**Liquid Scintillation for NORM in the Oil and Gas Industry**

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**Abstract.** Natural radionuclides of Radium, Lead and Polonium are trapped along with crude oil and gas and accumulate as scale deposits on equipment in the oil industries. Problems arise by residues and sludge where such NORM often becomes concentrated during the process of extraction, transport, and storage of crude oil. Additionally, Radon is accumulated in natural gas or is co extracted into oil as organic phase where it equilibrates with its Progenies. Thus NORM creates a possible hazard to workers both by external radiation exposure and internal due to incorporation during intervention work, and to the environment due to waste disposal. The determination of $^{222}\text{Rn}$, $^{226,228}\text{Ra}$, $^{210}\text{Pb}$, and $^{210}\text{Po}$ in the various production stages is a precondition for an efficient Radiation Protection Management. We have studied the applicability of Liquid Scintillation LS for the measurement of NORM in the oil and gas industry. Our investigations show that $^{226}\text{Ra}$ may be quantified by LS in solid scale deposits as carbonate and sulphate after grinding and as carbonate additionally after dissolution. Then, an organic LS scintillation cocktail like Betaplate Scint is added and the sample stored for Rn equilibration. While $^{222}\text{Rn}$ is quantitatively extracted from the solution, only 20 to 30% are emanated as free Rn from the powder into the organic phase. Emanation yield versus grain size and sample amount has been studied using synthetic Ra/Ca-carbonate powder and grinded Pitchblende ore samples. $^{226}\text{Ra}$, $^{228}\text{Ra}$ and $^{210}\text{Pb}$ in carbonate may be determined by $\alpha/\beta$-discriminating LS after dissolution, mutual separation on Radium Rad Disk filters and final elution with DHC and EDTA. From these results the isotopic ratio of Radium isotopes in the different scale fractions may be determined. $^{226}\text{Ra}$, $^{228}\text{Ra}$ and $^{210}\text{Pb}$ in production and waste waters may be quantified accordingly. Radon in oil fractions has been measured as 0.1 to 2% solution in Betaplate Scint with sensitivity down to 5 Bq/l. From our findings we conclude that LS provides an efficient, simple and in-situ applicable tool to detect Radon, Radium and Lead isotopes.

**KEYWORDS:** Liquid Scintillation, NORM, Oil and Gas Industry, $^{226,228}\text{Ra}$, $^{210}\text{Pb}$

1. **Scope and Objectives**

Radionuclides of the natural occurring decay series like those of Radium, Lead and Polonium are omnipresent as NORM in the petroleum industry. They are trapped along with crude oil and gas and accumulate as scale deposits in subsurface and surface production facilities. Problems arise from residues, sludge and “Produced Water” where NORM often becomes concentrated. The activity levels in the oil and gas production and processing are elevated but generally not large, however the quantity of material generated is enormous. Thus NORM creates a possible hazard to both workers by external radiation exposure, internal due to ingestion during intervention work, and to the environment due to waste disposal [1].

In this paper the applicability of LS Spectrometry has been studied for the analysis of NORM products in the petroleum industry.

2. **Theoretical Introduction**

Formation water in the oil and gas exploitation contains group II cations as being dissolved from reservoir rock. Thus Radium isotopes, being $^{226}\text{Ra}$ from the $^{230}\text{U}$ series (Fig. 1) and $^{226}\text{Ra}$ and $^{224}\text{Ra}$

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from the $^{232}$Th series (Fig. 2) can be found in the water co-produced with oil and gas. Drops in pressure and/or temperature can lead to the solubility products of their mixed Ca, Sr, Ba sulphates and carbonates being exceeded. Therefore they are precipitated e.g. as extremely insoluble barite deposits on the inner walls during the process of extraction (vessels, tubing), transport (pipelines, pumps, filters) and storage (ponds, tanks) of crude oil. If seawater is used to enhance oil recovery, it mixes with the formation water and enhances scale deposition.

