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Author

Budnitz, Robert J.

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Robert J. Budnitz

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LAWRENCE BERKELEY LABORATORY
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KRYPTON-85: A REVIEW OF INSTRUMENTATION FOR ENVIRONMENTAL MONITORING

Robert J. Budnitz

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

The aim of this review is to provide an overview of the techniques which have been developed for measuring krypton-85 in various media. The main empahsis is on measurements for surveillance and protection in environmental situations, especially around nuclear reactors and nuclear fuel reprocessing plants. Measurements in specialized research applications are not treated in detail. Overviews are first provided of the physical characteristics of krypton-85; of the sources of and typical levels of concentrations in the environment; and of the radiation protection guides. The various measurement techniques are then discussed, including both laboratory-type and field-type instrumentation.

1. INTRODUCTION

Krypton-85 is one of the main radioactive fission products normally released to the atomosphere in the reprocessing of nuclear reactor fuels. In fuel ready for reprocessing (150 days of cool-down) it is present in the amount of about 11,200 curies/metric ton of fuel (ORNL, 1971). In all reprocessing plants presently operating or under construction, the entire ^{85}Kr content of the fuel is released to the atmosphere. Since these plants operate at a through-put of from one to six tons per day, ^{85}Kr is a potential environmental pollutant, requiring measurement both in the plant stack during release and in the environment after dispersion. With the rise in nuclear power production, the world-wide ^{85}Kr inventory is expected to increase dramatically. One projection is shown in Figure 1 (From ONRL, 1971).

A recent study (Diethorn and Stockho, 1972) indicates that present world-wide dose to man averages about 10^{-3} mrad/year to the bare skin, and about 10^{-4} mrad/year to the whole body. Figure 1 can be used to determine approximately how these doses might increase in the next few decades.

Krypton is a noble gas, chemically inert, which is present (as stable Krypton-78, 80, 82, 84, 86) in normal air at a concentration of 1.14 ppm = 1.14 ml/m^3 (Sax, et al., 1968). The radioactive decay of ^{85}Kr has a half-life of 10.76 years. The principle decay mode is β^- emission, with a maximum beta energy of 672 keV. The beta has a broad energy spectrum shown in Figure 2 (Mantel, 1972). The range for the maximum-energy beta is 0.3 g/cm^2 (3 mm in water, 250 cm in air). A small (0.41%) branching ratio also exists for emission of a 514-keV gamma.

2. RADIATION PROTECTION GUIDE

For 168-hour occupational exposures, the International Commission on Radiological Protection (ICRP, 1959) has established a maximum permissible concentration in air, $(MPC)_a$. This occupational limit is

3×10^6 picocuries per cubic meter (pCi/m^3). For individuals in the general public, the applicable MPC values are a factor of 10 smaller (300, 000 pCi/m^3) and for exposure to a suitably large sample of the general public, another factor of 3 smaller still (100, 000 pCi/m^3). The U. S. Atomic Energy Commission's MPC values agree exactly with the ICRP MPC's just quoted (USAEC, 1973). Throughout this discussion, the MPC will be taken as 300, 000 pCi/m^3, since exposure to a few individuals in the general public at the 300, 000 level is undoubtedly more likely than to a larger population at the 100, 000 level.

This MPC is equivalent to fractional krypton-85 atomic concentrations of 2.0×10^{-7} (^{85}Kr/total Kr) or 2.3×10^{-11} (^{85}Kr/total air). At the fence around a typical fuel reprocessing plant, concentrations of a few percent of MPC are expected to occur periodically.

3. MEASUREMENT CONSIDERATIONS

In environmental samples, the measurement of ^{85}Kr is essentially always based upon detecting the decay β^-, with any of a number of detectors sensitive to ionization energy loss. Several detection systems exist, including liquid scintillators, plastic scintillators, Geiger-Muller counters and ionization chambers. Each of the methods has its advantages and disadvantages; the discussion below is intended to point out some of the factors involved.

