Prospects for Assessing Internal Exposure Examples from the Nuclear and Non-Nuclear Sector

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1. Introduction

The two methods presently operational at NRG for monitoring internal contamination with **uranium** are urine analysis by fluorimetry and alpha spectrometry. Most likely this will remain so for the near future. Only several tens of samples are offered per year for special monitoring. The published, apparently successful, application of other detection methods has led us to review the need and potentials for optimising both fluorimetry and alpha spectrometry.

Components from production facilities for oil and gas often contain **scales** arising from the deposition of insoluble sulphates containing the radium isotopes Ra-226 and Ra-228. The latter decays to Th-228, which builds up as the scale grows older. Specific activities in the order of a few hundred $Bq.g^{-1}$ are not really exceptional. Significant internal exposure can results from inhalation during mechanical operations such as sawing, cutting, grinding and polishing on scale contaminated components. Prospects for assessing body burdens from radioactive scale at radiologically meaningful levels by whole body counting are addressed in this paper.

2. Internal contamination with uranium

2.1 Background

NRG has been regularly requested to assess the internal contamination of workers with uranium. The typical circumstances of potential exposures involved:

- incidents in an uranium enrichment plant with potentials for internal contamination with UF_6,
- incidents of initially unnoticed exposure to depleted uranium, metal or oxide, from aeroplanes.

In the latter case the requests sometimes came many months after the period of potential exposure.

2.2 Availability of U detection methods at NRG

Currently applied methods of U analysis in urine and their availability at NRG are summarized in Table 1. Fluorimetry is the only method presently being applied at NRG on urine samples. Alpha spectrometry is used for analysis of uranium and other actinides in a number of different matrices, incidentally including urine. Although neutron activation and mass spectrometry are currently applied analytical methods at NRG their practical availability for special monitoring of urine is very limited.

Table 1. Methods for determination of uranium in urine and their availability at NRG

Analytical method	Chemical separation unconditionally required?	Yield tracer in sample processing?	Available at NRG ?
Fluorimetry	no	no	yes
Alpha spectrometry	yes	yes	yes
Neutron activation	yes	no	yes [a])
Mass spectrometry	yes	no	yes [a])
Inductively coupled plasma mass spectrometry (ICP-MS)	no [b])	no	no
Kinetic phosphorescence analysis (KPA)	yes	no	no

[a]) With limited availability
[b]) If direct dilution is high (Baglan et al., 1999)

Although ICP-MS and KPA are presently not available as analytical tools at NRG the lower limits of detection ascribed to the two methods in recent publications are given in Table 2 for comparison.

Table 2. Recently published lower limits of detection (LLD) of uranium in urine by ICP-MS and KPA

Publication	Method	LLD U-238 ng.l^{-1}	LLD U-238 mBq.l^{-1}
Karpas et al. (1998)	ICP-MS, direct	1.5	0.02
Baglan et al. (1999)	ICP-MS, direct, 20-fold dilution ICP-MS, direct, 100-fold dilution	3 7	0.04 0.09
Ting et al. (1996)	ICP-MS, direct, 10-fold dilution	10	0.12
Medley et al. (1994)	KPA, mineralisation and separation	7	0.09
Mc Diarmid et al. (1999)	KPA, mineralisation and separation Idem with preconcentration	60 20	0.7 0.3

With both fluorimetry and alpha spectrometry the sensitivity can only be increased by increasing the sample volume considerably. Estimated lower limits of detection which potentially can be reached are given in Table 3. Application of fluorimetry without preconcentration has a LLD of about 5000 ng.l^{-1}, not different from the LLD of 60 mBq.l^{-1} of U-238 in alpha spectrometry applied on a small sample.

Table 3. Sample size dependent sensitivities of fluorimetry and alpha spectrometry for U-238 in urine

Sample volume, pretreatment and method	Uranium detection limit ng.l^{-1}	U-238 detection limit mBq.l^{-1}
200 µl, mineralisation, fluorimetry	5000	60
10 ml, mineralisation, radiochemistry with yield tracer, _ -spectrometry	5000	60
100 ml, mineralisation, separation, fluorimetry [a]) 100 ml, mineralisation, radiochemistry with yield tracer, _ -spectrometry	500	6
500 ml, mineralisation, separation, fluorimetry [a]) 500 ml, mineralisation, radiochemistry with yield tracer, _ -spectrometry	100	1
1000 ml, mineralisation, separation, fluorimetry [a]) 1000 ml, mineralisation, radiochemistry with yield tracer, _ -spectrometry	50	0.5

[a]) Chemical yield has to be determined somehow. Volume of eluted uranium conservatively set at 10 ml.

