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Perspective

The radioactivity of atmospheric krypton in 1949–1950

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ABSTRACT **The chemical element krypton, whose principal source is the atmosphere, had a long-lived radioactive content, in the mid-1940s, of less than 5 dpm per liter of krypton. In the late 1940s, this content had risen to values in the range of 100 dpm per liter. It is now some hundred times higher than the late 1940 values. This radioactivity is the result of the dissolving of nuclear fuel for military and civilian purposes, and the release thereby of the fission product krypton-85 (half-life = 10.71 years, fission yield = 0.2%). The present largest emitter of krypton-85 is the French reprocessing plant at Cap-de-la-Hague.**

It is generally known that the chemical element krypton, isolated from the atmosphere in 1996, is radioactive. For example, Wilhelmova *et al.* (1) quote the air in Prague, Czechoslovakia, as having an average krypton-85 content of 0.8 Bq per cubic meter of air in the period 1983–1988. This radioactivity is the result of the dissolving of nuclear fuel both from past military and civilian programs and from present civilian power programs.

The largest current producer of radioactive krypton is the French reprocessing plant at Cap-de-la-Hague, which released 1.8×10^{17} Bq of krypton radioactivity in 1994.¶ If diluted by the whole world's atmosphere, this would produce a radioactivity of krypton of 2,400 dpm per liter (STP).‖ Cap-de-la-Hague's output may represent about half of the present input into the atmosphere of this radioactive nuclide.

The present paper provides the earliest known measurements of the krypton radioactivity in the United States, relates them to the output of the Hanford reactors and of the nuclear explosions that occurred before the samples were collected, and points out the special characteristics of krypton-85 for studying atmospheric mixing on a planetary and subplanetary scale.

The nuclear fission product krypton-85 was discovered independently by Thode and Graham in Canada (ref. 2; ref. 2 was based on ref. 3) and by Hoagland and Sugarman in the United States (4) in the mid-1940s. It was found to have a half-life of about 10 years [the presently listed value is 10.70 years (5)], to decay primarily by beta emission [a branch emitting a half million electronvolt (MeV) gamma ray was later found (6)], and to be formed in about 0.23% of the thermal neutron induced fissions of uranium-235.

Soon after the World War II, while writing up the fission product research of the war, A.T. pointed out the special characteristics of this fission product for, among other uses, tracing air masses on a worldwide scale (letter from A.T. to P. Morrison, Argonne National Laboratory, July 19, 1946).

Preliminary measurements made in a screen-wall counter by W. F. Libby (in 1947; unpublished work) and A.T. and W. F. Libby (in 1948; unpublished work) gave indications that these predictions were correct. The present report describes the technique that was used soon afterward to establish more precisely that atmospheric krypton in the late 1940s was much more radioactive than it had been, and gives the results of some early measurements of krypton samples isolated from the atmosphere at that time.**

Measurement Technique

The measurement technique that was used was influenced by those simultaneously being developed by Libby and Anderson (9) to measure the radiocarbon content of samples of archeological interest. In contrast to Libby's work, however, Geiger counting of gas samples was employed. The counters, made of brass, were 3 in. in diameter and 24 in. long, with an insulated central wire of 0.5 mil tungsten. The volume of the counters was about 2.3 liters.

The counters, filled with an inert gas, after shaking, had a background counting rate, in an open room, of about 1,000 cpm. When they were inserted into a "tomb" consisting of a shield of 8 in. of steel surrounded by 4 in. of lead, the background went down to about 350 cpm. A more drastic reduction was achieved by operating the counters not only inside the tomb but also inside a bank of 2-in. Geiger counters that were used in anti-coincidence to cancel out cosmic ray events. Only events that were not in coincidence with the shield counter discharges (1,900–2,000 per minute), within about 70 μs, were accepted.

There was provision for two counters inside this massive shielding and anti-coincidence counters. Use of this technique lowered the background of a counter to 16–35 cpm. The residual activity was mostly due to the construction materials of the individual counters. The dead time of the counter was about 5 ms, leading to a correction of less than 4% for the most radioactive samples measured. Typical counting times were 8–12 h in the work reported here. Assurance of statistical behavior was obtained from a 15-min printout of the disintegrations recorded during the long measurement times.

