INTAKES OF URANIUM NITRATE THROUGH THE SKIN AND EYES: IMPLICATION OF OCCUPATIONAL PHYSICIANS

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Abstract. In managing the consequences of incidents, the occupational physician of a nuclear installation has to solve various questions out of medical treatment in the field of modelling, risk management and dosimetry. Internal contamination constitutes one of the potential risks to which workers in the nuclear and uranium industries can be exposed. For inhalation, the biokinetics of uranium can be predicted by assignation of the compound to a particular Absorption Type, and combining the absorption parameter values with default parameter values describing particle deposition in, and particle transport from the respiratory tract according to the ICRP lung model for uranium which describes tissue deposition and clearance after entry into the blood stream. Despite the progress made in the development of physiological pulmonary and digestive models for interpreting individual monitoring data, there are no information on the skin contamination and intakes through eyes.

The authors present their medical experiences in the monitoring of such cases occurred during the last five years. They propose a treatment of skin burned by acid with uranium nitrate and a radiotoxicological monitoring of these workers exposed to skin and eyes projection, prescribed according to the kind of the incidents, the product manipulated and the industrial risk. This monitoring is performed by urinanalysis, depending on the chemical risk, on the time and the duration of collection of excreta. Virtually uranium nitrate compounds encountered in industry, can in broad terms be considered as highly soluble, after deposition on the burned skin or after a projection in the eyes.

1. Introduction

In the heart of nuclear fuel cycle in Pierrelatte (Drome), COGEMA and COMURHEX, firms inside AREVA group, worldwide leader in energy, convert uranyl nitrate, stemming from reprocessing, into stable oxides. Since the technological process is not always carried out in a confined zone, there is no absolute barrier between the uranium compounds and the workers. In normal operating conditions, atmospheric contamination (responsible for chronic low-level internal exposure of workers) can occur. The exposure may be higher when normal operation of equipment is disturbed (incident). The industrial compounds used are very diverse both in terms of their chemical nature and their isotopic composition (natural, enriched, depleted or reprocessed uranium). These factors affect the transferability of the compounds and their chemical and radiological toxicity. Industrial reality is complex and diverse. Atmospheric contamination may vary significantly from one work place to another; it may also vary in the course of a working day for a given work place or, even, from one work team to another. These variations affect the internal human contamination. During his working day, a worker undergoes all the events that occur at the different work places he occupies. To organise

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monitoring, the occupational health physician must be aware of the technological processes, the types of uranium compound used and of the conditions in which they are really implemented. In managing the consequences of incidents, the occupational physician of a nuclear installation has to solve various questions out of medical treatment in the field of modelling, risk management and dosimetry. Internal contamination constitutes one of the potential risks to which workers in the nuclear and uranium industries can be exposed. For inhalation, the biokinetics of uranium can be predicted by assignment of the compound to a particular Absorption Type, and combining the absorption parameter values with default parameter values describing particle deposition in, and particle transport from the respiratory tract according to the ICRP lung model for uranium which describes tissue deposition and clearance after entry into the blood stream.

The authors present their medical experiences in the monitoring of such cases occurred during the last five years. They propose a treatment of skin burned by acid with uranium nitrate and a radiotoxicological monitoring of these workers exposed to skin and eyes projection, prescribed according to the kind of the incidents, the product manipulated and the industrial risk. This monitoring is performed by urinanalysis, depending on the chemical risk, on the time and the duration of collection of excreta. Virtually uranium nitrate compounds encountered in industry, can in broad terms be considered as highly soluble, after deposition on the burned skin or after a projection in the eyes.

2. biokinetic and dosimetric data for uranium nitrate:

Uranium nitrate is a major compound in the nuclear fuel cycle. It is present as yellow liquid form, in an acid medium. Retention and excretion are heavily influenced by four parameters: the route of intake (inhalation, ingestion, percutaneous), the transferability, the particle size and the contamination rate (acute, chronic). This implies the following consequences:

- No single monitoring model can be established. For each installation, it should be based on theoretical knowledge, on the physical, chemical and biological data acquired from the work places studies (concentration, granulometry, dust solubility) and on the available detection means.
- Contaminations may be single or chronic and it may not be possible to determine exactly their relative importance. It is therefore desirable that routine monitoring elucidate that point. Given the diversity of the chemical forms used, the monitoring will necessarily depend on the exposure mode.

