

## <sup>85</sup>Kr in industrial krypton gas: origin, identification and dosimetry

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### Abstract

Industrial krypton gas is produced by fractionated distillation of liquefied air, in which it has a natural abundance of about 1 ppm<sub>v</sub>. The radioisotope <sup>85</sup>Kr is present in the atmosphere at a concentration of about 1.5 Bq/m<sup>3</sup>, due to continuous emissions from nuclear installations. Pure krypton gas thus will contain 0.35 MBq/kg of <sup>85</sup>Kr, and gas cylinders will contain many MBq of the isotope, making it detectable by radiation monitors. A case of an explosion of such a cylinder inside a factory building with subsequent detection of increased radiation levels by the fire brigade, followed by evacuation of the building and decontamination of persons, is reported in the U.S. press.

We report on a case of transcontinental transport of krypton gas, triggering of a radiation alarm and subsequent in situ measurement by different radiometric techniques. Quantitative in-situ gamma spectroscopy identified the isotope <sup>85</sup>Kr and revealed activity levels consistent with its atmospheric concentration and with measured and calculated dose rate values.

Possible other cases of such „TEARM“ (technologically enhanced artificial radioactive material) and possible techniques for detection and discrimination from attempts of nuclear smuggling are discussed.

### Introduction

The radioisotope <sup>85</sup>Kr is a main fission product and contributes significantly to the releases of nuclear power installations. The main emissions occur during fuel reprocessing and are estimated as about 10<sup>4</sup> TBq/GW·yr (UNSCEAR 2000). In 2008, the main emitter worldwide was the fuel reprocessing plant at La Hague, France, having released about 1.55·10<sup>17</sup> Bq of this isotope (BMU 2009). The atmospheric distribution is homogeneous and currently the equilibrium between atmospheric releases and radioactive decay results in a concentration of <sup>85</sup>Kr in air of about 1.5 Bq/m<sup>3</sup>, relatively constant with location and time.

The radiological properties of <sup>85</sup>Kr, apart from the well-known half-life of 10.756 yr and β<sup>-</sup> decay mode, include a low-abundance (0.43%) gamma emission of 514 keV.

Stable krypton is an inert gas, which is present in the Earth's atmosphere at a concentration of about 1.1 ppm<sub>v</sub> (CRC 1984, Aoki 2005). It is used industrially in the

production of halogen sealed beam headlights and high-efficiency dual-pane and triple pane windows. Pure krypton is obtained by fractionated distillation of liquefied air. Given the abovementioned concentration of <sup>85</sup>Kr in the atmosphere, a <sup>85</sup>Kr concentration in pure krypton of about 350 kBq/kg can be predicted.

The documentation for industrial krypton gas mentions the „slightly radioactive“ property (Air Liquide 2005a), in one case a value of 300 Bq/g is given for the activity concentration (Air Liquide 2005b).

Press records reveal an event involving the explosion of a krypton gas cylinder in a factory building located in Jacksonville, FL, USA, on January 31 2006 (New York Times 2006, First Coast News 2006). During rescue operations, a radiation alarm was triggered, and in consequence, about 40 persons were decontaminated. Apparently, the radioactive property of pressurized krypton was neither known to the company using it nor to the first responders, nor was the uselessness of decontamination measures known when dealing with an inert gas.

## Material and methods

### Record of events

A cargo of industrial krypton in 159 steel cylinders, each containing about 30 kg of pressurized gas, was shipped from Russia to the U.S.A. by truck and ship. On its way it had activated a radiation alarm during a border crossing in East Europe, but was allowed to continue its itinerary. No records of the measurement had been taken, and none of the persons involved was aware of the inherent radioactive properties of the cargo. The authors' institution was asked by the shipping company to identify the source of the radiation and to determine the possible dose to workers during a planned manual repacking of the cylinders.

### In situ measurements

The cargo was investigated using standard handheld instruments (beta/gamma contamination monitor and dose rate meter) in a first field trip, and by application of in-situ high-resolution gamma spectroscopy, using a hpGe detector of 10% relative efficiency, performed one day later. A photograph of the cargo with the dose rate meter in measurement position is shown in Fig. 1. A sketch of the measurement geometry for gamma spectrometry (with the detector in the same place) is displayed in Fig. 2.

### Dose and dose rate calculations

External and internal doses and dose rates were calculated by different methods, in order to take into account radiation protection issues of the current situation and of the reported gas cylinder explosion.