We shall concentrate upon measurements in the air around nuclear reactors and their fuel-reprocessing plants. Here the principle beta emitter besides ^{85}Kr is tritium (^{3}H); however, the tritium β^- has such a low energy (E_{max} = 18.6 keV) that its interference in the ^{85}Kr measurement is usually not significant. (The reverse is not true.)

There are two quite different classes of ^{85}Kr measurement systems: those which operate in the field, designed to run unattended except for periodic maintenance; and those which require laboratory procedures. The latter are invariably the more sensitive and the more precise. We shall discuss these two classes separately.

a) Laboratory Techniques

There are a number of ^{85}Kr techniques which have been developed for use in the laboratory. They all involve one substantial handicap, namely, that the volume of gas which can be sampled at some remote location and then transported to the laboratory for analysis is not large. This disadvantage limits sensitivity, but is counterbalanced by the ability to concentrate the krypton before counting and to perform other analytical procedures which are impossible to carry out in the field.

The two most common laboratory techniques use plastic-scintillator shavings contained within a gas-tight vial, and liquid scintillator as a solvent for the ^{85}Kr-containing gas.

(i) Plastic Scintillator

We shall discuss the technique of Sax, Denny, and Reeves (Sax *et al.*, 1968), which is typical of the plastic scintillator methods.

Plastic scintillator shavings of 20-40 mesh (an inexpensive by-product from any of several scintillator manufacturers) are encased in a glass vial of volume about 4 ml. A sample of pure krypton gas is prepared using vacuum-cryogenic techniques. The vial is evacuated and then filled to a known pressure (near 600 torr) with the krypton samples.

A scintillation counter then measures the pulse-height spectrum.

Calibration of the counting efficiency (the fraction of the β spectrum above the counting threshold) is determined using a known ^{85}Kr standard acquired from NBS (NBS, 1962). The counting efficiency is about 95%. Given about 0.5 ml of nearly pure krypton (equivalent to that present in about 0.5 m^3 of air), measurements can be made of normal ^{85}Kr background levels in the 10 pCi/m^3 range to about ±10% (Sax et al., 1968). The limit of detection is about 1 pCi/m^3 of air sample, with a 100-minute counting time, at the two-standard-deviation level above background.

(ii) Liquid Scintillator

Here we shall discuss that aspect of liquid-scintillation counting which is unique to or particularly relevant to ^{85}Kr.

The liquid scintillator method relies upon the high solubility of krypton in many of the commonly used liquid scintillators. Krypton is soluble (Linke and Seidell, 1965; Shuping et al., 1969) in aromatic solvents to ~ (1 ml Kr)/(ml solvent).

The earliest descriptions of liquid scintillators used for ^{85}Kr counting are those of Horrocks and Studier (1964), and Curtis, Ness and Bentz (1966). Those early methods suffered from a limit on the amount of krypton which could be introduced into the solution.

Shuping, Phillips, and Moghissi have reported a method in which about 25 ml of toluene-based liquid scintillator acts as solvent for about 10 ml of gas (Shuping et al., 1969). The gas is introduced into an evacuated glass vial, filled with deaerated scintillation solution.

"If the ^{85}Kr concentration in air is sufficiently high, the sample may be introduced directly into the solution and successfully counted" (Shuping et al., 1969). More commonly, krypton is concentrated cryogenically. A rate of 1 cpm above background corresponds to 0.025 pCi ^{85}Kr/m^3 of air, so that levels of that order of magnitude are detectable with the method. Accuracies in the ±4% range are achieved, when ^{85}Kr activities of ~10 pCi/m^3 of air are present.