Internal contamination constitutes one of the potential risks to which workers in the nuclear and uranium industries can be exposed. Current occupational standards for uranium are based either on radiation dose (ICRP 1991, OJEC 1996), or on chemical toxicity (NIOSH 2000, ACGIH 2000).

Radiological toxicity of uranium nitrate

ICRP recommends in case of inhalation to assess uranium nitrate intakes as a transferable compounds, type F (fast). Despite the progress made in the development of physiological pulmonary and digestive models for interpreting individual monitoring data, there are no information on the skin contamination and intakes through eyes.

In case of a direct intake, the modelling of uranium excretion via urine can be made assuming no local setting of uranium nitrate on the skin. Table 1 and Figure 1 show the magnitude of the evolution of urinary excretion after a single intake of 1 Bq via the skin. These data are useful to assess the impact of an incident with uranium nitrate.
### Table 1  predicted values of urinary excretion for percutaneous route

<table>
<thead>
<tr>
<th>days</th>
<th>daily urinary excretion in Bq per Bq intake</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.45E-01</td>
</tr>
<tr>
<td>2</td>
<td>2.21E-02</td>
</tr>
<tr>
<td>3</td>
<td>1.80E-02</td>
</tr>
<tr>
<td>4</td>
<td>1.63E-02</td>
</tr>
<tr>
<td>5</td>
<td>1.48E-02</td>
</tr>
<tr>
<td>6</td>
<td>1.34E-02</td>
</tr>
<tr>
<td>7</td>
<td>1.23E-02</td>
</tr>
<tr>
<td>8</td>
<td>1.12E-02</td>
</tr>
<tr>
<td>9</td>
<td>1.03E-02</td>
</tr>
<tr>
<td>10</td>
<td>9.43E-03</td>
</tr>
</tbody>
</table>

**Chemical toxicity of uranium nitrate**

The procedure used to generate the biokinetic data can also be used to calculate the maximum fractional uptake by the kidneys and the interval after exposure when this occurs. In turn, these fractions can be used to calculate the intake that would result in the recognised maximum recommended uranium concentration in the kidneys, 3 μg g⁻¹, assuming a kidney mass of 310 g (ICRP 1975). The Official Journal of the European Communities (OJEC 1980) has incorporated this toxicity with the statement "In view of the chemical toxicity of soluble compounds of uranium inhalation and ingestion should not exceed 2.5 mg and 150 mg respectively in any one day regardless of isotopic composition".

The recommended monitoring of renal dysfunction is:

- For severe clinical symptoms (e.g., oliguria, anuria, rhabdomyolysis, acute renal failure)
- Biochemical indicators (e.g., albuminuria, glycosuria, casts)
- Indicators of renal dysfunction (e.g., non-protein nitrogen, β₂-microglobulin, alkaline phosphatase)
Table 2 summarizes acute human exposures to uranium resulting in effects on the kidney, find in literature.

<table>
<thead>
<tr>
<th>Intake route</th>
<th>Chemical form</th>
<th>Subjects</th>
<th>Intake (mg)</th>
<th>Kidney (µg g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dermal, burn</td>
<td>Nitrate</td>
<td>1</td>
<td>130</td>
<td>35</td>
<td>Zhao, 1990</td>
</tr>
<tr>
<td>Injection</td>
<td>Nitrate</td>
<td>2</td>
<td>10</td>
<td>5</td>
<td>Luessenhop, 1958</td>
</tr>
<tr>
<td>Dermal, burn</td>
<td>Nitrate</td>
<td>1</td>
<td>10</td>
<td>3</td>
<td>Butterworth, 1955</td>
</tr>
<tr>
<td>Injection</td>
<td>Nitrate</td>
<td>3</td>
<td>5</td>
<td>2</td>
<td>Luessenhop, 1958</td>
</tr>
<tr>
<td>Ingestion</td>
<td>Nitrate</td>
<td>1</td>
<td>470</td>
<td>1</td>
<td>Butterworth, 1955</td>
</tr>
</tbody>
</table>

