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The Encounter and Analysis of Naturally Occuring Radionuclides (NORs) in Gas and Oil Production and Processing

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THE ENCOUNTER AND ANALYSIS OF
NATURALLY OCCURRING RADIONUCLIDES
IN GAS AND OIL PRODUCTION AND PROCESSING

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SUMMARY

As a result of oil and gas production, radioactive daughter elements from the uranium and thorium decay series can be mobilised and be transported away from the reservoir. Due to changes in flow regime, temperature, pressure or chemical environment Naturally Occurring Radionuclides (NOR's) may build up in products, by-products or waste streams from gas and oil production and processing facilities. Products containing NOR's are commonly denoted by the acronym NORM (Naturally Occurring Radioactive Materials).

The encounter of NORM in the E&P industry has also drawn the attention of (inter)national legislative and advisory bodies, hence, legislation on NORM is currently being drafted or is already in place. Licensing and disposal limits generally are based on NOR activity concentration levels. In view of these (forthcoming) regulations, understanding NORM and accurate, standardised analysis protocols are essential for the oil and gas industry.

With respect to the encounter of NOR's in oil and gas exploration and production, the uranium decay series can be sub-divided, according to the radionuclide transport mechanisms, in five sub-series which are headed by ^{238}U , ^{226}Ra , ^{222}Rn , ^{210}Pb and ^{210}Po , respectively. ^{238}U and its progeny is only encountered, in non-enhanced concentrations, in reservoir material, whereas ^{226}Ra and its daughters are transported with the aqueous brine phase. Consequently ^{226}Ra -containing NORM, and to a lesser extent ^{210}Pb , is found in oil production facilities at spots where water chemistry plays a dominant role. The noble gas ^{222}Rn is transported with natural gas or in live crude; its progeny is mainly detected in natural gas processing and treatment installations. Both the gas and the hydrocarbon phase may, especially in the gas industry, transport ^{210}Pb and ^{210}Po from the reservoir to the (sub)surface structures, whereas ^{210}Po can also migrate with hydrocarbon condensate.

By analogy, the ^{232}Th decay-series is sub-divided in four sub-series: in reservoir material, ^{232}Th and associated NORs can be found, whereas the radium isotopes, ^{228}Ra and ^{224}Ra , are co-produced with the brine phase. Being short-lived, ^{220}Rn and ^{212}Pb and associated daughters are not encountered without their parent nuclides.

Based on the above information, a sampling and analysis scheme can be proposed. In order to validate the protocols for NORM analysis in samples from the E&P industry, a multi-stage round-robin test amongst eleven Dutch institutes, with experience and expertise in NORM analysis, has been carried out. Results obtained from this test were compared with reference values, obtained from certifying institutes in Germany, France and Great Britain. Whereas initially, for relatively simple production water samples a large spread in NOR specific activity concentrations was found (up to $\pm 50\%$), results in the last stage on complex sludge samples deviated by less than 10% from the certified values. In particular the use of different γ -emission probabilities for the NOR γ -emission lines (γ -yields') and their branching ratios have been found responsible for the initial spread in results.

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INTRODUCTION

E&P NORM Characteristics

Naturally Occurring Radionuclides (NOR's) which are omnipresent on the planet earth, can be subdivided into cosmogenic (e.g. ^7Be , ^{14}C) and primordial (e.g. ^{40}K , ^{87}Rb , ^{138}La , ^{190}Pt , ^{232}Th , ^{238}U) radionuclides. While cosmogenic radionuclides are continuously formed in the outer atmosphere by cosmic irradiation, primordial (or terrestrial) radionuclides have been present ever since the earth (life-time 5.5×10^9 y) has been formed.

Uranium and thorium

Uranium (U) and thorium (Th) are spread throughout earth's crust, at an average concentration of 4.2 and 12.5 ppm(w/w)¹. The naturally occurring U- and Th-isotopes [being ^{235}U (natural abundance: 0.72%), ^{238}U (99.28%) and ^{232}Th ($\approx 100\%$)] are radioactive.

Consequently, 'radioactivity' is also wide-spread in the environment, on average 0.05 Bq [^{238}U]/g and 0.05 Bq [^{232}Th]/g^a. Because of its low isotopic abundance, ^{235}U or its progeny is rarely encountered in E&P NORM and therefore this series will not be further discussed in this paper.

These primordial radionuclides ^{232}Th and ^{238}U , are special radionuclides, as they each are heading a series of successive nuclear decays (Figs. 1 and 2). Both these NOR's decay through essentially the same elements, all of which are radioactive. As such, these radioactive daughters can be present in gas and oil bearing formations, where next to gas and oil also brine/formation water is present in varying amounts.

Under reservoir conditions, all U and Th compounds are highly insoluble in the aqueous/brine phase. Transport of Th-isotopes almost completely takes place in suspension, whereas U-isotope transport can also take place on clay minerals or with heavy organic matter, in stable complexes. In the E&P industry, ^{238}U and ^{232}Th are only encountered in non-enhanced concentrations in reservoir material.

Radium sub-series

If a geological formation containing ^{232}Th and ^{238}U has not been disturbed ('closed system') for more than 10^6 years, all members of both decay series will have the same activity concentration (Bq/g) and the series is said to be in *secular equilibrium*. However, as the chemical concentration (mole/g) is proportional to the half-life time ($t_{1/2}$) of a radionuclide, their number of atoms varies considerably. This is shown in Fig. 3, where the 'chemical concentrations' of the individual NOR's at equal activity concentrations are plotted.

When a formation is not 'closed' to radionuclide migration, e.g. ^{226}Ra becomes mobilised and is 'deposited' somewhere outside the formation, the secular equilibrium will be disturbed. At the site of deposition the only way the ^{226}Ra concentration can stabilise or increase is by influx of (geo)chemical/physical transport phenomena. No ingrowth of ^{226}Ra via radioactive decay of its ancestors will occur as all radionuclides above ^{226}Ra (cf. Fig. 2b) will stay close ^{238}U . In this way at the site of deposition ^{226}Ra is *unsupported*, i.e. ingrowth is not supported by radioactive decay. ^{228}Ra can also be encountered as an unsupported radionuclide (cf. Fig. 1b).

