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Full Length Article

Development of a method for on-line determination of chlorine impurity in crude oil by using fast neutrons

Hao Ping Chang [a,*], Ilker Meric [a,b,c], Davorin Sudac [c], Karlo Nađ [c], Jasmina Obhođaš [c], Robin P. Gardner [a]

[a] Center for Engineering Applications of Radioisotopes (CEAR), North Carolina State University, Raleigh, NC 27695-7909, United States
[b] Department of Electrical Engineering, Western Norway University of Applied Sciences, Inndalsveien 28, Bergen, Norway
[c] Ruder Boskovic Institute, Bijenička c. 54, 10000 Zagreb, Croatia

HIGHLIGHTS

- A proof of principle measurement system for on-line monitoring of chlorine impurity in crude oil was developed.
- 14 MeV neutrons have been used for analyzing chlorine content in fuel oil samples.
- Simulation models were implemented using MCNP6 and CEARCPG for design optimization of the measurement set-up.
- The chlorine impurity detection limit achieved in this research was 71 mg/L.

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ABSTRACT

An important challenge in the petroleum industry is to reduce the salt content to acceptable levels in crude oil. Continuous monitoring of crude oil salinity is thus an important aspect. However, development of safe and reliable on-line and non-intrusive monitoring systems is still a challenging task. In this work, a method for non-intrusive, on-line monitoring of the chlorine impurity in crude oil based on prompt gamma-ray neutron activation analysis (PGNAA) in conjunction with a portable pulsed neutron generator producing 14 MeV neutrons in deuterium-tritium (DT) nuclear reactions is proposed and tested. Simulations with Monte Carlo N-Particle version 6 (MCNP6) transport code combined with Center for Engineering Applications of Radioisotopes Detector Response Function (CEARDRF) and a specific purpose Monte Carlo code called Center for Engineering Applications of Radioisotopes Coincidence Prompt Gamma-Ray (CEARCPG) were used for the design optimization of the experiments. Preliminary results indicate that a minimum detection limit for chlorine impurity of about 71 mg/L is achievable for an integration time of 30 min.

1. Introduction

It is a well-known fact that crude oils contain various amounts of undesirable impurities including water, salt, sand, drilling mud, minerals, trace elements, etc. prior to the refining processes. Of these, salts represent a major challenge in the sense that they can cause corrosion in the pipelines and other equipment. Furthermore, byproducts of corrosion such as particulates of iron sulfides and oxides can cause pipe plugging and fouling. More important, the crude oil containing high salt concentrations will cause formation of hydrogen chloride gas and subsequently formation of liquid hydrochloric acid resulting in heavy corrosion of equipment. Thus, an oil desalting system is needed prior to the refinery processing, and the overall salt content in crude oil has to be monitored in the entire production system [1] to keep the salt content in crude oil below the standard concentration of 20 lbm per thousand barrels [2] (approximate concentration of 35 mg/L chlorine in crude oil). The overall concentration of salt in crude oil depends on the producing well and geological conditions in different oilfields [3,4]. Typical inorganic salts in crude oil include sodium, magnesium, and calcium chlorides that are dissolved in small water droplets diffused in crude oil. Hence, determination of salt content in crude oil can be reduced to determination of chlorine.

In order to monitor the overall salt content in crude oil samples, various techniques have already been developed. These include infrared (IR) spectroscopy, silver nitrate titration with chromate indicator (Mohr's method), electrometric and emulsion treating methods [1,3–5]. Although these methods are widely utilized and provide reliable information, they are off-line methods requiring tedious sample preparation.

* Corresponding author.

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In this work, the focus is on on-line and non-intrusive measurements. For this purpose the application of prompt gamma-ray neutron activation analysis (PGNAA) is proposed for the determination of chlorine content of crude oil samples in conjunction with a pulsed DT neutron generator emitting 14 MeV neutrons. Fast neutrons are not very efficient for determination of the chlorine content, however chlorine thermal neutron capture cross section is one of the highest in the periodic table of elements (35.5 barns in thermal neutron energy range 0–0.026 eV). Thus, fast neutrons need to be thermalized for PGNAA in conjunction with DT neutron generator to be applicable for the determination of chlorine concentration. On the other hand, it should be pointed out that fast neutrons are very efficient for oxygen and carbon content determination due to neutron inelastic scattering events. This makes pulsed DT neutron generator a promising tool for on-line monitoring of both chlorine and the water content in crude oil. However, in this work, the focus was on chlorine determination and the method may be further developed for simultaneous analysis of oxygen.

The application of PGNAA for the determination chlorine impurity concentrations in crude oil is justified by its successful utilization in various applications, including on-line and non-intrusive analysis of bulk samples in industry, security sector and especially in oil industry [6,7]. Several radioisotope neutron sources have been used in industry such as spontaneous fission Cf-252 (Californium) source, and alpha-neutron sources Am-Be (Americium-Beryllium) and Pu-Be (Plutonium-Beryllium) which have long half-lives. However, the replacement of radiological neutron sources with accelerator driven neutron sources is a long term goal promoted worldwide [8]. Accelerators are safer in terms of radiological protection and nuclear proliferation. These factors along with portability and relatively simple set-up, justify the use of a neutron generator for on-line monitoring of chlorine content in crude oils. It should also be noted that, to the best of the authors' knowledge, this is the first time the application of the PGNAA technique in conjunction with a pulsed neutron generator is proposed and tested for the purposes of determining the chlorine impurity in crude oil samples.