Table 2  Acute human exposures to uranium resulting in effects on the kidney

3. Uranium nitrate monitoring :

3.1 Implication of the medical service :
In industry, uranium nitrate can be present, often in association with other radionuclides or inert materials. Usually, there is insufficient high quality data from accidental inhalation by workers to derive the absorption parameters for uranium and hence describe the biokinetics of the material which form the bases for assessing radiological constraints or optimising monitoring procedures. The nature and the frequency at which examinations are carried out depends on what is known about the work place and on the handled products. Systematic controls may take place on a quarterly or six-monthly basis. Medical judgment cannot be based on a single isolated result. Examinations need to be repeated, first of all to confirm results and, secondly, to establish individual radiotoxicological monitoring profiles (excretion graphs plotted over time). With some exposures, regular examinations make it possible to observe the way in which uranium excretion evolves. Thus, the real biological period required for a realistic internal dose calculation may be derived.

The assay of uranium in urine can be used for intake and dose assessment after the uptake of uranium nitrate. The measurement of uranium excreted in urine at known times after exposure is a sensitive method for determining the intake of uranium. In case of incident, the occupational health physician has two types of examinations at his disposal:
- immediate urine ($U_i$), by micturation just after the intake
- 24-hour urine ($U_{24h}$)

3.2 Implication of the medical laboratory :
Urine monitoring is used for uranium nitrate exposures. Laboratories have tended to direct their efforts towards refining their analytical methods since the fraction detected in the sample is very small. Medical laboratories have two methods at their disposal for determining uranium in urine. The first one, determination by weight, is a quick and sensitive analytical examination which allows the chemical toxic risk to be assessed. The second technique is the determination of the urine activity and isotopy. With workers who may have been exposed to mixtures of varied isotopic composition, we recommend measuring the activity of the biological sample by $\alpha$ spectrometry. Scientific rigour requires that the two types of toxic risk related to uranium (chemical and radiological) be evaluated both by weight (results expressed in mg) and by radioactivity (measurement expressed in Bq). The main techniques available for measurement of uranium in urine are alpha spectrometry, fluorimetry and mass spectrometry (ICP/MS). Their advantages and disadvantages have been discussed elsewhere (WHO 2001). Essentially, alpha spectrometry must be used if the ratio of $^{234}$U to $^{235}$U and $^{238}$U is unknown. For natural or depleted uranium, mass spectrometry will be important due to their low limits of detection, and for providing information to assess the likelihood of chemical toxicity.

Urine sample conformity
The ratio between the quantity of uranium excreted and creatininuria frees scientists of the urine collection and dilution problems. Creatinin is eliminated in the urine after glomerular filtration. Tubular secretion exists, but it has little significance for physiological plasmatic concentrations. The elimination of creatinin, which is independent of food consumption, is fairly constant for a given
individual over a 24-hour period. This makes it possible to check that the 24-hour urine collection is complete. Sampling duration, and the time at which the sample is taken, are key parameters that need to be defined before establishing the monitoring procedure. All the urine results are expressed in creatininuria-related units.

Natural content in urine samples

Uranium is present in urine as a consequence of dietary intake and potential environmental exposure. Generally, individuals can excrete between about 10 ng and 400 ng of natural uranium per day in urine, although values between about 10 ng and 40 ng are more usual (ICRP 1975, Roth et al 2001, Dang et al 1992, Riddell 1995, Ting et al 1999, Minoia et al 1990, Lorber et al 1996). However milligram amounts have also been reported (Ting et al 1999). Further complications are that there may also be appreciable individual daily variation, that dietary excretion appears to be age dependent (Roth et al 2001) and that uranium excreted as a consequence of accidental or occupational exposure may not be in radioactive equilibrium.

