# IN SITU CHARACTERIZATION OF NORM WASTE FROM THE OIL INDUSTRY

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**Abstract**

In the oil industry, radioactive wastes are generated in the oil production platforms containing natural radionuclides, such as $^{226}Ra$ and $^{228}Ra$, the NORM waste. This waste is mainly in the form of produced water, sludge and scales which should be characterized for the correct final destination. The Brazilian laws establish that the NORM wastes from the oil production must comply with Law 10308 of November 20, 2001, which determine in its article 7, "The disposal of radioactive waste of any kind in the oceanic islands, the continental shelf and the Brazilian territorial waters is prohibited." Therefore, the NORM waste from offshore oil extraction rigs should be transported to onshore facilities. There are two options for the destination of this material: industrial landfill, in the case of activity concentrations are below clearance limits established by Brazilian Nuclear Commission, CNEN; or on the contrary, to intermediate storage facilities, until final disposal is decided. Currently, the oil production companies take samples from the waste and send them to radiometric laboratories in order to evaluate their activity concentration by gamma spectrometry. The complete process takes more than six months to be concluded. Nuclear and Energy Research Institute, IPEN, is making efforts to solve the management problems of NORM waste from oil extraction, including conduct research aiming at characterizing the waste. The objective of the paper is to present the results of in situ characterization of drums containing oil sludge using portable gamma spectrometers.

## 1. INTRODUCTION

Technologically Enhanced Naturally Occurring Radioactive Materials, TENORM, here referred to as NORM waste, are continuously produced in oil production platforms. It is a mixture of waste oil, wastewater, sand and other mineral compounds that accumulates inside pipes, tanks and other equipment of the platform and is produced during the operation, cleaning and maintenance.

This NORM waste is mainly in the form of produced water, sludge and scales mainly constituted by sulphates, carbonates, silicates of alkaline-earth metals (Mg, Ca, Sr and Ba) and lead. The main radionuclides present in this waste are $^{226}Ra$ and $^{228}Ra$ and their concentrations range from 0.2 to 560 kBq $kg^{-1}$, in addition to lower levels of uranium, thorium and lead isotopes.

In Brazil the NORM waste from the oil production must comply with Law 10308 of November 20, 2001, which establishes in its article 7, "The disposal of radioactive waste of any kind in the oceanic islands, the continental shelf and the Brazilian territorial waters is prohibited." [1]. Therefore, the NORM waste from offshore oil extraction rigs should be transported to onshore facilities.

There are two options for the destination of this material: industrial landfills, in the case of activity concentrations are below clearance limits established by Brazilian Nuclear Commission, CNEN [2]; or on the contrary, to intermediate storage facilities, until final disposal is decided. It's worth mentioning that the activity concentrations of the material should be previously determined (NORM waste characterization), since this information will define the type of final disposal.

Currently, characterization programme conducted by the oil production companies takes more than six months to be concluded and includes: sampling from the packages; samples transport to the continent; samples transfer to the analysis laboratory; samples preparation; equilibrium between the radionuclides; the measures; the report issuance; the report submission; and the decision-making.

Nuclear and Energy Research Institute, IPEN, one of the CNEN research centers, conducts research and development work on characterization, treatment, conditioning and final disposal of radioactive waste and is

making efforts to solve the management problems of NORM waste from oil extraction, including conduct research aiming at characterizing the NORM waste.

The development of a new methodology for in situ characterization of NORM waste is promising because it will be able to reduce the time required for decision-making on the destination of the NORM waste. It would reduce the area needed for storage, minimizing the risks associated with storage, and, in addition, it would facilitate the logistics of transferring the NORM waste to the continent. All these consequences directly imply a cost reduction for the process.