It was established that the response of a counter was adequately insensitive to position in the tomb, to the presence of the other counter, or to the krypton radioactivity in it. At the time of these measurements, a typical sample had a counting rate of 150 cpm when filled to a pressure of 20 cmHg (1 cmHg = 13.3 Pa).

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¶J. Pellissier-Taanov, private communication to L. Machta, World Meteorological Congress, 1995, Vienna.
‖In this regard, STP means 0°C and 760 torr (1 torr = 133 Pa) pressure. The abundance of krypton in the atmosphere is taken as 1.12×10^{-6} parts by volume.
**This paper is based, in large part, on refs. 7 and 8.

The work reported here was carried out in the old ruling engine room for grating production in the basement of the Ryerson Physics Laboratory of the University of Chicago.

The counters were filled to a pressure of 100–500 torr of the gas to be measured (krypton or argon) and 15 torr of a quench gas. Ethyl alcohol was used for this purpose for most of the measurements; later measurements were made with ethyl ether as quench gas. After filling the counters and shaking with an internal shaker to promote mixing, the applied high voltage was increased until the counting rate indicated a plateau region (less than 10% change in counting rate per 100-V change in operating voltage). Counters filled with a gas having no radioactivity had larger slopes). A 2.0-V output pulse was obtained at a voltage of 2,200 V when the counter was filled with a krypton pressure of 300 torr and 15 torr of a quench gas. The plateau measurements and a monitor of counter behavior were facilitated by use of a capsule of a radium solution that could be placed in a reproducible position near the counter.

Early measurements, made on three different krypton samples, established that the radioactivity being measured was due to the krypton in the counters. Successive measurements showed that nothing shorter lived or appreciably longer lived than the 10.7-year half-life was present in detectable amounts.

Special efforts were made to ensure the chemical purity of the samples that were measured. These always included adsorption and desorption from activated charcoal under controlled conditions, and removal of reactive components by treating the gas with finely divided calcium prepared by dissolving the calcium in liquid ammonia and then evaporating the ammonia (10). The purified krypton had to show the correct vapor pressure at liquid nitrogen temperature (1.9 ± 0.2 torr).

Although the specific origin of the radioactivity that was found in post-1945 gas samples could not be pinned down completely, three samples of gas that had been isolated from the atmosphere before 1934 (gases 3, 5, and 38) showed no radioactivity, whereas all samples isolated from the atmosphere after mid-1947 had easily measurable radioactivity (see below). This makes assignment to nuclear fuel production or nuclear tests most probable.

Sample Procurement

All the samples measured for this report were procured by B. R. Balcar (Special Consultant to U.S. Government Agencies) from operating commercial liquid air plants in northeastern United States. Until October 1949, the samples represent plant operations lasting several days with perhaps 10% representing a "heel" from previous operations. After that date, the plant operation period was restricted to the day listed, except as noted. However, even here, only about 50% of the krypton produced represented the air processed that day; some 13% came from air that had entered the plant the day before, and so on. Thus, these early samples represent an average over several days of the krypton-85 content of the ambient air.

Sample Measurement Procedure

Each sample was measured at least twice, in different counters or at different pressures. The duration of each measurement was at least 8 h. The 15-min records of each measurement were examined to be sure that they were consistent with the totals, that they exhibited no trends, and that the fluctuations were compatible with statistics. The number of events that had been canceled by the anti-coincidence counters was noted and had to be within a small range. The results from the two measurements, after background subtraction, had to agree within the statistical accuracy of the measurements before the results were accepted. Occasionally, a third measurement, sometimes after gas purification, was required.

The routine activity measurements of a gas were made relative to the activity of a "standard gas" (gas 21, collected at Philadelphia, PA, between April 26 and May 10, 1949). This was done by periodically measuring the standard gas in the counter involved. Typically, some 10–20 routine gas measurements were made between standard gas measurements. The standard gas had an activity of about 200 dpm at STP on its collection date.