4 - Emergency procedures of medical service

When an incident has occurred, intervention teams composed with 4 physicians and 10 nurseries have to rescue, assist, and treat the workers involved, with a minimum 1 physician and 1 nursery for 24/24h assistance.

- In case of burns by acids different from the hydrofluoric acid, the medical instructions impose a quickly and \textit{in situ} washing with water, abundant and prolonged (10 minutes) and evacuation into infirmary for immersion of the member in the frozen water during 20 minutes.
- In case of ocular projection, the medical instructions impose a quickly and \textit{in situ} eyes washing with water (10 minutes) and evacuation into infirmary for administration of an anaesthetic collyrium to prevent the blepharistic reflex followed by a second eyes washing.

If the person presents a wound supposed contaminated, a measurement with a X ray detector and one spectrometry with a hyperpure Germanium detector will be done. The burns are treated following to the incriminated acid, with precaution to prevent the passage of uranium through the skin. The part of the skin is dressed with Biafine\textsuperscript{©}. The bandages are kept for analysis. Urinary examinations are prescribed.

5 – Results of the cases of five year period

During 1999-2003, examinations of all incidents reveal that the localization of skin diseases depends widely on the industrial risk.

5.1 Global overview of incident during the period

<table>
<thead>
<tr>
<th>Place</th>
<th>localization</th>
<th>number</th>
<th>total number</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>upper limbs</td>
<td>hand</td>
<td>9</td>
<td>16</td>
<td>47%</td>
</tr>
<tr>
<td></td>
<td>arm</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lower limbs</td>
<td>knee</td>
<td>3</td>
<td>4</td>
<td>12%</td>
</tr>
<tr>
<td></td>
<td>leg</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Head</td>
<td>face</td>
<td>8</td>
<td>13</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td>hair</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chest</td>
<td>torso</td>
<td>1</td>
<td>1</td>
<td>3%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>34</td>
<td>34</td>
<td>100%</td>
</tr>
</tbody>
</table>

Table 3  Localization of contaminated areas
Table 3 and figure 2 summarize the frequencies and localizations of skin events during 1999-2003 period.

Table 4 shows the amplitude of uranium results between excretion in immediate urines ($U_i$) and in 24-hour ($U_{24h}$). A large majority of results is inferior to detection limit of the two determinations. Inside all these events, skin burns represent 59% and projection into eyes 9%. As they are together the majority of the route of intakes, the authors have studied these clinic cases.

Figure 3  speed of uranium excretion in urines

The authors observe that there is a difference in the rapidity of systemic way and in the urinary excretion of uranium with the circumstances of incidents (Figure 3). After one projection in the eyes,
instead of the speed of the eyes washing, uranium goes very rapidly in the kidneys. For the burns with uranium nitrate, there is a protection of the blood by the burned skin.

For all these incidents, a following monitoring was engaged for both radiological and chemical risk. The results of uranium in urine and of renal dysfunctions with kidney indicators confirm that there is no consequences for these workers involved. The maximum effective dose assessment is 0.15 mSv and widely less than chemical limits.

6 - Discussions

The occupational physicians underline in this rapport during 1999-2003:
- the efficiency of the emergency team,
- the good appropriateness of medical orders,
- the suitable organization of emergency department,
- the correct correlation with facilities (number of showers, baths, medical beds, etc.)

The authors highlight:
- the broad number of major events,
- the repartition of circumstances (skin burns represent 59 % and projection into eyes 9 %);
- the wide impact in internal dose assessments
- the absence of renal dysfunction and chemical effect of uranium

The major medical conclusions are:
- the rapidity of uranium transfer after a projection in the eyes,
- after burns by the nitric acid containing uranyl nitrate, the death tissue layer formation stops the effect of the acid and the contamination,

This medical overview show the minor radiological and chemical impact for all the incidents occurred during the years 1999-2003 but provide significant experience for the treatment protocols, the monitoring of workers involved and the training of occupational medicine department.

REFERENCES

1. ACGIH (2000). American Conference of Government Industrial Hygienists. Threshold limiting values for chemical substances and physical agents and biological exposure indices, Technical Affairs Office ACGIH, Cincinnati, Ohio, USA.