^a Becquerel (symbol Bq) is the SI unit of activity and has replaced the 'old' unit curie (Ci). One becquerel equals one nuclear disintegration per second; 1 Bq equals approximately 2.7×10^{-11} Ci. Activity concentrations, which are commonly referred to in legislation, are expressed in Bq per gram.

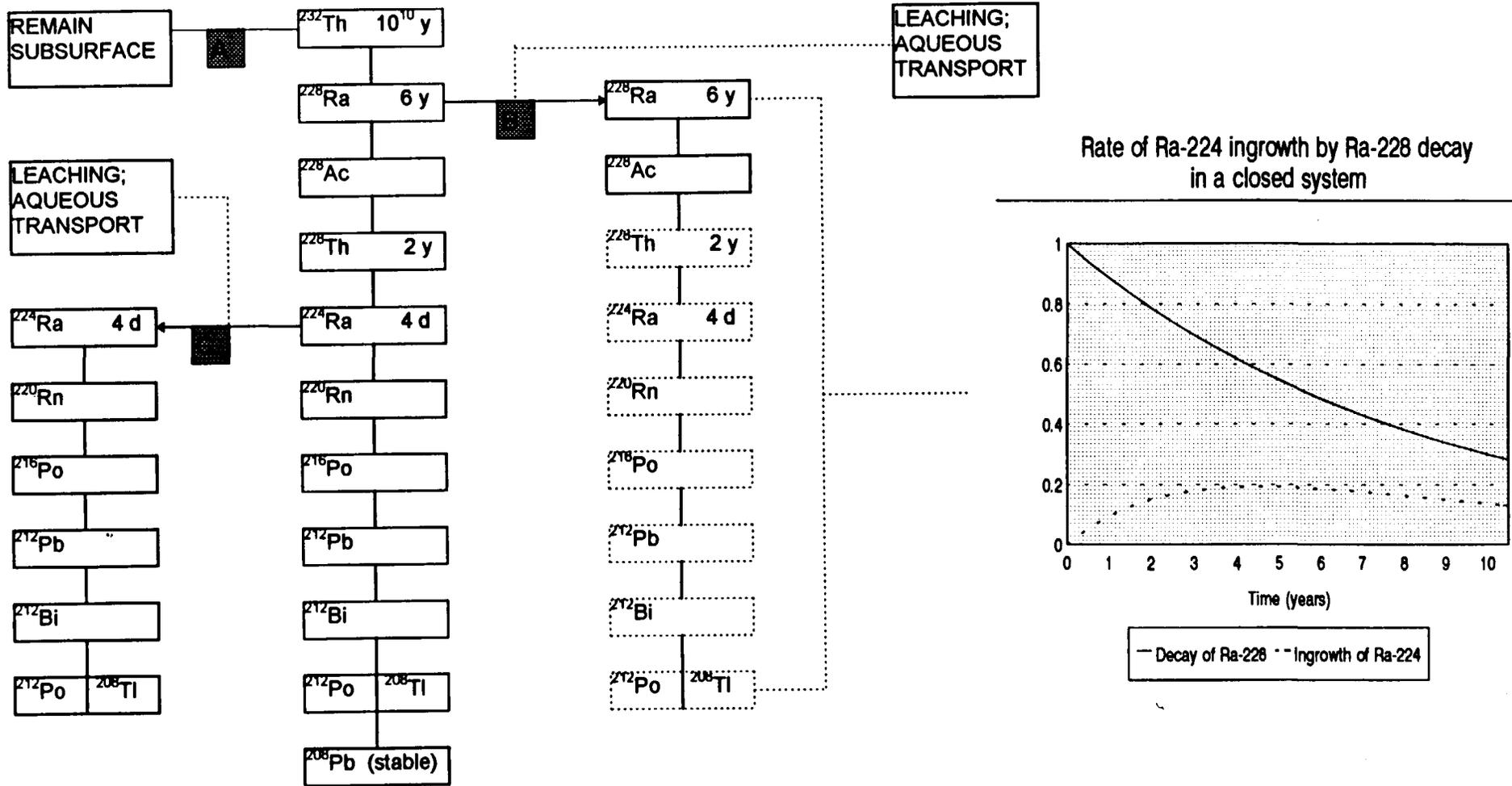


FIGURE 1

The ^{232}Th decay series and its sub-series: **A:** geochemically immobile ^{232}Th ; **B:** ^{228}Ra sub-series; **C:** ^{224}Ra sub-series. Nuclides in the sub-series, which do not readily reach secular equilibrium, are noted in dotted boxes. The figure shows the rate at which (unsupported) ^{228}Ra decays and the rate at which this decay produces ^{228}Th and ^{224}Ra and its short-lived progeny.