Similarly, the background of a particular counter was determined, usually at the time of standard gas measurements, by a measurement of the activity of pre-nuclear-age krypton (see below). The measurement of the standard gas and of the background of a counter represented a "calibration" of the counter.

Absolute Radioactivity

Thus, the routine gas measurements provided the activity of the gas in question relative to the activity of the standard gas. The absolute activity of this standard gas was determined in two different ways. In the first, a sample of this gas was given to A. Engelkemeier (Argonne National Laboratory, Argonne, IL), who was collaborating with W. F. Libby at the time and using a screen-wall counter. She added a known amount of radioactive krypton to the gas. From the decrease in radioactivity, the activity of the standard gas could be determined.

In the second method, two counters were constructed in this laboratory, identical in diameter and in other construction details, but of two different lengths. The lack of efficiency at the walls of these large counters was estimated to be small (about 0.6%), and the difference in counting rate per unit volume could be assigned to the inefficiencies of the counters at the ends. The two methods agreed, with the method using counters of different lengths having a smaller error. The effective volume of a typical counter was thus determined to be 98.0% of the value calculated from the length of the bare central wire [the effective volume of one of the counters was 2.43 (±2%) liters]. In this way it was determined that the standard gas had a disintegration rate of 191 dpm per liter (standard conditions) on the collection date. This corresponds to an isotopic abundance of 5.5×10^{-14} of krypton-85 in the standard gas on collection date.

All routine gas measurements were corrected to the time that the particular gas was collected (separated from the ambient atmosphere) and were then converted to absolute

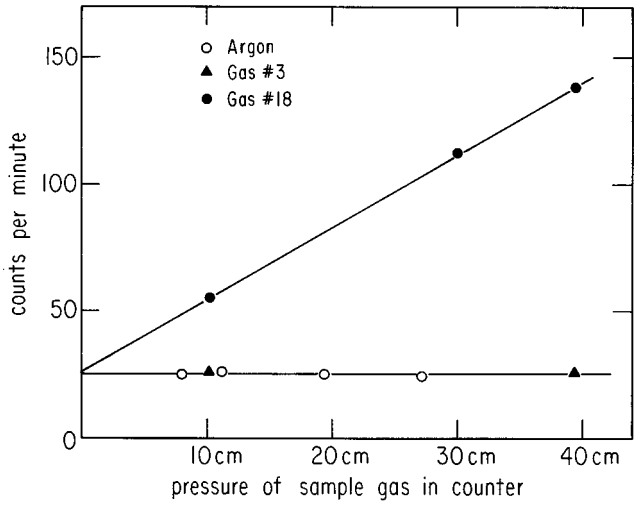

FIG. 1. The radioactivity of early nuclear age atmospheric krypton. Shown is the radioactivity, in counts per minute (abscissae), as a function of pressure (ordinates) of argon, krypton collected before 1945 (gas 3), and krypton collected in 1948 (gas 18).

values using this value for the activity of the standard gas. The corrections for decay between collection time and measurement time were usually less than 4% for the samples discussed here.

The statistics of counting of the duplicate measurements of the routine gas samples were well below 1%. The agreement of the duplicate measurements suggest that the radioactive assays carry a 1 σ uncertainty of 3%, with most of this coming from the manipulation of the gas samples.

Radioactivity of Pre-Nuclear-Age Krypton

At the time that this program was initiated, it was important to establish a limit to the radioactivity of pre-nuclear-age krypton. This was done in the following way. Three samples of krypton that had been isolated from the atmosphere before 1945 were obtained (B. R. Balcar): gas 3, prepared in July 1932; gas 5, prepared before 1934; and gas 38, old, but the date of isolation uncertain. They were measured in our counters at several pressures. A sample of argon was measured in the same counter, as well as a sample of gas collected after 1945 (gas 18, collected in Buffalo, NY, during July 1948). The results of one of the comparisons are presented in Fig. 1. Shown in the figure are the counting rates of the three gases (pre-nuclear-age krypton, argon, and krypton collected in 1948) as a function of pressure. The figure indicates that the counting rate with pre-nuclear-age krypton (isolated from the atmosphere before 1945) was very nearly the same as that when argon was in the counter, and that the counting rate of these two gases did not increase with pressure. In contrast, the counting rate when the krypton collected in 1948 was in the counter was much higher and increased linearly with the pressure of the filling. The extrapolated value of the radioactivity at zero pressure of gas 18 is indistinguishable from that of argon and pre-nuclear-age krypton.