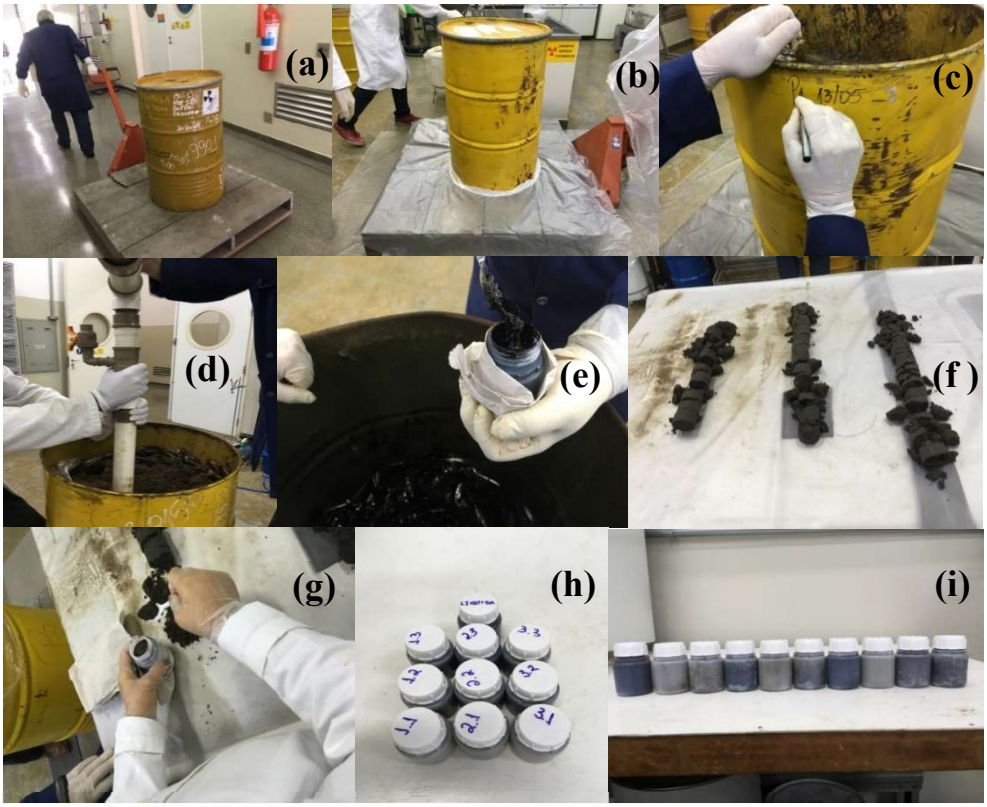
The objective of the paper is to present the results of in situ characterization of drums containing oil sludge and scales, using portable gamma spectrometers.

## 2. METHODOLOGY

All studies for the methodology development were carried out using 12 packages (200 litters drums) containing NORM waste that were selected according to their external dose rate. These drums were transferred from oil production platforms to the Radioactive Waste Department, SEGRR, at IPEN. Each drum was opened and the height of the NORM waste inside the drum was checked and labelled. Ten samples (10 – 15 g) were taken from each drum using auger, spoon or suction depending on the NORM waste characteristics. Some data about the drums and the NORM waste characteristics are presented in Table 1 and some images of sampling procedures one can see in Fig. 1.

TABLE 1. DATA ABOUT PACKAGES CONTAINING NORM WASTE

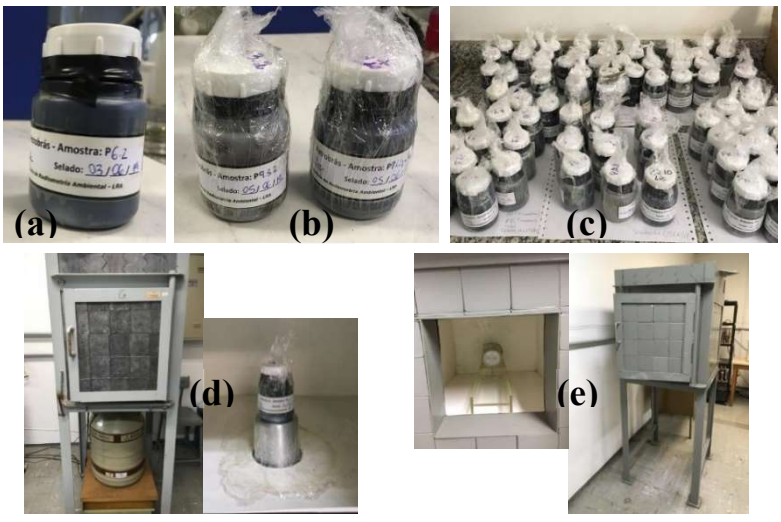
| SEGRR code | Dose rate microSv/h | NORM characteristics | Drum weight (kg) | NORM height (cm) | Sampling |
|---|---|---|---|---|---|
| P1 | 0.4 | Homogeneous and dry. Liquid phase on the bottom. | 284 | 70 | Auger and suction |
| P2 | 0.6 | Homogeneous and sandy. | 197 | 55 | Auger |
| P3 | 0.9 | Oily. Several plastic bags inside the drum and presence of liquid fraction outside the bags. | 169 | 60 | Spoon |
| P4 | 2.4 | Sludge with a lot of oil. Some plastic bags with the solid phase. | 143 | 40 | Spoon and suction |
| P5 | 3.6 | Homogeneous, dry and sandy. Reddish coloring. | 209 | 53 | Auger |
| P6 | 4.0 | Sludge | 128 | 50 | Spoon |
| P7 | 5.0 | Sandy and compacted, with liquid fraction. | 191 | 50 | Auger |
| P8 | 5.7 | Jelly/grease aspect, segregated in several bags. Strong and characteristic sulfur odor. | 160 | 60 | Spoon |
| P9 | 8.6 | Clayey on the surface and sandy in the background. | 249 | 60 | Auger |
| P10 | 8.7 | Homogeneous and sandy. Liquid phase on the bottom. | 221 | 43 | Auger |
| P11 | 10.9 | Clayey and very compacted. | 166 | 60 | Spoon |
| P12 | 15.8 | Sandy with supernatant liquid. | 309 | 39 | Auger |