One of the more difficult problems in the procedure just described is the separation of krypton gas from the main air sample. To overcome this problem, a separation system for krypton, by Cummings, Shearin, and Porter employs ^{83m}Kr as a spike in the air sample, in order to determine directly the ^{85}Kr yield after a complicated separation procedure involving "charcoal and molecular sieve cold traps, calcium sulfate, ascarite, and a titanium furnace (900°C) for the removal and separation of other air constituents from krypton" (Cummings et al., 1971). A description of a method for generating ^{83m}Kr (2-hour half-life) from ^{83}Rb in the laboratory has been given by Moghissi and Hupf (1971).

Another ^{85}Kr system, described by Stevenson and Johns, uses a battery-operated air compressor to collect 1 m^3 of air in the field. After a series of cryogenic absorptions and elutions in the lab, the krypton is dissolved and counted in a liquid scintillator. The krypton recovery ranges from 50 to 70%, measured volumetrically. These workers report a minimum detectable sensitivity (three standard deviations above background) of about 2 pCi ^{85}Kr/m^3 of air, with a 4-hour counting time (Stevenson and Johns, 1971).

b) Field Instruments

For measurements in the field, the ideal goal is an instrument which can record continuously, with reasonably short time-integration periods, at sensitivity levels well below the current average background of about 10 pCi/m^3 of air. The ideal instrument must also be rugged enough to withstand temperature and humidity extremes and shock; and should require little maintenance.

A study (Smith et al., 1970) of several possible field instruments was carried out in 1969 by the Northeastern Radiological Health Laboratory, U.S. Public Health Service. Four ionization chambers and four Geiger-Muller counters were studied. Calibrations were performed in the laboratory, followed by determinations of the minumum detectable concentrations. Some of the instruments were then used in the field around a fuel-reprocessing plant, to determine performances under actual field conditions.

None of the field instruments came close to the sensitivity required for background measurements in the pCi/m^3 range. However, all were sensitive enough to measure fractions of the MPC for individuals in the general public (300,000 pCi/m^3).

(i) Flow-through Ionization Chambers

The four flow-through ionization chambers were tested in the laboratory using dry, radon-free air. They ranged in size from 0.5 to 4.3 liters in volume. After calibration against an NBS standard (NBS, 1972), the minimum detectable concentrations (MDC, defined as twice the standard deviation in counting) were determined: they ranged from 130,000 to 40,000 pCi/m^3. The calibrations were performed with errors (2σ) in the ±7% to ±17% range. These ionization chambers have several undesirable properties: first, they must be used downstream of a radon holdup trap and filter (or equivalent). Second, because of the use of the radon trap, the averaging time is in the 30-minute range, which is much longer than the few-minute time for a significant change in ^{85}Kr concentration when a fuel-reprocessing-plant plume passes directly overhead. Third, it is necessary to make appropriate measurements of pressure, temperature, humidity, and external background variation to obtain reasonable accuracy. Finally, maintenance requirements are high. To quote from Smith _et_ _al._, (1970):

> "It should be noted that although the ionization chamber systems can be made to operate in the field, the degree of care, number of precautions, and amount of operator training required to obtain usable data for environmental levels, and the questionable nature of the data obtained when the field levels passing the instrument are fluctuating rapidly, all weight heavily in favor of using simpler systems for this purpose."

(ii) Geiger-Muller Counters

Several Geiger-Muller (G-M) tubes were also studied by Smith _et_ _al._ (1970). These were calibrated against the flow-through ionization chambers described above, and then minimum detectable concentrations were determined. The calibration errors (2σ) were in the ±13% region for all of the G-M detectors. The most sensitive G-M detector was found to be the Eon 8008H, a double end-window pancake detector, of 2" diameter with 3.5 mg/cm^2 mica windows. It had an MDC of 12,000 pCi/m^3 with a counting time of 10 minutes (sample) and 10 minutes (background). Unfortunately, this detector was so fragile that its use in the field was precluded.