The calculated limit on the radioactivity of pre-nuclear-age krypton (from the lack of increase of the counting rate with pressure) is 5 dpm per liter (STP) of krypton. The other two pre-1945 gases behaved similarly.

The only value available to compare with this number is the estimate of Styra and Butkus (11). They have calculated that the cosmic-ray production of krypton-85 by neutrons in the atmosphere is 5.2×10^{13} Bq per year. This would lead to an activity of about 10 dpm per liter of krypton. This estimate is in adequate agreement with our upper limit.

Several samples of gases collected after 1945 were measured several times, often after extensive purification. They showed no change in specific radioactivity, nor any decay other than what could be attributed to krypton-85. Finally, one sample

Table 1. Radioactivity of atmospheric krypton before mid-1950

Sampling location	Gas no.	Collection date	Observed activity	Activity due to U.S. operations
Philadelphia	21	4/28/49–5/10/49	191	110
	33	8/4/49	163	118
Johnstown, PA	7	Before 9/1/47*	101	70
	22	1/1–7/49	198	100
	25	1/1–7/49	198	100
	26	3/12–14/49	166	109
	53	7/25–28/49	156	115
	31	8/4/49	188	115
	73	1/29/50	304	
	74	1/31/50	264	
	75	2/16/50	331	
	76	2/18/50	325	
	77	2/20/50	307	
	78	2/21/50	296	
	79	2/23/50	266	
	80	2/25/50	296	
	82	3/6/50	272	
	83	3/13/50	250	
	84	3/23/50	260	
	85	3/30/50	278	
	89	4/7/50	268	
	91	4/19/50	240	
	92	4/27/50†	300	
	132	5/28/50	277	
	133	6/3/50	269	
	151	6/30/50	295	
Pittsburgh	35	1/28/49	173	102
	60	5/12/49	171	111
	61	5/16/49	171	113
	28	6/28–29/49	177	113
	36	7/24/49	184	115
	37	8/11–13/49	195	
	54	8/20–26/49	176	
	55	9/13–17/49	212	
	56	9/25–28/49	189	
	62	10/19/49	211	
	57	10/28–29/49	194	
	58	11/11/49	197	
	59	11/23–24/49	236	
	63	12/8/49	232	
	64	12/21/49	335	
	65	1/6/50	227	
	66	1/15/50	261	
	68	1/23/50	302	
	69	1/25/50	237	
	70	1/27/50	227	
	67	1/28/50	308	
	71	2/1/50	250	
	72	2/10/50	264	
	90	2000/4/11/50–0800/4/12/50	253	
Boston	20	10/48	138	94
	27	6/10–16/49	160	113
	29	6/17–19/49	152	113
	32	8/4/49	203	115
	41	8/26–27/49	165‡	
	42	8/27–28/49	177	
	43	8/28/49–9/10/49	161	
	44	9/11–12/49	164	
	45	9/12–13/49	164	
	46	9/13–14/49	164	
	47	9/14–14/49	167	
	49	9/14–15/49	165	
	50	9/15–16/49	159	
	51	9/16–16/49	163	
	52	9/16–17/49	197	
	108	5/22/50	248	
Buffalo, NY	17	5/1/57	103	63
	18	7/11–25/48	97	89
	19	12/10/48–1/13/49	202	99
	34	8/4/49	199	115

All activity is in disintegrations per minute per liter (STP).
*Probably collected during the first 6 months of 1947.
†Collected from 0800 to 2000 on April 27, 1950.
‡Only one measurement was possible.

was analyzed mass spectrometrically, after radiochemical assay, and found to have, at most, 0.5% xenon.

As mentioned earlier, atmospheric krypton in the 1990s has a radioactivity of tens of thousands of disintegrations per minute per liter. It is now about a hundred times more radioactive than the samples reported on here.