2.3 Required sensitivity

The required sensitivity of uranium analysis in urine depends strongly on the long clearance type of the inhaled particles. For Type F particles the predicted levels of uranium in urine after in intake of 1/10 ALI are well above the 5000 ng.l^{-1} LLD of direct application of fluorimetry even at 7 days after intake (see Table 4). For special monitoring of potential exposure of workers to airborne Type F U compounds direct fluorimetry has adequate sensitivity.

Table 4. Derived investigation levels (DIL) in special monitoring for U-238 in urine based on intake of 0.1 ALI for 5 µm AMAD and Type F compounds (from ICRP Publication 78 ,1997).

Time after intake (d)	Daily urinary excretion (Bq per Bq intake)	DIL Daily urinary excretion (Bq)	DIL of U-238 in urine ($mBq.l^{-1}$), [a])	DIL of U in urine ($ng.l^{-1}$), [a])
1	1.80E-01	6.2E+02	4.4E+05	3.6E+07
2	6.40E-03	2.2E+01	1.6E+04	1.3E+06
3	5.10E-03	1.8E+01	1.3E+04	1.0E+06
4	4.60E-03	1.6E+01	1.1E+04	9.2E+05
5	4.20E-03	1.4E+01	1.0E+04	8.4E+05
6	3.80E-03	1.3E+01	9.4E+03	7.6E+05
7	3.50E-03	1.2E+01	8.6E+03	7.0E+05
8	3.20E-03	1.1E+01	7.9E+03	6.4E+05
9	2.90E-03	1.0E+01	7.1E+03	5.8E+05
10	2.70E-03	9.3E+00	6.7E+03	5.4E+05

[a]) Based on daily urine production of 1.4 l.

This picture changes dramatically if the inhaled particles are likely to be of Type S. From Table 5 it follows that at a level of incidental inhalation of 1/10 ALI the uranium concentration in urine can be expected to decrease rapidly below the LLD of both direct fluorimetry and alpha spectrometry on small samples. In order to be of use in special monitoring intakes at a level of 1/10 ALI or lower both methods have to be optimised.

Table 5. Derived investigation levels (DIL) in special monitoring for U-238 in urine based on intake of 0.1 ALI for 5 µm AMAD and Type S compounds (from ICRP Publication 78, 1997).

Time after intake (d)	Daily urinary excretion (Bq per Bq intake)	DIL Daily urinary Excretion (Bq)	DIL of U-238 ($mBq.l^{-1}$), [a])	DIL of U concentration in urine ($ng.l^{-1}$) , [a])
1	7.00E-04	2.5E-01	1.8E+02	1.4E+04
2	4.40E-05	1.5E-02	1.1E+01	8.9E+02
3	2.60E-05	9.1E-03	6.5E+00	5.3E+02
4	2.40E-05	8.4E-03	6.0E+00	4.9E+02
5	2.20E-05	7.7E-03	5.5E+00	4.5E+02
6	2.00E-05	7.0E-03	5.0E+00	4.1E+02
7	1.90E-05	6.7E-03	4.8E+00	3.9E+02
8	1.80E-05	6.3E-03	4.5E+00	3.7E+02
9	1.70E-05	6.0E-03	4.3E+00	3.5E+02
10	1.60E-05	5.6E-03	4.0E+00	3.2E+02

[a]) Based on daily urine production of 1.4 l.

2.4 Optimisation of fluorimetry and alpha spectrometry for special monitoring

From Table 5 it is clear that the sensitivity required for special monitoring within a few days after suspected uranium exposure by inhalation of Type S particles is a few $mBq.l^{-1}$ This applies when the incidental intake of a significant fraction (1/10) of the ALI is to be detected. Both fluorimetry and alpha spectrometry will then require the processing of urine sample sizes in the order of 200 – 500 ml. Consequently, a yield tracer has to be used to assess the chemical yield from the separation and purification steps. The steps required for concentration and mineralisation of the samples are common to both methods. While the use of a yield tracer is inherent to alpha spectrometry, with fluorimetry it is not.