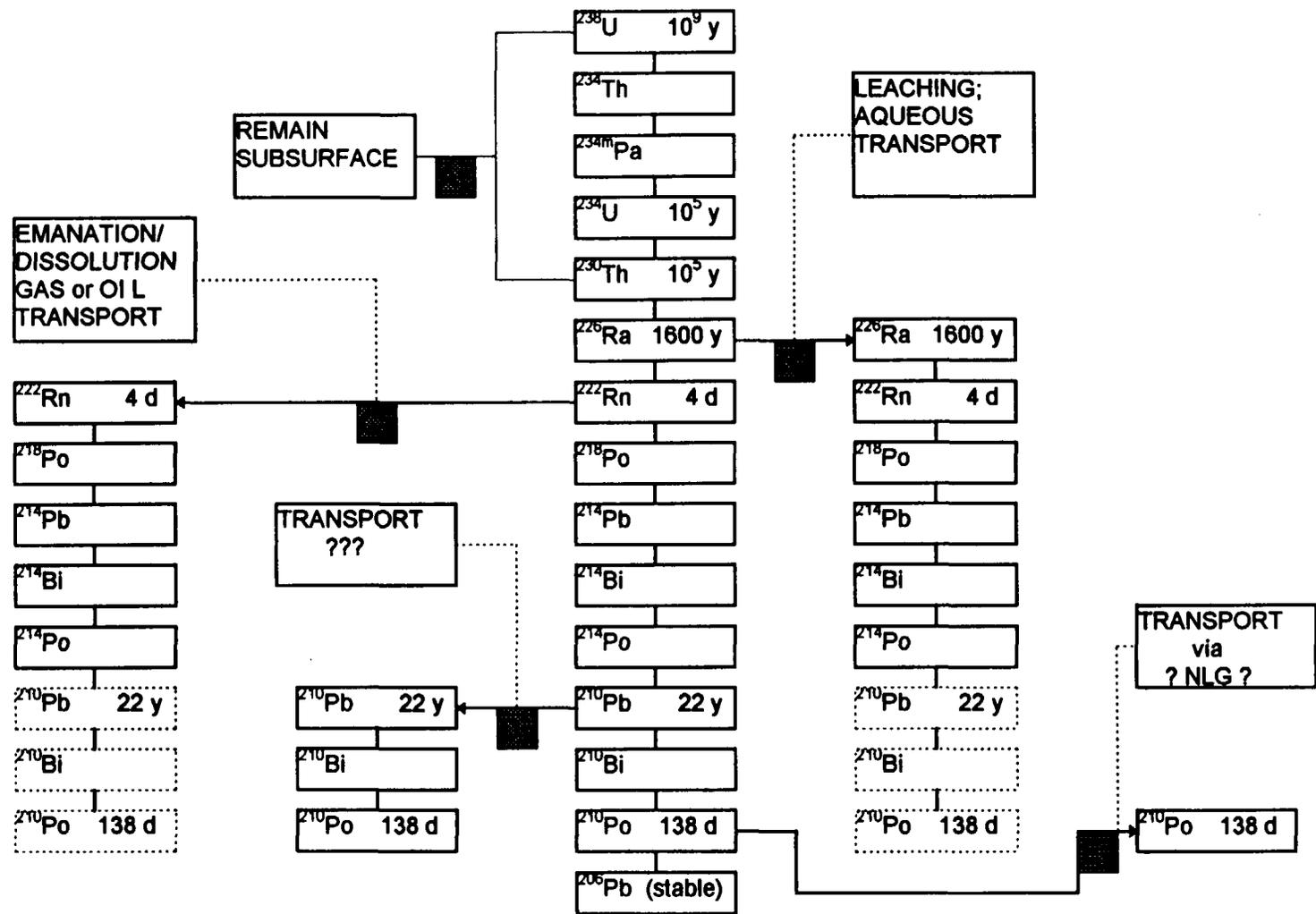


FIGURE 2

The ^{238}U decay series and its sub-series: A: geochemically immobile ^{238}U ; B: ^{226}Ra sub-series; C: ^{222}Rn sub-series; D: ^{210}Pb sub-series; E: ^{210}Po sub-series. Nuclides in the sub-series, which do not readily reach secular equilibrium, are noted in dotted boxes.

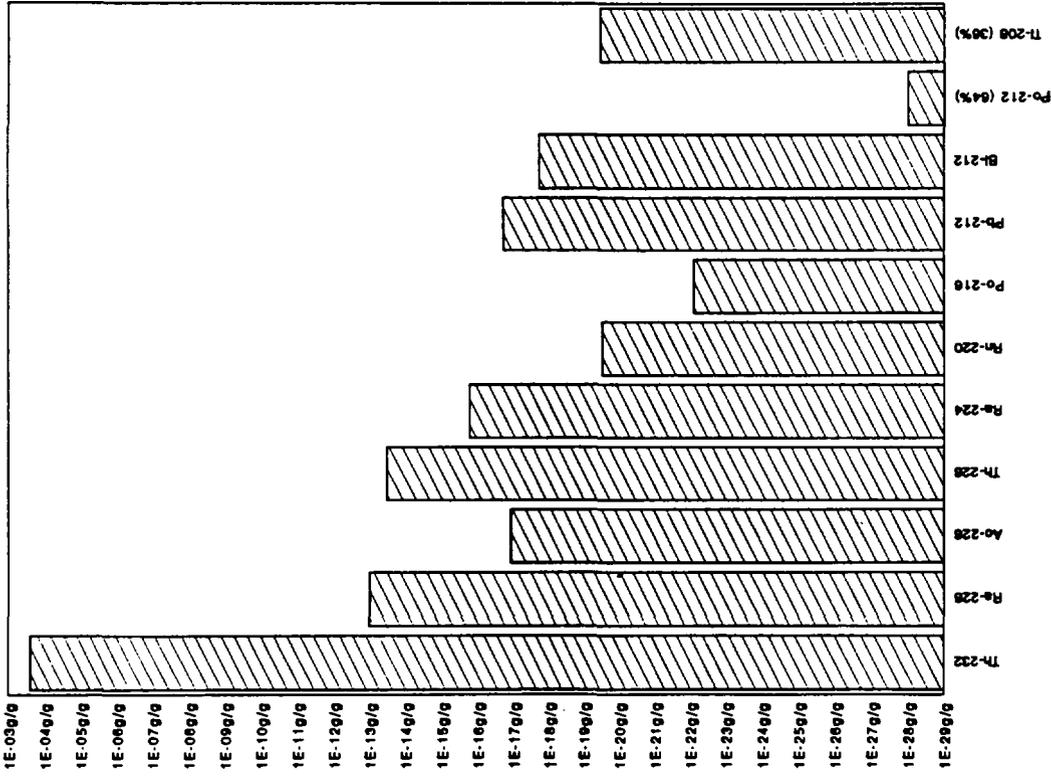
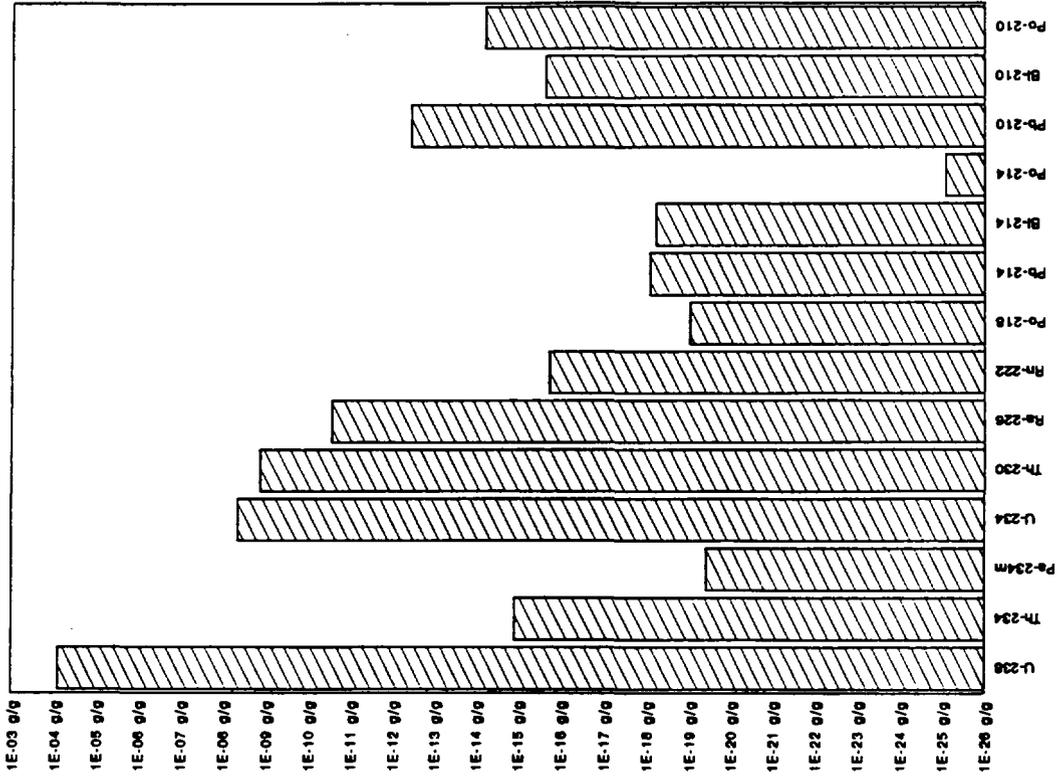