Also the noble gas $^{222}$Rn, which is generated in the reservoir rock as decay product of $^{226}$Ra, is carried along as mixed stream of oil, gas and water. Being transported as dry “Export Gas” it forms $^{210}$Pb and $^{210}$Po as long lived solid decay products. Thus $^{210}$Po accumulates and deposits as thin lead film, known as “Black Powder”, on the internal surfaces of production equipments. $^{210}$Po is observed at levels in excess of its precursor $^{210}$Pb, indicating direct emanation from the reservoir [1]. Produced water may contain $^{226,228,224}$Ra and $^{210}$Pb in concentrations of up to a few hundred Becquerel per litre, but is virtually free of $^{222}$Th [2]. Mean concentrations of 4.1 Bq/l of $^{226}$Ra and 2.1 Bq/l of $^{228}$Ra were recorded in Norwegian offshore oil production installations [3].

Generally the activity concentrations of Radium isotopes are lower in sludge than in scales [1, 4, 5]. The opposite applies to $^{210}$Pb, which usually has a relatively low concentration in hard scales but may reach a specific activity of more than 1000 Bq/g in Lead deposits and sludge [6].

Which nuclides occur in which concentration and appearance, chemical form, grain size etc. depend on the kind of facility (gas or oil), flow rate, type of rock or geological setting, composition of production waters and physical and chemical conditions [7, 8]. The activity concentration is time dependent and may appear considerably in a later stage.

Therefore simple and fast measurements are imperative for regular essay in order to ensure an effective radiation protection for both staff and the environment.

For identification and quantification of NORM nuclides the method generally reported is high resolution $\gamma$-spectrometry. Problems arise from interferences of the 186 keV $\gamma$-line of $^{226}$Ra with $^{235}$U. Thus it has to be estimated through its progenies $^{214}$Pb or $^{214}$Bi if secular equilibrium may be ascertained e.g. in gas-tight containers for solid samples. Additionally coincidence losses and $^{222}$Rn escaping from water samples cause uncertainties. The assessment of the $^{210}$Pb concentration is influenced through self absorption of the low energy $\gamma$-photons of 46 keV in the matrix.

In Produced Water at activity concentrations of some Bq/l or less the counting efficiency for direct $\gamma$-measurements of the low intense $^{226}$Ra-line will not be sufficient. Thus time consuming and laboratory intensive chemical treatment is obligatory.

For the estimation of the $^{210}$Po activity concentration chemical separation and auto deposition followed by $\alpha$-spectrometry is precondition.

During the recent conferences on “Advances in Liquid Scintillation Spectrometry” e.g. in [9] liquid scintillation as counting method for radionuclides has proved to be simple in sample preparation, efficient, and efficiency independent over a large range of $\beta$-energies. For $\alpha$-emitters it may even be considered as absolute method.

3. Methodology

3.1 Instrumentation and Materials

- Triathler (HIDEX) was the preferred instrument for our LS studies. The equipment is mobile, relatively simple to handle, and equipped with an effective $\alpha/\beta$ pulse shape discrimination PSD technique to ensure a low background in the $\alpha$-channel. Ra measurements after selective Rad Disk filtration were done with Beckman LS 6000LL.

- Betaplate Scint (Wallac), Toluene Scint and MaxiLight (HIDEX) as organic cocktails, and Ultima Gold AB (Packard) for gel samples were used.

- Standard solutions of $^{226}$Ra, $^{210}$Po and $^{210}$Pb, aged Th-nitrate in equilibrium with daughter nuclides, and a multi-nuclide $\gamma$-standard (QCYB410, QSA Global) were applied for calibration measurements and preparation of simulated scale samples.