2.4.1 Alpha spectrometry

The approach followed by NRG in optimising alpha spectrometry has been focussed on automation of the separation of actinides by ion exchange using TRU-resin. This semi-automated method involves computer-controlled loading of the sample on a TRU-resin column followed by sequential elution of americium, plutonium, thorium and uranium from the column. Yield tracers used are Am-243, Pu-236, Th-228 and U-232. Table 6 provides a summary of results obtained in analyses of U-238. The method has also been applied successfully to the analyses of plutonium isotopes in a 350 ml urine sample from an intercomparison exercise. The gain from the automation is a reduction with about a factor of four of the man-hours needed for sample processing.

Table 6. Summary of the application of the semi-automated separation process for analysis of U-238 at NRG.

Sample type	Measured concentration U-238 (Bq/kg)	Reference concentration U-238 (Bq/kg)	Origin
Fecal ash	0.025 ± 0.001	0.023	PROCORAD 98
Model water	1.37 ± 0.05	1.33	BfS 98
Ore	4845 ± 184	4939	IAEA RGU-1
Sediment	34.3 ± 3.7	30 (CI 27 – 36.5)	IAEA-135

2.4.2 Fluorimetry

Once uranium has been concentrated from a large urine sample and eluted in the semi-automated actinide separation process, fluorimetry becomes a potential analytical tool, requiring no electroplating and long alpha counting. However, fluorimetry without a yield tracer would not constitute a method of choice. In principle the yield can be determined by simple alpha counting of a subsample of the extracted uranium provided that the sample is spiked sufficiently high relative to U-238 to be determined. U-232 presently used in our alpha spectrometric method is not very useful for this purpose because of the rather rapid ingrowth of its alpha emitting daughter Th-228 and its short lived decay products which also include alpha emitters. Therefore, the preferred yield tracer for application of fluorimetry would be U-233 which has a rather long-lived daughter Th-229 and has itself not a too long half-life to cause significant uranium addition with the spike. The method offers good prospects for optimising U determination in urine but has still to be tested in the laboratory.

3. Internal contamination with radioactive scale

3.1 Background

Incidentally NRG has been requested to assess the intake of radioactive scale from oil and gas production by whole body counting. In these cases potential exposure was suspected because of initially unnoticed presence of radioactive scale on tubulars being cleaned with abrasive methods.

3.2 Radiological characterisation of scale

Sulphates of alkaline earth elements are known to deposit in oil and gas production facilities as sulphates containing Ba, Ca, Sr and Ra. They are mobilised from the reservoir and appear in produced water from which they precipitate if sulphate is present and pressure and temperature drop down stream. Dry abrasive techniques and high temperature cutting techniques applied on scale-covered surfaces can produce airborne scale particles involving risk of internal contamination by inhalation.

Sulphate scales are very insoluble. Consequently, particles of scale are without doubt of Type S. Moreover, as many times confirmed by alpha spectrometric analyses of scales at NRG, Rn-222 is very well trapped in the scale matrix. As a result, the effective dose coefficient from inhalation to be used for these scales should take into account these characteristics. In addressing the same aspects for ore mineral sands Silk et al. have calculated effective dose coefficients taking into account both the low solubility and radon trapping of the particles. The results shown in Table 7 were confirmed by calculations at ECN (now NRG). The table includes not only the radium isotopes but also Th-228 and its daughter Ra-224 as these radionuclides arise in scale from the decay of Ra-228. For the same reason Pb-210 is included as it, however more slowly, growths into the scale from decay of Ra-226.

For exposure of workers ICRP-78 (1997) considered Type M particles only and the effective dose coefficients were calculated with allowance for radon removal from the lungs. For both reasons together the 5 µm AMAD

dose coefficient of 2.2 10^{-6} $Sv.Bq^{-1}$ for Ra-226 given in ICRP-78 and in the EU BSS for workers are lower by a factor of 17 than the value of 3.8 10^{-5} $Sv.Bq^{-1}$ we would recommend for sulphate scales.