FIGURE 3
 Correspondence between a secular equilibrium of 1 Bq/g ^{232}Th (left side) and ^{238}U (right side) and the chemical quantity of the individual radionuclides in grams per gram.

The (geo)chemical/physical properties of all radium isotopes, *i.c.* ^{226}Ra , ^{228}Ra and ^{224}Ra , are identical. Differences between these isotopes are caused by their radiation decay characteristics and hence by the associated potential radiation hazards. A NOR should 'live' long enough to develop the (geo)chemical properties of the element. In gas and oil production two typical time scales are important, a *geological* (say, far longer than 1,000 years) and a *production time scale* (order of magnitude: days to decades). Therefore, for processes taking place on a time scale of one day, only isotopes of thorium, radium, lead, uranium, radon and polonium may become unsupported. From considerations on the generation of hydrocarbons from source rocks under reducing conditions² and based on knowledge of geochemical transport phenomena³ and taking into account the results from a literature survey recently carried out by us, it is concluded that only a limited number of NOR's actually may appear unsupported in E&P (by-)product streams.

The survey showed that both ^{238}U (and its immediate daughters: ^{234}Th , $^{234\text{m}}\text{Pa}$, ^{234}U and ^{230}Th) and ^{232}Th have only been detected in minute quantities ($\ll 0.05$ Bq/g), which is in agreement with transport phenomena under reservoir conditions. Consequently in E&P samples these NOR's (the 'head' of the series) do not constitute a radiological hazard. This is in marked contrast with the experience in ore exploration, production and treating industries, where the parent nuclides themselves may impose a radiological safety risk.

Furthermore, it is noted, that radium isotopes actually mark a clear separation line for the encounter of NORM in gas/oil production, treating or processing facilities. The most likely cause for this separation is a distinct difference in geochemical properties (mobility under reservoir conditions) in combination with the effective^b half-life of ^{238}U and ^{232}Th on one hand, and that of ^{226}Ra and ^{228}Ra and their progeny on the other hand. As in the ^{232}Th series in between ^{228}Ra and ^{224}Ra , rather long-lived (with respect to a production time scale) and (geo)chemically immobile ^{228}Th is encountered, ^{228}Ra and ^{224}Ra are normally not in secular equilibrium.

Unsupported ^{228}Ra however will produce ^{228}Th (*cf.* Fig. 1), which on its turn will decay into ^{224}Ra . Since ^{228}Th is *not* transported with the production fluids or gases and because of the relatively short half life of the (transportable) ^{224}Ra , all ^{224}Ra detected in E&P NORM results from ^{228}Ra decay *at the site of deposition*. For 'operational' timescales, the ratio $^{228}\text{Ra}/^{224}\text{Ra}$ thus allows one to calculate the average age of the deposit (see Fig. 1).

For radiological safety assessment studies, production water and production water associated deposits have to be analysed both for ^{228}Ra and ^{224}Ra , where the ^{224}Ra concentration is considered to be equal (because of the rapid establishment of secular equilibrium) to the concentration of the (more restrictive and more radiotoxic) ^{228}Th .

After radium isotopes have been mobilised, they can become incorporated in sulphates, carbonates *etc.* of the other earth alkaline metals (Ca, Mg, Ba, Sr) and are deposited at those spots where 'ordinary' (*i.e.* non-radioactive) scaling or sludge formation is also observed. The presence of radium isotopes in scales, sludges or deposits in E&P facilities can relatively easily be detected with an external γ -radiation monitoring device, which triggers on the

^b The effective half-life of a radionuclide under reservoir conditions is defined as a linear combination of its physical half-life ($t_{1/2}$) and its 'mean residence time' in a phase during production from the reservoir or even during maturation, migration or accumulation processes in the subsurface.

penetrating γ -radiation of the radium daughters. Upon the encounter of this type of NORM, appropriate Standard Operating Procedures (SOP's) should be in place to protect the workforce against exposure (both external and internal) to ionising radiation and to prevent the uncontrolled spread of NORM containing waste.

