an active neutron-based approach was employed, leveraging the exceptionally high neutron capture cross-section of ¹⁵⁷Gd. The results confirmed that the PFTNA technique can be used to reliably detect gadolinium concentrations even in low-concentration samples, with an experimentally achieved MDL of 12 ± 1 ppm in the gamma-energy region (2.55–3.3 MeV). This detection limit is sufficient for identifying gadolinium concentrations in both the Pacific (68 ± 2 ppm) [108] and Indian (39 ± 2 ppm) Oceans [109].

To complement the findings on gadolinium, the detection of lutetium was performed using passive gamma-ray spectroscopy, focusing on the measurement of ¹⁷⁶Lu gamma lines at 202 keV and 307 keV. Monte Carlo simulations were used to optimize lead shielding, minimizing the influence of unwanted background radiation. The active part of the germanium detector was enclosed within a 5 cm lead shield to enhance detection sensitivity. The MDL for lutetium after a 50-hour passive measurement was found to be $(3.8 \pm 0.7 \text{ ppm})$, which is lower than the lutetium concentration in the Pacific Ocean $(6.0 \pm 0.3 \text{ ppm})$ [108] but higher than that in the Indian Ocean $(2.55 \pm 0.29 \text{ ppm})$ [109]. Achieving the same 95% confidence level for Indian Ocean concentrations would require a longer measurement time. This detection limit could be further reduced if testing were conducted at sea, as the natural background radiation in the ocean environment is generally lower than in a laboratory setting.. Future efforts will be directed toward developing a compact sensor designed to fit within a small ROV, enabling its deployment to the ocean floor for the active detection of gadolinium.

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