$^{222}$Rn containing oil samples were prepared by contacting Pitchblende material from Menzenschwand former U-mine, Germany, with various mineral oils (Mineral Oil Divinol 10/40, Crude Oil Shell, Grundöl GO1).
Figure 1: Mobilisation of $^{238}$U-decay products [1]

Figure 2: Mobilisation of $^{232}$Th-decay products [1]
Radium Rad Disk filters (3M EMPORE) have been used for selective Ra-separation and enrichment. The procedure was adopted according to our recent findings [10, 11]. All chemicals were of “analytical grade”.

3.2 Analytical Procedures

3.2.1 Preparation of Materials

1. Synthetic Ra/Ca-carbonate samples have been prepared from CaCl₂ and NH₄-carbamate (NH₄CO₂NH₂) by adding a ²²⁶Ra-standard spike to a calculated specific activity of 20 Bq/g. The real value of the carbonate standard has been determined using the Radium Rad Disk Filter Method after dissolution of small amounts in HNO₃. Additionally, the ²²⁶Ra value was verified by ²²²Rn extraction from the aqueous solution after neutralisation with NH₄OH and super layering with both Betaplate and Toluene Scint cocktail after 20 to 30 days storage time.

2. For exhalation studies Pitchblende ore was ground with a pebble mill (MM200, Retsch) and sieved to various grain size fractions (<60 µm, 60-125 µm, 125-300 µm and 300-500 µm) using metal sieves (Type 1171, Retsch). After drying varying sample amounts were weigh into 20 ml LS glass vials and covered with organic LS cocktail.

3.2.2 Sample Preparation for Analysis and Measurement

1. ²²⁶Ra in ore was analysed by γ-spectrometry according to the following procedure: Grinded mineral samples of 1.5 g each from 60 to 500 µm were sealed air-tight in a 2 ml glass mini vial. After 30 days storage the ²²²Rn content was measured by high resolution γ-spectrometry and quantified through the ²¹⁴Bi/²¹⁴Pb-γ-lines in secular equilibrium and cross-checked by the 186 keV ²²⁸Ra-line for possible interferences with ²³⁵U. Furthermore the ²²²Rn content was quantified 3 hours after sample preparation. For efficiency calibration a multi-nuclide γ-standard was measured in the same counting geometry.

2. Additionally, ore samples of each grain size fraction were dissolved by evaporation with conc. HF and Aqua Regia and then analysed through Radium Rad Disk filtration. Because of the presence of other alkaline elements (e.g. Sr and Ba) only small amounts of 37.5 to 150 mg have been taken for analysis.

3. Samples for emanation measurement were prepared by contacting carbonate powder with 20 ml Betaplate Scint as organic cocktail in glass vials. The vials were sealed and stored for 5 to 20 days in the fridge with the cover down to avoid Rn losses. The free ²²²Rn in grown was finally extracted by vigorous shaking. After further 3 hours storage for equilibration with the direct daughter nuclides an aliquot of the organic phase has been transferred into a mini vial for more effective α/β PSD measurement.

4. Ore samples for emanation measurements were prepared analogous to (3) by weighing the grinded dry ore fractions and covering with MaxiLight and Toluene Scint Cocktail. Measurements were done 7 days and 20 days after sample preparation.

5. To simulate Produced Water both drinking and sea water samples were spiked with ²²⁶Ra- and ²¹⁰Pb-standard and taken for analysis. The samples were acidified to 2M HNO₃ and filtered through the selective Radium Rad Disk material according to the procedure described in detail in [10]. After elution with 6 ml 0.25M alkaline EDTA, OptiPhase HiSafe III was added for measurement as gel.