The other G-M detectors all had MDC's in the region of about 25,000 pCi/m^3. These instruments were Amperex 18546 and an Eon 8001T (both one-window pancake detectors of 2" diameter); and an LND 719 and and Eon 5108E (both cylindrical probes, 5-1/2" long, 0.6" diameter, 30 mg/cm^2 wall thickness). The cylindrical instruments were found to be durable against mild shock and rain in the field; the single-window detectors were less durable against shock. However, all performed in the field with sensitivities nearly identical to those measured in the laboratory. The conclusion can be taken directly from Smith et al., (1970):

> "Long-term (weeks to months) environmental monitoring would demand the most sensitive detectors and systems that could endure the environment with a minimum of attention. The choice at present is between the single windowed pancake tube (Amperex 18546) and the thicker walled (30 mg/cm^2) cylindrical probes (Eon 5108E or LND 719) which, though slightly less sensitive,

are certainly the most durable of the detectors evaluated."

4. SUMMARY AND CONCLUSIONS

Two important numbers determine the sensitivity required of instruments for measuring ^{85}Kr in environmental air:

1. the maximum permissible concentration for individuals in the general public is 300,000 pCi/m^3 (ICRP, 1959; USAEC, 1973)
2. the typical "background" level of ^{85}Kr in air today is in the range 10 to 15 pCi/m^3 (Sax *et al.*, 1968).

The ideal instrument is one capable of measuring the background level to a small fractional accuracy; several of the laboratory techniques described have this sensitivity. These techniques, which use liquid or plastic scintillation counting, all suffer from a common problem: a complicated series of laboratory steps is required to concentrate the krypton from the original gas sample.

In contrast, the *field* monitoring instruments (Smith *et al.*, 1970) are all several orders of magnitude less sensitive, with MDC's ranging from 12,000 to 28,000 pCi/m^3 (for the G-M detectors) and from 39,000 to 190,000 (for the ion chambers). All of these instruments are thus capable of detecting ^{85}Kr at levels well below the 300,000 pCi/m^3 for individuals in the general public, but cannot measure ^{85}Kr in "background" samples.

At present, there does not exist (to our knowledge) a commercially available *Krypton-85 Monitor* which can be purchased off-the-shelf. The G-M detectors described by Smith *et al.* are worthy of commercial development, to meet the need for monitoring in the field around fuel-reprocessing plants and nuclear power reactors. Any commercial instrument would have to satisfy several requirements besides sensitivity:

(1) Rugged construction, insensitivity to changes in temperature and humidity.

(2) Some method of continuous recording of the data: at least a strip-recorder, or preferably a direct magnetic-tape record.

(3) Some method of calibration: perhaps a frequent, rapid check with a high energy source, and a less-frequent check in a controlled chamber of known ^{85}Kr concentration.

For the more sensitive measurements of levels below the natural background of a few pCi/m^3, field instruments are presently out of the question. Some kind of cryogenic concentration method is required to increase the specific activity to the point where reasonable counting times ($\lesssim$a few hours) are possible.

One key problem here is with the accuracy and reproducibility of the concentration mechanism. Accurate determinations of the fractional yield through a multi-stage sequence are notoriously difficult. This is true especially if a known volume of "ordinary" krypton is introduced as a carrier, since all krypton today unfortunately contains ^{85}Kr at levels in the ppm region. One solution is the use of ^{83m}Kr as a tracer to determine the yield.

There are a few technological developments on the horizon which will provide some increased sensitivity. The most important of these is the recent development of substantially better photomultiplier tubes

(Leskovar and Lo, 1972). These tubes have higher quantum efficiency, lower noise, and generally superior operating characteristics. This will improve the scintillation counting method considerably.

The incorporation of integrated circuit electronics into the G-M detector systems will also be important, helping to increase the ruggedness and reliability of the technique. Also, read-out systems are being developed which will enable the data to be collected, recorded, and analyzed remotely, bypassing the strip-chart-recorder step entirely.

Finally, it should be noted that some of the instruments designed to measure <u>tritium</u> in gaseous environmental samples are also capable (or adaptable) for the ^{85}Kr problem, with some modifications and changes in procedure.