**(a)** drum transfer; **(b)** drum positioning; **(c)** drum identification; **(d)** auger sampling; **(e)** spoon sampling; **(f)** samples from auger sampling; **(g)** samples transfer to measurement vials; **(h) and (i)** samples from drum P1.

*FIG. 1. Sampling of NORM waste from 200 liters drums.*

The samples were labelled, sealed and stored to reach secular equilibrium (minimum of 30 days) and after this time, they were measured by gamma spectrometry in order to determine the activity concentration of $^{226}$Ra, $^{228}$Ra and $^{228}$Th. It was used two spectrometry system: ORTEC and INTERTECNIQUE both with 15% of nominal relative efficiency (in 1.33 MeV) and the counting time used varied from 5,000 to 50,000 seconds depending on the sample activity. Some pictures of the sealed sample and the spectrometry systems used in the radiometric analysis one can see in Fig. 2.




**(a)** sample closed; **(b)** samples sealed with PVC film; **(c)** samples stored for secular equilibrium; **(d)** ORTEC spectrometry system; **(e)** INTERTECH spectrometry system.

*FIG. 2. Sealed samples and the spectrometry systems used in the radiometric analysis.*

Simultaneously to the radiometric analyses, direct measurements were performed using two portable gamma spectrometers: a Germanium detector (Falcon 5000®) and a cadmium and zinc tellurite detector (RayMon®). The measurements were performed together because they used the same arrangement and parameters.

Each drum was positioned on a lifting/rotational station and the measurements were performed at the half height of the volume of NORM waste contained in the drum (height already indicated on the external side of the drum according to measurements performed during the sampling step).

The measurements were made in four quadrants and at three different distances, 1cm, 20cm and 40cm. Measurement times ranged from 2 to 5 minutes, being longer for those with lower dose rate. Drums P1, P2 and P3 were measured for 5 minutes; P4, P5 and P6 for 4 minutes; P7, P8, P9 and P10 for 3 minutes; and drums P11 and P12 for 2 minutes.

In Fig. 3 one can see some images of the drums direct measurements procedure.


**(a)** lifting/rotational station; **(b)** drum transport; **(c)** drum positioning; **(d)** portable gamma spectrometers; **(e)** measurement at 1cm; **(f)** measurement at 20cm; **(g)** measurement at 40cm.

*FIG. 3. Direct measurements procedure.*

## 3. RESULTS

The results of gamma spectrometry measurements were presented as a report of each drum. In Fig. 4 one can see the report of results for Drum 1.

The results of direct measurements with portable gamma spectrometer Falcon 5000® were presented graphically. Each drum generated two graphics: one for the $^{228}$Ra family (including $^{228}$Th) and other for the $^{226}$Ra and $^{235}$U. As an example, one can see in Fig. 5 the graphic generated form drum 1 ($^{226}$Ra and $^{235}$U).

The results of direct measurements with portable gamma spectrometer RayMon® were not finished because there was a problem with data acquisition and they will not be presented in the paper.

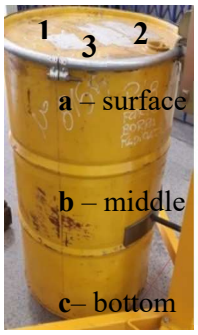
All data of gamma spectrometry measurements and measurements with portable gamma spectrometer Falcon 5000® were statically treated and a summary of results one can see in Table 2.

**Drum 1**

Sampling date - May 15th, 2019

Dose rate: 0.40 microSv/h

| Sample codification | |
|---|---|
| Drum identification – **P1** | |
| Place where the samples were taken | Number after drum identification – place where the sample was taken (see figure)<br>Variyng from **1 to 3.**<br>Letter after place where the sample was taken – height where the sample was taken (see figure)<br>"**a**" surface; "**b**" middle; and, "**c**" bottom.<br>"**LIQ**" – liquid sample from the bottom. |





Height of NORM waste: 70 cm.