4. Results and Discussion

4.1 Calibration Measurements

Standard solutions of the relevant NORM nuclides have been measured for LS calibration. The high counting efficiencies of nearly 100% as described earlier [5-7] could be confirmed for α-nuclides like ²¹⁰Po and ²²⁶Ra in the relevant cocktails (Table 1). Due to the low intense β-energy of 16 keV (35%) and because of discriminating the lower part of the β-window (channel 0 to 170) avoiding
luminescence interferences with the Triathler instrument, a reduced counting efficiency of 25% has been determined for \(^{228}\text{Ra}\). As \(\alpha/\beta\) PSD in organic phases is excellent an overall efficiency for Rn in the \(\alpha\)-channel of up to 295\% has been found (\(^{222}\text{Rn},^{218}\text{Po},^{214}\text{Po}\)). In this value the extraction yield is included, showing a lower efficiency for Toluene Scint as organic cocktail. \(^{214}\text{Pb}\) (0.7 MeV) and \(^{214}\text{Bi}\) (1.5 MeV) were detected with 90 and 95\% efficiency respectively. The results confirm LS as efficient and efficiency independent method for \(\beta\)-energies at least over a large energy range. No quenching for \(\alpha\)-emitters has been recognised thus confirming LS as being an absolute method.

**Table 1:** Decay properties and LS counting efficiencies for relevant NORM nuclides

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<td>(^{210}\text{Po} (\alpha))</td>
<td>(\alpha): 5.3 MeV</td>
<td>Ultima Gold AB</td>
<td>100%</td>
</tr>
<tr>
<td>(^{226}\text{Ra} (\alpha \text{ PSD}))</td>
<td>(\alpha): 4.8 MeV</td>
<td>OptiPhase HiSafe III</td>
<td>100%</td>
</tr>
<tr>
<td>(^{228}\text{Ra} (\beta))</td>
<td>(\beta): 0.016 MeV (35%)</td>
<td>OptiPhase HiSafe III</td>
<td>25% **</td>
</tr>
<tr>
<td>(^{214}\text{Pb})</td>
<td>(\beta): 0.7 MeV</td>
<td>Ultima Gold AB</td>
<td>485%</td>
</tr>
<tr>
<td>(^{214}\text{Bi})</td>
<td>(\beta): 1.5 MeV</td>
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\* in equilibrium with direct daughter nuclides (after 3h storage time)
\** channel 170 - 420

**4.2 \(^{222}\text{Rn} \text{ in Mineral Oil}\)**

Optimum concentrations for three different \(^{222}\text{Rn}\)-enriched mineral oil samples in organic cocktails have been studied. An increasing concentration of oil in the organic cocktail results in a yellowish to brown colour shifting the energy spectrum to lower values as can be seen from Fig. 3. Thus the amount of quenching increases and the counting efficiency in the \(\alpha\)-channel is reduced from 295\% (\(^{222}\text{Rn},^{218}\text{Po},^{214}\text{Po}\)) with MaxiLight and 3\% oil to 240\% for 7\% oil. Additionally, the decay

**Figure 3:** 3-dimensional \(\alpha/\beta\)-plot for mineral oil (Divinol 10/40) in Betaplate cocktail
a) 1\% mineral oil
b) 7\% mineral oil (corresponds to 1 ml oil and 15 ml cocktail)
time of α-pulses decreases and thus the time valley between α- and β-pulses for PSD is diminished. Consequently the α/β separation by setting a Pulse Length Index PLI is aggravated. The maximum amount of oil and consequently the Lower Limit of Detection LLD value greatly depends on the kind of oil and its characteristic colour. It varied from 1 Bq/l for mineral oil (7% Divinol 10/40 and a yellowish crude oil sample) to 40 Bq/l for black crude oil (e.g. 0.2% “Grundöl GO1”). No differences for the two organic cocktails have been found. 

222Rn in production gas may as well easily be quantified through LS by simply flushing the mineral gas through organic cocktails using an impinger (diffuser). The method has been described in detail by us in [13].

4.3 Synthetic Scale Materials

Synthetic Ra/Ca-carbonate and Ra/Ba-sulphate were used in our investigations as substitute due to lack of real scale material. Additionally, ore fractions of different grain size were taken for Rn emanation studies. No emphasis was put on any preliminary purification step for scale contaminated with organic material as procedures can be found elsewhere [14].