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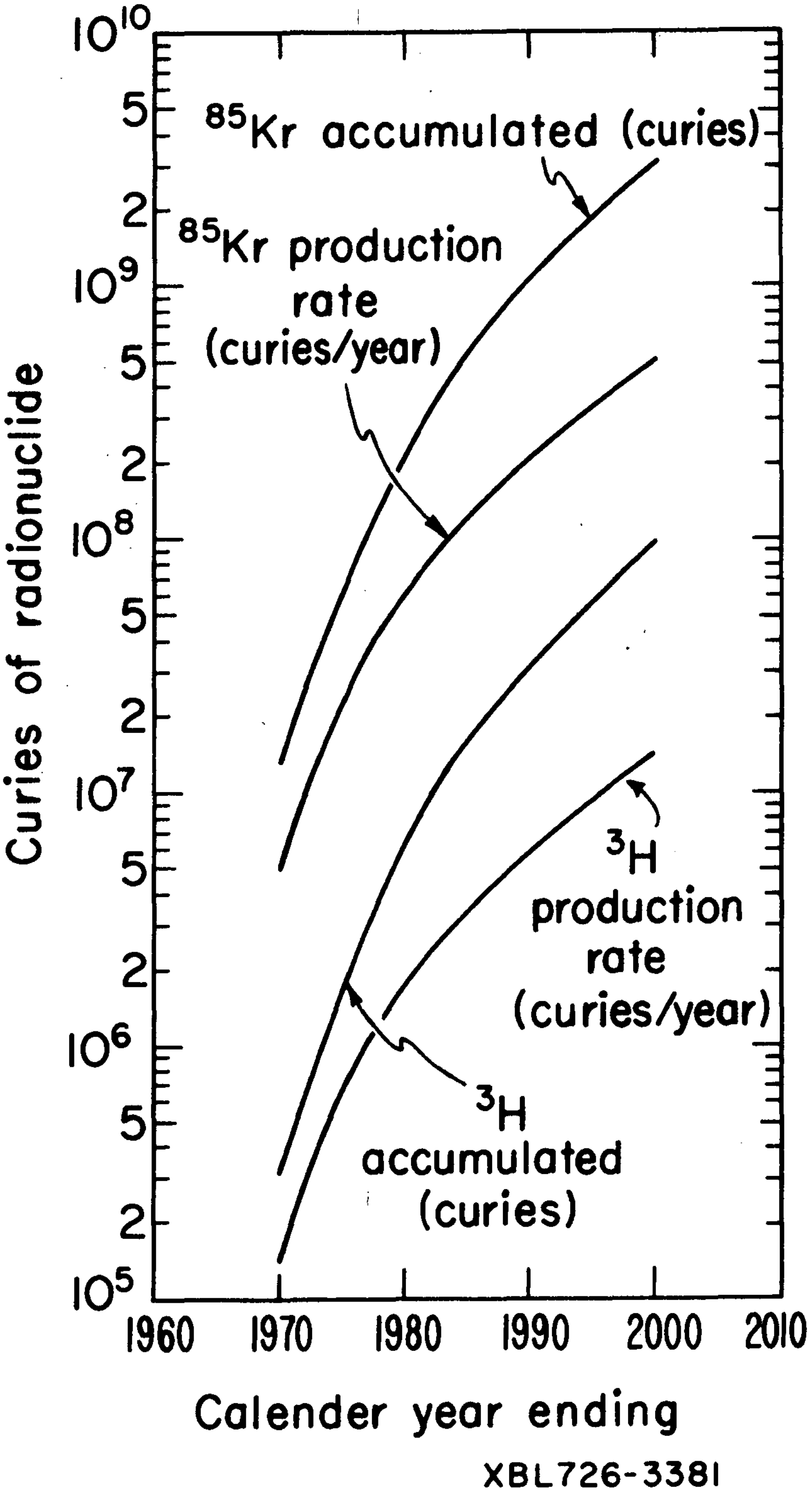
FIGURE CAPTIONS

Figure 1. Estimated production of Krypton-85 and ^{3}H (Tritium) from the Nuclear Power Industry of the Free World (ORNL, 1971).