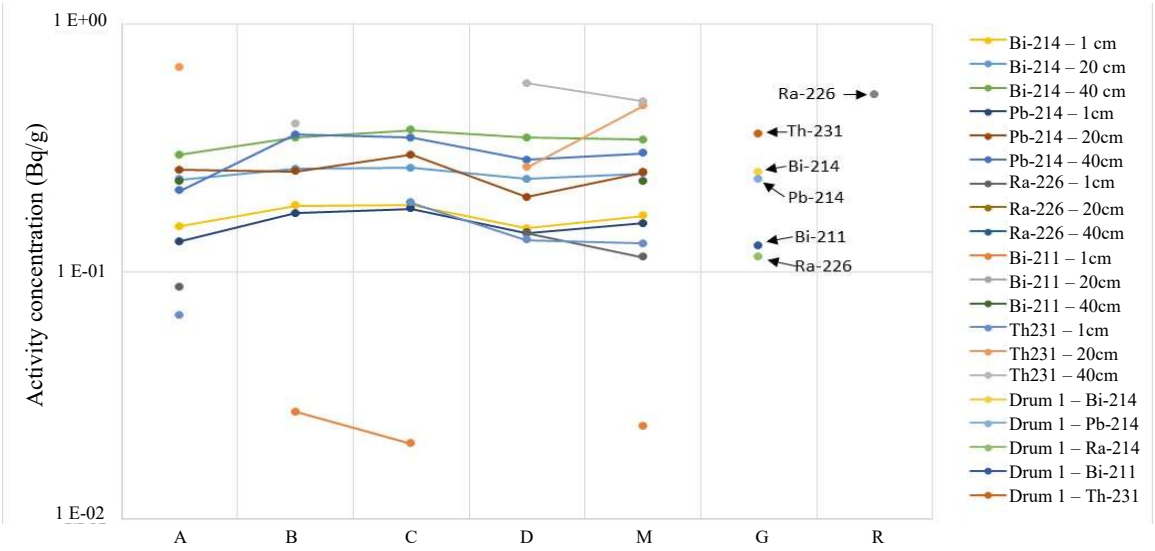
Characteristics: Homogeneous sample, apparently dry, but with the presence of liquid phase in the bottom, after sampling. Due to the NORM waste height, it was decided to take samples from three places and due to the presence of liquid it was decided to take a sample of this phase. The results of the activity concentration measurements of radionuclides $^{226}$Ra, $^{228}$Th and $^{228}$Ra, in Bq.kg$^{-1}$, are presented in the following table.

| Simple code | Bq kg$^{-1}$ | | |
|---|---|---|---|
| | $^{226}$Ra | $^{228}$Th | $^{228}$Ra |
| **P1.1.a** | 528 ± 55 | 181 ± 30 | 132 ± 13 |
| **P1.1.b** | 497 ± 52 | 119 ± 25 | 108 ± 11 |
| **P1.1.c** | 429 ± 44 | 102 ± 18 | <LID |
| **P1.2.a** | 655 ± 56 | 185 + 30 | 131 ± 13 |
| **P1.2.b** | 483 ± 50 | 151 ± 25 | 106 ± 10 |
| **P1.2.c** | 486 ± 50 | 105 ± 18 | <LID |
| **P1.3.a** | 724 ± 75 | 199 ± 31 | 141 ± 14 |
| **P1.3.b** | 463 ± 48 | 142 ± 23 | <LID |
| **P1.3.c** | 484 ± 51 | 192 ± 27 | 138 ± 12 |
| **P1.LIQ** | 441 ± 48 | 134 ± 26 | 88 ± 10 |

LDL – Lower Detection Limit

LDL $^{226}$Ra - 95 Bq kg$^{-1}$; LDL $^{228}$Th - 22 Bq kg$^{-1}$; LDL $^{228}$Ra - 90 Bq kg$^{-1}$

*FIG. 4. Drum 1 - report of results.*




A to D = quadrant; M = quadrant average for each distance and radionuclide;
G = general average for all quadrants and distances; R = average of results from samples gamma spectrometry

*FIG. 5. Portable spectrometer measurements of drum 1 ($^{226}$Ra and $^{235}$U).*