4.3.1 Ra/Ca-Carbonate

Synthetic carbonate “scale” was prepared according to 3.2.1 (1). The specific activity of the Ra/Ca-carbonate material has been determined after dissolution in 2 M HNO₃ and successive Rad Disk extraction to 18.2 Bq/g, which has been assumed as true value instead of the anticipated 20 Bq/g. The selective disk method allows the simultaneous determination of the 228Ra quantity from the low energy β-spectrum. Thus the isotopic ratio of Radium isotopes in the different scale fractions may be determined. Additionally 226Ra was quantified by dissolution in HCl, neutralisation with NH₄OH and covering with organic cocktail phases. After storage 222Rn was extracted and the 226Ra activity determined to 18.7 and 13.1 Bq/g in Betaplate and Toluene Scint respectively (Fig. 4). Thus Safe Cocktails showed a lower extraction capacity compared to Toluene based LS cocktails. However, phase separation often is more difficult.

The 222Rn emanation of Ra/Ca-carbonate powder into the organic phase varied according to the sample amount used. A maximum value of 21% was observed for samples below 0.5 g. The in growth corrected emanation yield decreased for storage times exceeding 25 days, probably due to alteration of the powder. Toluene Scint again showed a lower extraction yield for Radon compared to Betaplate and MaxiLight.

**Figure 4:** Specific activity of 226Ra/BaCO₃ found for different sample preparation techniques in relation to the calculated standard activity (100%).

**Figure 5:** 222Rn emanation yield of ore powder vs. sample amount and grain size (100% corresponds to the free Rn content, being 34% for 60-125 μm, 28% for 125-300 μm, and 24% for 300-500 μm).
4.3.2 Ra/Ba-Sulphate

A dependency of the Rn emanation capacity from the sample amount has been found as well with Ra/Ba-Sulphate powder material with a maximum of 20% of the theoretical value with 100 mg samples and a considerable decrease for amounts exceeding 200 mg analogous to carbonate scales.

4.4 Ore Samples

The specific Radon emanation capacity in dependency of grain size and sample amount has been studied with a mineral sample (Pitchblende Ore) milled and sieved to different grain sizes. As an inhomogeneous distribution of Radium in the various fractions was expected, quantitative analysis of the $^{226}\text{Ra}$ content in the different grain size fractions has been performed. Methods used were $\gamma$-spectrometry as described in 3.2.2 (1) and LS measurement after dissolution and Rn extraction into organic cocktails according to 3.2.2 (2). The specific activity of $^{226}\text{Ra}$ varied by 25% in the different fractions with 1330 Bq/g being highest for 125 to 300 $\mu$m grain size. The free $^{222}\text{Rn}$ fraction has been calculated from the $^{222}\text{Rn}$ content after sample preparation and the $^{222}\text{Rn}$ equilibrium value through $\gamma$-spectrometry. As assumed the highest value with 34% has been found for the smallest grain size of 60 to 125 $\mu$m investigated, decreasing constantly to 28% for 125 to 300 $\mu$m and 24% for 300 to 500 $\mu$m grain size. This is explained by the fact that the greater the grain sizes the less Rn atoms are free to migrate through the grain boundary as gaseous Rn and as such are available for $^{222}\text{Rn}$ emanation analysis. The specific $^{222}\text{Rn}$ emanation yield, measured in the LS cocktail after equilibration showed higher values for small sample amounts with saturation below 100 mg to 200 mg. A considerable decrease can be seen for sample amounts exceeding 200 mg (Fig. 5). 100% emanation yield corresponds to the free Rn-content determined by $\gamma$-spectrometry. The lower values for less than 60 $\mu$m are result from considerable quenching from particles not depositing after $^{222}\text{Rn}$ extraction. Detailed data are published elsewhere [15].

4.5 Water Samples (Produced Water)

Production Water mainly contains $^{224}\text{Ra}$, $^{226}\text{Ra}$, $^{228}\text{Ra}$ and $^{210}\text{Pb}$ as NORM nuclides. Their activity concentration generally is low; however, the volumes are enormous.