2. Methods

2.1. Simulation tools

Monte Carlo N-particle code version 6 (MCNP6) [9], Center for Engineering Applications of Radioisotopes Detector Response Function (CEARDRF) and Center for Engineering Applications of Radioisotopes Coincidence Prompt Gamma-Ray (CEARCPG) were the Monte Carlo (MC) codes used in this work for the design optimization of the measurement system. The results of simulations were compared to the experimental results. MCNP6 was used to generate neutron flux spatial distribution maps and detector pulse-height spectra for a total of 10^9 neutron histories. CEARDRF is a MC code that has been developed at Center for Engineering Application of Radioisotopes (CEAR), Raleigh, NC, United States, for generating gamma-ray detector response functions (DRFs) for scintillation detectors [10]. CEARDRF was used to generate the DRFs from 0.00605 to 12.3892 MeV to match the energy range of the experiments. The DRFs pre-computed using CEARDRF were then convoluted with the spectra obtained using the tally type 4 in MCNP6, i.e. the flux averaged over a cell, (F4 card) for photons, to obtain pulse-height spectra [10]. The so-called TMESH tally card, i.e. geometry independent mesh tally, type 1 was used to generate the thermal neutron flux spatial distribution in the sample holder. Default physics options for both neutrons and photons were used. The neutron source was defined as a 14 MeV isotropic, point-like source. CEARCPG simulations were run for 10^7 neutron histories. CEARCPG tracks each prompt gamma-ray until termination by means of absorption or escape. It incorporates also DRFs, thus producing realistic prompt gamma-ray spectra as its output. In this work, CEARCPG was utilized to generate elemental prompt gamma-ray libraries (or spectra) [11] which were then used to calculate the total prompt gamma-ray spectra of the samples of interest.

Two separate simulation models were considered. Each consisted of a 14 MeV neutron source, small or large sample holder, and $3'' \times 3''$ NaI detector as shown in the Fig. 1. To simplify the modeling, the DT neutron generator was modeled as an isotropic 14 MeV point-like source, and the sample in each case was assumed to be a homogeneous mixture of crude oil, salt and water. The surrounding materials were neglected and only the neutron source, sample mixture, sample container and detector with an aluminum shield were considered in the simulation models.

In the simulations, relatively high salt concentrations were considered in order to evaluate the influence of background on the chlorine prompt gamma-ray peaks. The weight fraction of the sample constituents as modeled in MCNP6 and CEARCPG codes are given in Table 1.

2.2. Experimental system arrangement for chlorine impurity measurements

Two experimental set-ups built at Ruđer Bošković Institute, Zagreb, Croatia, were used for chlorine impurity measurements, one with small cylindrical sample holder, 23×23 cm^2 (Fig. 2 left) and the other with larger cylindrical sample holder, 35×65 cm^2 (Fig. 2 right). In the experiments, diesel fuel was used instead of crude oil. The small sample holder was utilized for the initial testing of the experimental arrangement to reduce the diesel consumption and for avoiding safety issues. The second experimental set-up with large sample holder was used to obtain enhanced thermalization of fast neutrons.

The DT neutron source was Sodern's Genie 16 which gives pulsed neutron beams with pulse durations ranging from 10 μs to 100 ms, with repetition rates from 100 μs to 0.1 s. The generator gives a maximum 14 MeV neutron yield up to $2 \cdot 10^8$ neutron $\cdot s^{-1}$ in 4π. In the experiments described in this paper, a lower neutron intensity of $3 \cdot 10^7$ neutron $\cdot s^{-1}$ was used in order to reduce the intensity of prompt gamma-rays from the activation of the surrounding materials as well as to ensure the stability of the neutron generator. The parameters of neutron generator were set as 80 kV and 20 μAmp, 10 μs pulse width and 100 μs repetition rate (10,000 Hz). These parameters were tailored to the experiments to ensure a high thermal neutron component and to minimize the interference from decay gamma-rays from the possible activation of oxygen. This was confirmed by MC simulations where the ratio between thermal and fast neutron components between pulses were compared for different pulse repetition times. Longer pulse repetition times gave the desired higher ratios. Ideally, longer pulse repetition rates would be needed. However, this is limited by the duty cycle (ratio between the pulse width and repetition time) of neutron generator which must be equal or larger than 10%. The minimum duty cycle was implemented in this work. The integration time was 30 min. In the experimental set-up presented in Fig. 2. left (small sample holder), three $3'' \times 3''$ NaI(Tl) scintillation detectors were placed on the opposite side of the neutron generator. The sample itself acted as a neutron moderator thus minimizing detector activation. In the experimental set-up presented in Fig. 2. right (larger sample holder), two diametrically opposite holes were cut into the sample container, and a plastic tube was placed through the central part of the container from side to side in order to place the neutron generator in the center of the