TABLE 2. AVERAGE OF ACTIVITY CONCENTRATION FROM SAMPLES AND DIRECT MEASURMENTS OF NORM WASTE

| Nuclide | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | P9 | P10 | P11 | P12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^{226}$Ra (a) | 0.11 | 0.37 | 0.66 | 2.20 | 3.29 | 1.42 | 2.80 | 3.30 | 8.60 | 3.50 | 7.60 | 2.00 |
| $^{226}$Ra (b) | 0.52 | 0.53 | 1.95 | 4.30 | 5.20 | 4.00 | 6.50 | 7.00 | 16.90 | 7.80 | 22.40 | 13.50 |
| $^{228}$Ra (a) | 0.12 | 0.49 | 0.36 | 1.20 | 2.06 | 0.73 | 4.80 | 3.60 | 5.00 | 2.70 | 1.20 | 3.80 |
| $^{228}$Ra (b) | 0.08 | 0.73 | 0.56 | 1.60 | 3.00 | 2.10 | 2.20 | 7.70 | 2.10 | 4.20 | 2.80 | 14.50 |
| $^{228}$Th (a) | 2.28 | 4.05 | 6.70 | 16.50 | 15.00 | 9.25 | 12.60 | 29.60 | 28.30 | 16.20 | 21.20 | 11.10 |
| $^{228}$Th (b) | 0.15 | 0.45 | 0.77 | 1.70 | 1.70 | 1.90 | 3.30 | 6.80 | 2.90 | 5.70 | 4.10 | 16.00 |
| Total (a) | 2.50 | 4.90 | 7.70 | 19.80 | 20.40 | 11.40 | 20.20 | 36.50 | 41.90 | 22.40 | 30.00 | 16.90 |
| Total (b) | 0.75 | 1.70 | 3.30 | 7.60 | 9.90 | 8.00 | 12.00 | 21.50 | 21.90 | 17.70 | 29.30 | 44.00 |

(a) Average measurements using Falcon5000®
(b) Average of gamma spectrometry measurements of all samples taken from each drum

## 4. DISCUSSION

The analysis of samples taken from different locations within the drum shows some variability in the concentrations of radionuclides, which is expected since the presence of material from different batches in the same drum can occur. The lowest concentration of $^{226}$Ra was observed in the liquid phase, indicating that this radionuclide tends to be trapped in the solid phase. This trend is less pronounced for the $^{228}$Ra / $^{228}$Th radionuclide pair.

It is observed that the concentration of $^{228}$Th is systematically higher than that of $^{228}$Ra for each sample, showing activity ratio $^{228}$Th / $^{228}$Ra within the range 1.1 – 1.5. This is consistent with the situation in which the drum was left undisturbed for a few months and thus is in the way to achieve transient radioactive equilibrium, which is reached when that ratio is 1.5. This value corresponds to the expression:

$\frac{T_{Ra}}{T_{Ra}-T_{Th}}$ where $T_{Ra}$ = 5.75 y and $T_{Th}$ = 1.91 y are respectively the half-lives of $^{228}$Ra and $^{228}$Th.

The results obtained through direct measurements using the Falcon 5000® detector indicate uniformity in the activity concentration of the radionuclides, regardless of the drum quadrant, the drum-detector distance and the degree of homogeneity of the NORM waste. In several drums, the heterogeneity in the distribution of activity in the sludge was well established and, however, the measurements results were not affected.

The direct implication is that concentrations can be estimated from a single measurement, on either position of the drum (quadrant) and at the distance that is most convenient considering time measurement – the lower the dose rate, the longer the data acquisition time to obtain results with acceptable uncertainty – and by considerations of the level of background radiation and space at in situ measurement.

## 5. CONCLUSION

The analysis of samples taken from different locations within the drum shows some variability in the concentrations of radionuclides, which is expected since the presence of material from different batches in the same drum can occur. The lowest concentration of $^{226}$Ra was observed in the liquid phase, indicating that this radionuclide tends to be trapped in the solid phase. This trend is less pronounced for the $^{228}$Ra / $^{228}$Th radionuclide pair.

The use of portable gamma spectrometer Falcon 5000® to estimate activity concentrations of NORM waste is feasible as a radioisotopic characterization method, in view of the correlation between the results of direct gamma spectrometry and radiometric analyses made with the samples of NORM waste in the reference laboratory of IPEN. Some discrepancies are within acceptable uncertainties and there is also the fact that concentrations are sometimes overestimated by a factor that can reach an order of magnitude.

## ACKNOWLEDGEMENTS

The authors thank Petrobras - Petroleo Brasileiro S.A. for the financial support for the development of this research project.

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