## Results

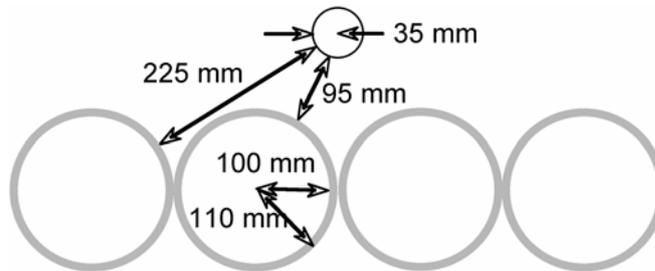
### Handheld instruments

The measurements using handheld instruments revealed values about 50% above background (dose rate and count rate of the contamination monitor), at various positions on top of the cargo. Background subtraction resulted in a net mean dose rate

of 0.058  $\mu\text{Sv/h}$  at the cargo surface. Shielding of natural background radiation from the ground by the cargo was assumed to increase this value.



**Fig. 1. Cargo of steel cylinders containing pressurized krypton gas, with the dose rate meter in measurement position**



**Fig. 2. Schematic representation of the geometry applied in the gamma spectrometry measurements**

### Calculation of dose rate from activity concentration

After the first set of handheld meter measurements, an attempt was made to estimate the expected dose rate under the hypothesis of <sup>85</sup>Kr being responsible for the increased values. This was done using a handbook developed for photon shielding calculations (Foderaro 1976). The handbook did not provide the complicated geometry present in the measurement (similar to the gamma spectroscopy geometry shown in Fig. 2). Instead, a simplified planar geometry of 20 cm of pressurized krypton gas below 1 cm of steel was used. Including build-up effects, a dose rate of 0.074  $\mu\text{Sv/h}$  was obtained. The measured dose rate increase above the cargo was 0.058  $\mu\text{Sv/h}$ , plus an unquantified contribution from shielding of natural background. In view of this uncertainty, the result could be considered satisfactory.

In a second calculation, the Monte Carlo code EGS-Ray (Kleinschmidt 2001), which is based on the code EGS4 (Nelson 1985), was used with the same goal. Here, the geometry could be modelled more precisely, resembling the structure shown in Fig. 2. The obtained result was 0.77  $\mu\text{Sv/h}$ , in good agreement with the estimate based on tables.

### Calculation of internal and external dose after a krypton gas release

Internal and submersion doses for the case of a release of krypton gas were obtained by applying tabulated dose conversion factors. The applied scenario was the complete release of the content of one gas cylinder (about 30 kg) and its homogeneous distribution within an air volume of 10,000  $\text{m}^3$ , like it could be expected in a factory building, leading to an activity concentration of about 1000  $\text{Bq/m}^3$ . The exposure time was taken as 10 minutes, and no ventilation was assumed (both values together were intended to be conservative for most situations). Dose conversion factors were obtained from ICRP Publication 72 (ICRP 1996) and German state regulations (BfS 2001). The former include doses from inhalation together with beta and gamma submersion, whilst the latter, also based on the ICRP model, allow for discrimination between the different dose contributions. Results are shown in Table 1 and reveal the dominant contribution of beta submersion. In general, doses are low, but the isotope concentration might trigger radiation alarms.

**Table 1. Organ and effective doses resulting from a 10-minute exposure to the content of one krypton gas cylinder released accidentally into the air volume of a 10,000  $\text{m}^3$  building.**

Exposure path	Conversion factor (Sv d/Bq $\text{m}^3$ )	Data source	Dose type	Dose value ( $\mu\text{Sv}$ )
Inhalation, beta and gamma submersion	$2.2 \cdot 10^{-11}$	ICRP 1996	Effective	$1.5 \cdot 10^{-4}$
Gamma submersion	$1.4 \cdot 10^{-13}$	BfS 2001	Skin	$9.6 \cdot 10^{-7}$
Gamma submersion	$7.8 \cdot 10^{-14}$	BfS 2001	Effective	$5.4 \cdot 10^{-7}$
Beta submersion	$1.1 \cdot 10^{-9}$	BfS 2001	Skin	$7.8 \cdot 10^{-3}$

### In situ gamma spectrometry

Spectra recorded on the cargo surface (in the geometry shown in Fig. 2) and at 1 m lateral distance both revealed a prominent peak at 514 keV, proving the involvement of <sup>85</sup>Kr. The spectra also revealed the 511 keV  $e^+/e^-$  annihilation peak and several signals from natural isotopes (indicated in Fig. 3).

After performing a numerical efficiency calibration for the detector in measurement geometry by means of a commercial program (LabSOCS, Canberra Inc.), the obtained activity concentration in the cargo was 0.37 MBq/kg, in very good agreement with the expected value of 0.35 MBq/kg. Furthermore, the comparison of the spectra on top of the cargo and at the side of it revealed a decrease of the peaks resulting from natural background by about 40% or more. This finding supports the assumption of a decreased natural background dose rate above the cargo.