Radon sub-series

For relatively dry natural gas wells, ^{222}Rn (*cf.* Fig. 2c), forms a second distinct separation line for the potential encounter of NORM. Most likely the ^{222}Rn stems from (reservoir) rock near the perforation. Very often it is observed that with increasing depletion of gas reservoir due to production also increasing ^{222}Rn concentrations are found.

Upon decay of ^{222}Rn very thin (almost invisible) layers of ^{210}Pb can be formed at the inner surface of gas transport lines, treating- or storage installations, with activity concentrations up to 1,000 Bq/g. This isotope is the grandparent of the radiotoxic α -emitter ^{210}Po ; inhalation or ingestion of $^{210}\text{Pb}/^{210}\text{Po}$, during inspection or maintenance, might easily lead to effective doses in excess of the recommended ICRP dose limits.

Especially in treating installations and NGL storage tanks with relatively long mean residence times of ^{222}Rn a significant concentration of ^{222}Rn may take place. Especially in C_2 and C_3 fractionators concentration factors of more than 1,000 for this noble gas (boiling point of -61.8°C , with great affinity for these liquid hydrocarbons) have been observed⁴. Under these circumstances, a (significant) fraction of the radon may decay and produce very thin ^{210}Pb deposits. The presence of these deposits can be established externally from the increased γ -radiation levels from the short-lived ^{210}Pb ancestor ^{214}Bi ; this radiation quickly disappears once the supply from ^{222}Rn is stopped (*e.g.* when the vessel is vented). The radioactive lead deposits remain present; the γ -radiation from ^{210}Pb however is too weak to be measured externally ($E_\gamma = 47\text{ keV}$, 4%; $E_{\beta(\text{max})} = 61\text{ keV}$; half-life 22 years).

The observation of external γ -radiation from NORM surveys during operations, will provide adequate warning signals to the radiation safety adviser for the presence of $^{210}\text{Pb}/^{210}\text{Po}$. The implementation of adequate SOP's for inspection or maintenance activities will be sufficient to prevent unintended exposure of the workforce.

Lead sub-series

From the literature survey and based on our own experience, we have also observed that ^{210}Pb may mark an independent separation line in the ^{238}U decay series, as this radionuclide can be encountered unsupported⁴ (Fig. 2d). When carried with the water phase, this is likely caused by its specific (geo)chemical properties.

Recently, it has been observed⁵, that ^{210}Pb can also be present in gas processing/treating facilities as an unsupported radionuclide, *i.e.*, in amounts which are much higher than can be explained from the ^{222}Rn concentrations in the gas which is treated or processed in the facilities⁶. The external "warning" radiation from ^{214}Bi which can be detected in NGL processing units, is lacking here and unintentional exposure might easily take place.

This type of unsupported ^{210}Pb has been observed in two morphologies:

- as yet unidentified chemical forms in hydrocarbon condensate and in sludges, but also in scrapings from clean (to the naked eye) tubing and even on spheres used for pipe

⁶ Both unsupported ^{210}Pb and unsupported ^{210}Po has been observed in hydrocarbon condensates co-produced with natural gas.

cleaning purposes ("pigs") with activity concentrations in the order of 10 Bq[²¹⁰Pb]/g and

- as part of massive "metallic" lumps (sizes of up to several centimetres), consisting of either elemental lead or distinct lead compounds^d, such as laurionite (Pb[OH]Cl) with activity concentrations of circa 1,000 Bq[²¹⁰Pb]/g.

"On site" detection of unsupported ²¹⁰Pb, with rigid explosion proof monitors, is unfortunately not possible. In the case of the nearly invisible films, the weak γ -radiation is readily absorbed by the steel walls. Even in the case of films with relatively high surface activity, external radiation detection is not possible, because of the lack of total activity in the field of view of the monitor. In the case of massive lumps, self-absorption of the γ -radiation will very much obscure the picture. The use of very sensitive γ - or β -radiation monitors generally is prohibited at E&P treating and production sites because of safety reasons.

Polonium sub-series

Only occasionally unsupported (highly radiotoxic) ²¹⁰Po (Fig. 2e) in hydrocarbon condensate has been reported, notwithstanding the fact that one should be aware that this radionuclide may be encountered. Detection of this radionuclide can only be done on with the aid of dedicated analysis methods (see below).

Incentives for NORM analysis

NORM as discussed above, will constitute a radiological hazard, *i.e.* delivering a so-called TENR (Technologically Enhanced Natural Radiation) dose to human beings. Two pathways for exposure can be distinguished:

- enhanced *external* radiation fields near and in production and treatment facilities *c.q.* equipment may deliver a TENR dose to (contractor) *personnel*, and
- *internal* contamination of (contractor) *personnel* during maintenance and repair practices (inhalation or ingestion of NORM) and of the *public at large* through uncontrolled disposal of NORM or NOR contaminated equipment into the environment (ingestion of NOR's via human food chain).

Any TENR dose delivered to (contractor) personnel can be minimised by bringing in place Standard Operational Procedures (SOP's)⁶ whereas any TENR dose delivered to the public at large has to be controlled by competent national authorities regulating NORM disposal practices. Presently, there is an increasing international environmental concern on the occurrence and build-up of NORM in the Non-Nuclear Industries (NNI). In the Malaysian federation, in various gas/oil producing US states as well as in the European Union (EU), stringent guidelines to control NORM in oil and gas production and in the processing/treating facilities are implemented⁷ or being drafted⁸ and will be implemented into national legislation in the forthcoming years. Besides, a group of international bodies^e has issued 'basic radiation

^d The identity of these compounds has been determined by elemental analyses techniques, in combination with X-ray diffraction and IR spectroscopy. In the paragraphs below, these two specific samples shall be denoted as "lead" and "laurionite".