Atmospheric Measurements and Interpretations

Many samples were collected and measured during the period covered by this report. The results of krypton radioactivity assays made on some of these are presented in Table 1. All results presented in the table are for samples collected at commercial liquid-air plants, with varying control of operating characteristics. Some of these conditions are mentioned below.

The first Soviet explosion of a nuclear device occurred in August 1949. The data reported here on samples collected before about this date have been analyzed on the assumption that the only significant emitter of krypton-85 affecting them was the Hanford, WA, reprocessing plant of the United States and the nuclear tests carried out by this country. The yearly and monthly emissions of the Hanford plant have been published (R. L. Stutheit, personal communication; ref. 12). Ref. 12 gives the monthly dissolvings in terms of mega-watt days of neutron exposure of the fuel that was dissolved. These have been converted to curies of krypton-85 released in a way to be consistent with the data of R. L. Stutheit.

Table 1 presents measurements made on krypton isolated from the atmosphere at several locations in northeastern United States before mid-1950. For each location, the second column identifies the gas. The third column gives the date(s) of operation of the liquid-air plant involved. The fourth column gives the result of the measurement of the specific activity of the isolated krypton, in disintegrations per minute per liter (STP). The last column gives, for dates before about Aug. 10, 1949, the expected specific activity of krypton if the Hanford output were diluted by the whole world's atmospheric inventory of krypton, taken here as 4.506×10^{15} liters (STP). The collection dates listed should be considered with the following points in mind. The dates correspond to plant operating dates when the krypton was removed from a commercial liquid-air plant. If a range of dates is given, it indicates that the air sampled came from at least this period. Even if only one date is indicated, it probably still involves the processing of air from several days, about half of the krypton coming from the air of the date listed, the rest coming from previous days' operations. The output from Hanford was calculated on the assumption that the numbers given in ref. 12 were emitted evenly through the year.

Although detailed analysis of the data presented here would involve specific meteorological information about conditions on the days involved, some general remarks can be made.

(*i*) The absolute amounts of radioactivity observed are, in all cases, significantly higher than would be expected from instantaneous mixing with the whole world's atmosphere. For example, the four samples taken on Aug. 4, 1949, at different locations in northeastern United States, measure 163, 188, 203, and 199 dpm per liter (STP). They were each measured five times. The Hanford output as of this day, diluted by the world's krypton, would lead to an activity of 115 in the same units. The small (a few percent) contribution of nuclear explosions have been included. This discrepancy is not surprising in view of the faster production of krypton-85 by the U.S. military program than the decay of this nuclide in the atmosphere. Because the plutonium production plants were in the Northern Hemisphere and because mixing with the Southern Hemisphere takes time (13, 14), it is to be expected that the average Northern Hemisphere values would be higher than worldwide averages.

(*ii*) The ratio of observed specific activities to those expected from infinitely fast diffusion seems to take an abrupt rise at the end of 1949. This may be due to meteorological conditions—faster flow from Hanford to the sampling sites and less vertical mixing on the way. However, an accelerated Soviet reprocessing schedule during those early days of their program cannot be excluded from the contribution.

(*iii*) Even though the sampling times cannot be defined to as little as 1 day, the variability observed, for example, in the Aug. 4, 1949 samples, is greater than the experimental errors. Similarly, the time sequence of the measured specific activities at a given location indicates a larger scatter than can be explained from the experimental errors. This suggests that the northeastern U.S. sampling sites are randomly situated relative to a meandering plume from Hanford, WA.

In any case, these observations of the krypton-85 content of the early-nuclear-age atmosphere provide data on the rate of large-scale mixing of the components of the world's atmosphere. They provide quantitative data on how activities in one part of the globe affect the rest of the world.

Many people contributed to the work reported here. Even at this late date it is easy to remember the support provided by S. G. English (U.S. Atomic Energy Commission), Tom Brill (Argonne National Laboratory), and W. F. Libby (University of Chicago). B. R. Balcar, special consultant to the project, provided the samples. L. Machta of the U.S. Weather Bureau provided meteorological support. Finally, W. Nicholson of Batelle Northwest, in addition to his statistical analyses, located records of early Hanford operations.

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