The results of the analysis of fresh water, sea water and dissolved ore samples with the Radium Rad Disk Method demonstrate that $^{210}\text{Pb}$ and $^{226}\text{Ra}$ as main radionuclides present may easily be determined simultaneously after 3 hours storage for decay of $^{214}\text{Pb}$ and daughters. Fig. 6 shows the energy spectrum of EDTA fractions of the dissolved ore sample (125-300 $\mu$m) measured by LS directly after separation (Fig. 6a, b) and after one week storage (Fig. 6c). $^{210}\text{Pb}$ and $^{226}\text{Ra}$ are separated from all other NORM nuclides and are concentrated in the EDTA fraction. $^{228}\text{Ra}$, if present, would overlap with $^{210}\text{Pb}$, but can be determined separately by an additional stripping step with dihydrogen citrate DHC as weaker complexing agent [10].

Formation water according to [1] might be rich on cations like Na, K, Ca, Sr, Mg and especially Ba, which may compete with the Ra extraction because of the similar ionic radius (Ba$^{2+}$: 0.136 nm; Ra$^{2+}$: 0.143 nm). In this case the volume of water for analysis has to be limited accordingly and water samples might have to be filtered repeatedly in order to secure quantitative extraction. For the dissolved ore sample used in our experiments an upper amount of 50 mg per analysis has been found, for Mediterranean Sea water the maximum volume for quantitative extraction was 150 ml. The LLD for $^{226}\text{Ra}$ has been calculated to 15 mBq/l for a 1 litre water sample (120 counts/h background, $\alpha/\beta$ PSD Triathler).

5. Conclusion

1. With counting efficiencies of 90 to 100% for $\alpha$- and medium- to high-energetic $\beta$-emitters LS provides an efficient and simple tool for the analysis of NORM nuclides in the oil and gas industry like Radon, Radium and Lead. $^{210}\text{Po}$ with 100% efficiency as pure $\alpha$-emitter is additionally accessible for analysis. Thus scales containing NORM as residues from inner walls, vessels, tubing, pipelines or tanks, as well as Production Water can easily be determined using LS.
2. Radon ($^{222}$Rn) in oil fractions has been measured in organic Betaplate cocktail as 0.1% solution for crude oil and up to 7% for yellowish mineral oils with LLDs down to 5 Bq/l. These results confirm our recent findings [11]. LLDs depend on batch, but with 40 Bq/l are sensitive enough as well for black crude oil samples.

3. $^{226,228}$Ra as carbonate scale may be measured after dissolution in small quantities of HNO$_3$ and addition of a gel forming cocktail like Ultima Gold AB applying $\alpha/\beta$ PSD spectrometry. Using the modified Radium Rad Disk Filter Method the isotopic ratio of Radium isotopes in the different scale fractions may be determined additionally.

4. The $^{226}$Ra content may be estimated directly both in solid carbonate and sulphate scale materials after grinding and Rn exhalation into an organic LS cocktail like Betaplate Scint after storage. However emanation yield with 20% is not quantitative confirming the results made recently by White and Rood [7].

5. Our investigations on the Rn emanation yield of ore powder showed that the Rn release depends on grain size and porosity, amount of sample and distribution of Ra within the material. Maximum values of 30% have been found for sample amounts lower 200 mg and 60 to 125 $\mu$g grain size.

6. $^{226}$Ra, $^{228}$Ra and $^{210}$Pb in Production Water can easily be determined after acidification to 2M HNO$_3$, and mutual separation on Radium Rad Disk filters by elution with DHC and EDTA successively using OptiPhase HiSafe III cocktail for measurement. The LS method overcomes the problems with $\gamma$-spectrometry, resulting from faults due to interferences of the 186 keV $^{226}$Ra $\gamma$-line and self absorption of the low energetic $^{210}$Pb $\gamma$-emitter.
REFERENCES