A typical scale encountered in practice does not only contain Ra-226 but also Ra-228 as well as Th-228 in more or less comparable concentrations. The effective dose coefficient applicable to such scales would than amount to 9.2 10^{-5} $Sv.Bq^{-1}$ Ra-226. From these considerations it follows that the prospects of assessing scale intake by inhalation at radiologically relevant levels should take into account the high dose coefficient.

Table 7. Effective dose coefficients ($Sv.Bq^{-1}$) for radionuclides encountered in sulphate scale from oil and gas production

Nuclide	Silk et al (1997), 5 µm AMAD	NRG- calculated, 5 µm AMAD	NRG- calculated, 1 µm AMAD	EU BSS (1996) 1 µm AMAD
Ra-226	$3.8\ 10^{-5}$	$3.8\ 10^{-5}$	$4.8\ 10^{-5}$	$9.5\ 10^{-6}$
Pb-210	$4.5\ 10^{-6}$	$4.6\ 10^{-6}$	$5.4\ 10^{-6}$	$5.6\ 10^{-6}$
Po-210	$2.8\ 10^{-6}$	$2.7\ 10^{-6}$	$3.9\ 10^{-6}$	$4.3\ 10^{-6}$
Ra-228	$1.2\ 10^{-5}$	$1.2\ 10^{-5}$	$1.5\ 10^{-5}$	$1.6\ 10^{-5}$
Th-228	$3.2\ 10^{-5}$	$3.3\ 10^{-5}$	$3.9\ 10^{-5}$	$4.0\ 10^{-6}$
Ra-224	$2.8\ 10^{-6}$	$2.7\ 10^{-6}$	$3.3\ 10^{-6}$	$3.5\ 10^{-6}$
Pb-210 + daughters	$7.3\ 10^{-6}$	$7.3\ 10^{-6}$	$9.3\ 10^{-6}$	$9.9\ 10^{-6}$
Ra-226 + daughters	$4.5\ 10^{-5}$	$4.5\ 10^{-5}$	$5.7\ 10^{-5}$	$1.9\ 10^{-5}$
Ra-228 + daughters	$4.7\ 10^{-5}$	$4.8\ 10^{-5}$	$5.7\ 10^{-5}$	$5.9\ 10^{-5}$
Th-228 + daughters	$3.5\ 10^{-5}$	$4.6\ 10^{-5}$	$4.2\ 10^{-5}$	$4.3\ 10^{-5}$

3.3 Scale detection by whole body counting

The facility for whole body counting at NRG comprises a P-type high purity germanium detector positioned above a „chair“ in a low background surrounding. Whole body counting for control of internal contamination with artificial radionuclides involves 20 minutes standard counting time. To obtain average background count rates in the peak areas relevant to sulphate scales 100 spectra of such routine subject counts were added. The results given in Table 8 were not significantly different from background count rates obtained with an empty chair. The background count rates apparently relate to the surroundings.

Table 8. Background count rates and sensitivity of whole body counting system at NRG for nuclides from sulphate scale.

Nuclide	Energy (keV)	Number of counts in 20 minutes averaged over 100 subject spectra	Calibration factor [a]) (Bq per count in 20 minutes)
Ra-226	186	4.5 ± 0.5	120
Pb-214	352	4.9 ± 0.4	20
Bi-214	609	1.8 ± 0.3	20
Ra-228	911	1.1 ± 0.2	40
Th-228	583	1.8 ± 0.2	30

[a]) Estimated from phantom calibration

A count rate of about 10 times the long-term average background in the ROI of Bi-214 is needed to positively identify the presence of the nuclide in a subject. This corresponds with an estimated body (lung) burden of the order of about 400 Bq. How this would relate to an estimated intake depends on the time between intake and the actual measurement and the clearance rate of the inhaled particles. We can assume that at the time of measurement the lung burden is about 10% of the intake. Therefore the minimal detectable body burden corresponds with an intake of 4000 Bq Ra-226. The effective dose from an intake equal to the detection limit would amount about 400 mSv. The prospects of detecting activity from inhaled scale by whole body counting at levels relevant to radiological monitoring are very low indeed. Therefore, we have concluded not to offer whole body counting as a tool to assess intake of radioactive scale, even when urgently requested.

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