^e FAO [Food and Agriculture Organisation], International Atomic Energy Agency [IAEA], ILO [International Labour Organisation], NEA/OECD [Nuclear Energy Agency of the Organisation for Economic Co-operation and Development], PAHO [Pan American Health Organisation] and WHO [World Health Organisation].

safety standards', which in the absence of national radioactive substance legislation may be utilised as NORM guidance.

This type of legislation either addresses NNI NORM specifically, or includes NNI NORM. This is achieved by defining notification, intervention and/or exempt activity concentration levels of the individual NOR's present. Besides, also schemes for compulsory, regular external and internal surveys of E&P facilities and equipment, may be an integral part of this type of legislation. Though activity concentrations form the heart of the legislation, references to standardised (analytical) methods on sampling, sample pre-treatment and NOR analysis are neither included, nor recommended. To the best of our knowledge no such standardised methods have been issued yet for E&P NORM samples, neither have analytical contractor laboratories been identified who are working according to (quality assurance) certified procedures.

NORM ANALYSIS

In view of the great (economic) impact the use of unreliable analysis procedures might have for E&P industry; the lack of certified procedures for E&P NORM sampling and analysis; the strongly growing awareness of the need for standardisation in environmental screening matters, and the potential liabilities, it is needless to state that both sampling and analysis methods, which both are reliable, standardised and acceptable to the competent authorities, are a critical need.

In practice, the availability of adequate and proper NORM sampling and analysis methods would allow:

- 1) to enable accurate determination of the strict radiological levels on-site,
- 2) to qualify and to process production facility parts as well as secondary streams and waste,
- 3) to enable reporting to authorities of NORM activity concentrations involved, and
- 4) to carry out reliable quantitative risk assessments.

The availability of these methods will also strengthen the negotiating position of the E&P industry in discussing NORM levels with national authorities.

The importance of sampling, being the first step in the analysis sequence, should not be neglected nor underestimated. In fact, poor sampling degrade all values of subsequent activities as it wastes time and effort thereby requiring repeat samples to confirm uncertain results. Currently standardised sampling protocols for NORM sampling in all relevant E&P product, by-product and waste streams developed in our institute.

The standardisation of NOR analysis has been the subject of a research project at Shell Research and Technology Centre, Amsterdam (SRTCA)^f. These samples have a heterogeneous character (*i.e.* gas, hydrocarbon condensate, water, scale and sludge) and varying chemical and NOR's composition and content. An interlaboratory test programme on NORM analysis using pre-treated, homogenised actual samples from the gas and oil production and treatment facilities has been set up, in order to achieve this goal. The way in which the interlaboratory test programme has been conducted, has extensively been described⁹.

^f Formerly: Shell Research B.V., Koninklijke/Shell-Laboratorium, Amsterdam (KSLA).

Based on our experience, on geochemical considerations and from observations in the literature, E&P samples should be analysed for NOR's according the scheme presented in Table 1. These analysis were requested from the participants (from eleven Dutch institutes) to the interlaboratory test.

Table 1: NOR's encountered in E&P samples

E&P (by-)product stream	^{238}U progeny	^{232}Th progeny
Natural Gas	^{222}Rn	none
- Natural Gas Liquids	^{222}Rn , ^{210}Pb , ^{210}Po	none
Crude Oil	none	none
Production water	^{226}Ra , ^{210}Pb	^{228}Ra , ^{224}Ra
- hard scale	^{226}Ra	^{228}Ra , ^{224}Ra
- medium hard to soft scale	^{226}Ra , ^{210}Pb	^{228}Ra , ^{224}Ra
- scrapings	^{226}Ra , ^{210}Pb	^{228}Ra , ^{224}Ra
- sludge	^{226}Ra , ^{210}Pb	^{228}Ra , ^{224}Ra

Interlaboratory Test Programme

The test programme, consisting of four stages, was conducted over a period of three years. The actual oil and gas production samples varied from relatively simple single phase (e.g. methane gas, hydrocarbon condensate, production water and scale) to complex multi-phase samples (e.g. various sludge samples). After a pre-treatment step to achieve homogeneity and a check via repeatability measurements, the samples were despatched to the participants. After 3 months results were collected, subjected to statistical evaluation and feedback was given to the institutes via a review meeting (*i.e.* discussion of the results, exchanging analytical expertise, agreeing on measures to be taken and on samples for the next stage).

Prior to the despatch, the homogeneity of each sample was determined at SRTCA by repeatability measurements using γ -spectrometry, except for (i) the condensate, where radiochemical ^{210}Po analysis (*vide infra*) was applied, and (ii) the methane gas where the ^{222}Rn analysis via the α -scintillation method (*vide infra*) was used. With reference to the estimated counting statistics error, the repeatability was less than 5% at 95% confidence level (2σ), while, the more laborious radiochemical technique (^{210}Po) did show a somewhat larger repeatability.

Except for the first stage of the test programme, in which results were compared to those obtained by SRTCA, the activity concentrations of γ -emitting NOR's in the samples were certified by the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig - Germany. To enable mutual comparison of the ^{210}Po results, an aliquot of an aqueous ^{210}Po standard has been analysed by the institutes in stage four of the test programme.

Analysis Techniques

The full radiometric analysis of E&P NORM samples generally requires at least three techniques for a complete determination of the activity concentrations of the various NORMs:

Lucas cell α -scintillation method for the determination of ^{222}Rn in natural gas

The inner surface of a cylindrical Lucas cell (± 250 ml) is coated with a high-efficiency α -scintillator material (e.g. zinc sulphide). Natural gas is introduced in the cell, which will be light-tight connected to a photomultiplier tube. After about two hours ^{222}Rn will be in secular equilibrium with its short-lived progeny, particularly its α -emitting daughters ^{218}Po and ^{214}Po (cf. Fig. 2). The ^{222}Rn concentration is computed from the number of detected scintillations (efficiency calibration required) due to α -decay. This measurement technique is fast, simple and easy to operate. Analytical results will be available at the same day.