Figure 2. Beta-particle energy spectrum from Krypton-85.



^{85}Kr accumulated (curies)
^{85}Kr production rate (curies/year)
^{3}H production rate (curies/year)
^{3}H accumulated (curies)
Curies of radionuclide
10^{10}
5
2
10^{9}
5
2
10^{8}
5
2
10^{7}
5
2
10^{6}
5
2
10^{5}
1960
1970
1980
1990
2000
2010
Calender year ending
XBL726-3381

Figure 1

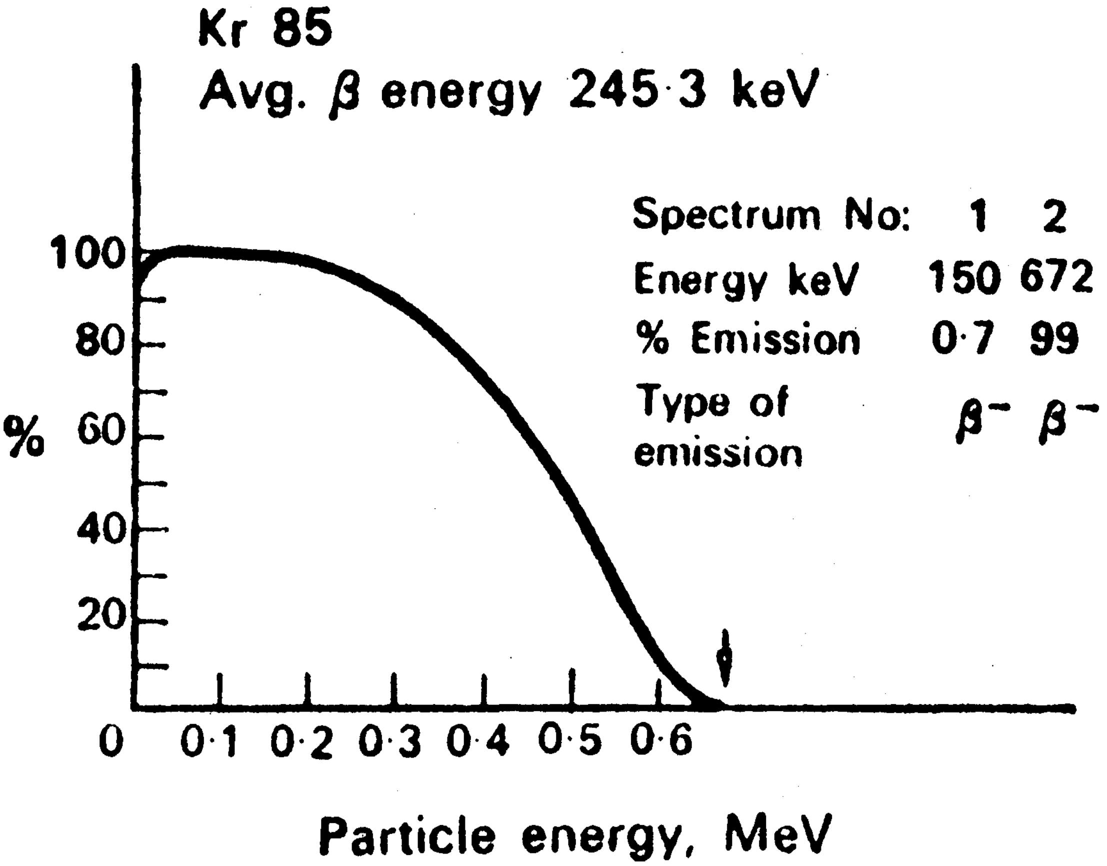


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Figure 2

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
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