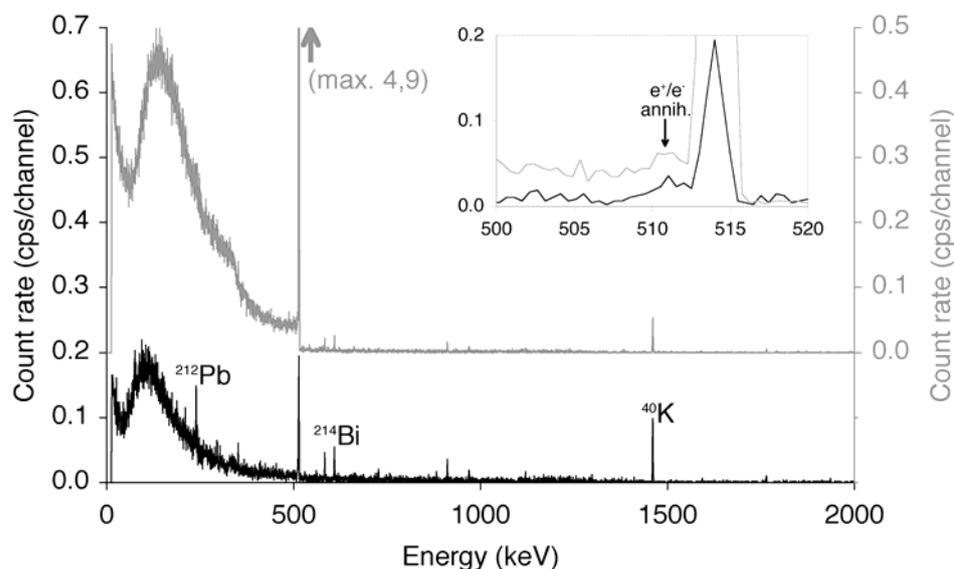


Fig. 3. In situ gamma spectra recorded on top (grey, right y scale) and at 1 m lateral distance (black, left y scale) of the gas cylinders. Spectra have been normalized for count rate. The insert displays the <sup>85</sup>Kr peak region, revealing also the 511 keV annihilation peak.

## Discussion

### By which methods could the isotope be identified unequivocally?

Knowing the concentration and the radioactive properties of <sup>85</sup>Kr in pressurized krypton gas, the measured dose rate is already a plausible indication for its presence. The increase of the reading of the (beta/gamma sensitive) contamination monitor by the same factor indicates the absence of external contamination by beta emitters. However, the expected dose rate is not readily available, e.g. in data sheets, and requires considerable knowledge and effort to be calculated. Judged from the present case, gamma spectroscopy appears to be the most straightforward way towards an unambiguous result. As in this case the characteristic gamma energy of 514 keV is extremely close to the 511 keV annihilation line, high resolution is required, requiring a semiconductor detector.

### Which occupational doses could be expected?

Due to the low gamma emission probability in <sup>85</sup>Kr decay, despite the high activity involved (about 1.5 GBq in total), expected and measured external dose rates are very low.

### Could an attempt of nuclear smuggling be excluded?

The overall consistency of the results revealed <sup>85</sup>Kr as the main radiation source. An additional source of radiation, which might have been hidden within the cargo, would have been detected in the gamma spectra in case of a gamma source of considerable activity. Pure alpha or low energy gamma emitters would not have been detected, but they would not have been found either by any other radiometric procedures.

### Can similar cases be expected in the future?

The authors expect similar findings to appear with increasing frequency, due to the increase of the numbers of radiation monitors at borders, ports, scrap yards and waste repositories. The author's laboratory experience includes findings of <sup>60</sup>Co in stainless steel, depleted uranium in scrap metal and <sup>131</sup>I in hospital waste. The common property of these objects is their artificial origin and their concentration in specific materials due to human technical action. The authors therefore propose the usage of the term "TEARM" (for technologically enhanced artificial radioactive materials) in analogy to "TENORM" (for technologically enhanced naturally occurring radioactive materials). Labeling of such materials might help to identify them as (often weak) radiation sources and to discriminate them from potentially more hazardous material.

### Conclusions

The measurements, calculations and considerations show that

- <sup>85</sup>Kr in industrial krypton gas is a weak source of radiation, often unknown to persons involved in its usage or transport;
- it might be advantageous to label materials like krypton gas as "slightly radioactive", indicating expected dose rate levels;
- high resolution in situ gamma spectroscopy appears to be the method of choice in the unambiguous identification of unknown radioactive materials.

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