γ -spectrometry for the determination of ^{226}Ra , ^{210}Pb , ^{228}Ra and ^{224}Ra in various types of E&P samples

A γ -spectrometer consists of a high efficiency, high energy resolution ($\Delta E/E < 0.2\%$), germanium detector, which is placed in a low background radiation area obtained by shielding with, amongst others, (old) lead bricks. In general E&P samples can be measured as received, but in some cases sample pre-treatment (e.g. for sludge the sample is separated into a liquid and solids part) is required. The sample is placed in a standard size, air-tight container on top of the detector and the current pulses in the biased semi-conducting germanium detector are registered. Spectrometer efficiency calibrations are performed using NORM reference materials. Both the quick analysis (results after about two days) and the accurate analysis (about one month) require expert knowledge and can not be carried out by a layman.

- The ^{226}Ra concentration can be computed accurately from the registered γ -emission intensity of its indirect daughter isotopes ^{214}Bi and ^{214}Pb . Therefore, an air-tight sample container has to be filled and stored in order to establish secular equilibrium between the isotopes, which is reached after about three to four weeks.
However, because of the absence of ^{235}U (a.o. γ -emission line at 185 keV), a quick and somewhat less accurate analysis can be performed in about one day by direct measurement of the 186 keV ^{226}Ra γ -emission line.
- The low γ -energy 46.5 keV line of ^{210}Pb can be determined only if a sensitive germanium detector is available. E&P NORM samples often have a relatively low activity concentration and a high density. As a result, γ -attenuation in the sample will occur, which has to be taken into account during calibration of the γ -spectrometer system. A correction for self-absorption of ^{210}Pb and/or other γ -photons of low energy has been made (e.g. via γ -transmission measurements¹⁰ or via computed efficiencies from effective solid angles¹¹). Correction factors between 1.5 and 2.5 are not exceptional, particularly when high Z elements (e.g. Ba, Pb) are present.
- After establishing secular equilibrium (in about one day) with its immediate daughter ^{228}Ac , the ^{228}Ra concentration can be computed from a selection of the most intense ^{228}Ac γ -lines.
- After establishing secular equilibrium (in about two days) with its indirect daughters ^{212}Pb , ^{212}Bi and/or ^{208}Tl , the ^{224}Ra concentration is computed from a selection of their most intense γ -lines present.

α -spectrometry for the determination of ^{210}Po in various kinds of E&P samples

An α -spectrometer is an evacuated (to enhance the mean free path of α -particles) chamber, in which a silver disc with the deposited α -emitter is placed opposite an α -energy discriminative detector. A fluid (*water* reduced by evaporation; *hydrocarbon condensate* acid extracted and subsequent reduction by evaporation) E&P sample is spiked with ^{208}Po , while a solid E&P samples is acid digested and the obtained solution is spiked with ^{208}Po and reduced by evaporation. Both ^{210}Po and ^{208}Po (internal calibration of deposition efficiency) are deposited onto the silver disc. The method is very labour intensive and requires expert knowledge. It has a low detection limit, while results may be available after about one day.

Details on the methods applied, such as detection limits, accuracy, preparation and measuring time, are listed in Table 2.

Table 2: Characteristics of the NORM analysis methods applied.

NORM Analysis Method	Type of sample material	Detection limits for each NOR	Accuracy (2σ at 95% conf. level)	Preparation time (hours)	Measuring time (hours)
γ -spectrometry ^{226}Ra , ^{210}Pb , ^{228}Ra , ^{224}Ra	Solid	0.02 Bq/g	10%	0.25 to 2.0	15
	Liquid	0.01 Bq/g	10%	0.25 to 0.5	15
α -spectrometry ^{210}Po	Aqueous solutions	4×10^{-6} Bq/g	10%	3	15
	Solid	4×10^{-3} Bq/g	10%	5	15
	Condensates	0.5×10^{-3} Bq/g	10%	3	15
α -scintill. cell ^{222}Rn	Natural gas	0.01 Bq/L (STP)	10%	0.25 to 0.3	3 to 5

Results and conclusions of the test programme

In the interlaboratory test programme, the need for standardisation of E&P NORM analyses on samples from the gas and oil industry was clearly demonstrated. After each stage, a steady improvement in the reproducibility and accuracy of the analytical results was shown which may partly be attributed to the open character of exchanging analytical expertise during the review in meetings. As such, the participation in the test programme on NORM analysis proved to be beneficial to all parties involved.

With few exceptions only, the NORM analyses methods used at the Dutch institutes were proven to be reliable and accurate. Next to locally standardised methods at several institutes, those used by SRTCA were proven to be reliable and accurate throughout the test, and were found to be a sound basis for broader standardisation of E&P NORM analyses.

As described above, it has been confirmed that only three distinct analytical methods (i.e. α -scintillation, γ - and α -spectrometry) are required to fully characterise E&P NORM samples, thereby yielding complete accurate and reliable results (Table 2).

Critical parameters in the application of these methods have found to be:

for α -scintillation:

the use of methane gas for counting cell efficiency calibration, by purging methane gas through a standard ^{226}Ra solution in secular equilibrium with ^{222}Rn . It is essential that the density of the purging gas should correspond to that of the sample to be measured, as the counting efficiency of the cell increases with the decreasing gas density inside the chamber¹². In case nitrogen is used as purging gas, the ^{222}Rn counting cell efficiency for natural gas will be too low by some 7%. Besides, ^{226}Ra calibration source available from manufacturers, from which ^{222}Rn is purged by air, is only suited for this purpose, if appropriate corrections for purge gas density are made.

for γ -spectrometry:

an accurate correction for self-absorption, in view of the low energy γ -emission of ^{210}Pb at 46.5 keV and the heavy matrix of the majority of the samples analysed. A simple and adequate correction technique for self-absorption is based on γ -transmission measurements⁹. This technique only requires the attenuated and un-attenuated beam intensity of a ^{210}Pb point source to correct for self-absorption due the sample matrix at the 46.5 keV γ -line.

a uniform NOR's γ -yield data set, based on recent insight/investigations in order to obtain reproducible/reliable results for the complex sludge samples. An inventory of the NOR ' γ -yields' applied by the institutes to calculate activity concentration, showed that amongst them values varying up to 30% were used. These γ -yields are often included with the commercially available data-acquisition and data-analysis software packages, whereas more recent literature values are also used. To exclude errors in results due to variation in ' γ -yields', it was found to be necessary to use a uniform set of recently revised ' γ -yield' data^{13, 14, 15} for all γ -spectrometry results reported (*cf.* Appendix), after which a clear improvement in accuracy of the results has been observed.

for α -spectrometry:

a well-calibrated ^{208}Po spike solution, for the ^{210}Po measurement. The accuracy of the ^{210}Po activity concentration analysis has been checked using a commercially available, aqueous ^{210}Po standard. Trends observed in the analytical results produced by the participants disappeared when corrected with the analytical results obtained for an aliquot of a commercially available ^{210}Po standard. Therefore, it could be concluded that the accuracy of the results is affected by that of the ^{208}Po standard rather than by sample digestion procedure and the α -spectrometry techniques.

The observed improvement in accuracy during the four stages of the test programme were shown to be independent of the applied instrumentation and data-analysis software packages. The improvement in the γ -spectrometric results averaged per stage, and normalised to PTB or SRTCA reference values is shown in Fig. 4. With reference to a range set by the average PTB result $\pm 10\%$, a gradual improvement in the results may be observed in comparison with each preceding stage, which is noteworthy, especially for the complex sludge samples in the third stage 3 of this study. For the ^{226}Ra results sludge 1 of stage 4, it should be noted that a general trend has been observed, indicating that the PTB result might be inaccurate. For the complex sludge samples of the final stage 4, all results reported are within $\pm 10\%$ of those reported by PTB, except for two institutes (04 and 09).

In view of the importance of these findings to all institutes as a first step to standardisation, the results of the interlaboratory test programme on NORM analysis have been published in a joint multi-institute co-authorship⁸.

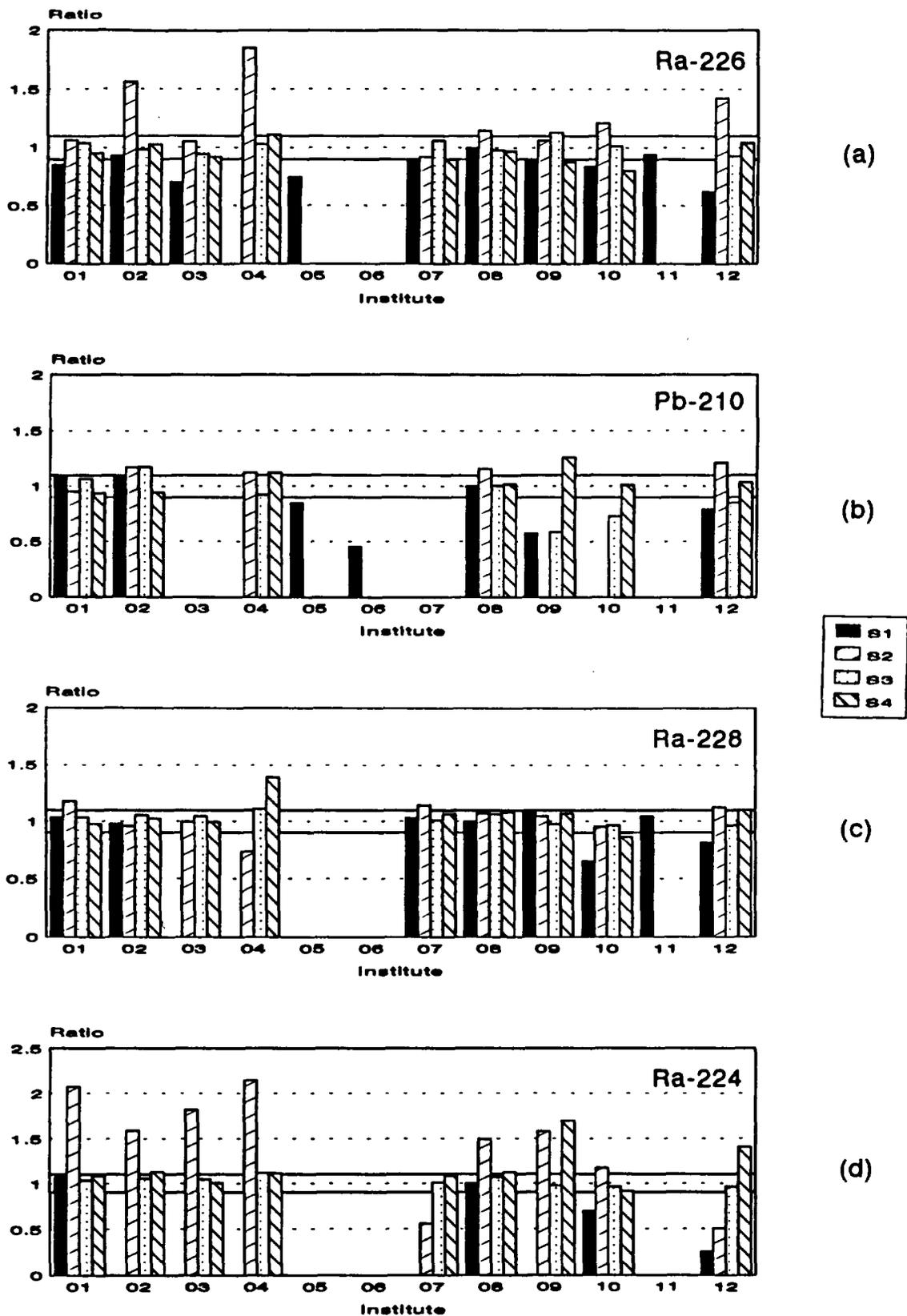


FIGURE 4 Accuracy improvement trends of averaged NOR gamma-spectrometrical results for each of the stages (S1, S2, S3, S4) of the interlaboratory test programme. Normalised results (relative to the reference institute) are shown, with a 10% error range.