Reprinted from

The International Journal of
APPLIED RADIATION
AND ISOTOPES

PERGAMON PRESS
OXFORD · LONDON · NEW YORK · PARIS

International Journal of Applied Radiation and Isotopes, 1972, Vol. 23, pp. 445–464. Pergamon Press. Printed in Northern Ireland

Low-Level Radioactivity Measurements on Aluminum, Steel and Copper*

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(*Received* 26 *May* 1972)

The radioactive contamination levels in samples of aluminum, steel and copper, supplied by a number of producers of these materials have been measured and activities have been assigned to possible natural radioelements. These activities were found to lie in the range of 0·02–0·6 pCi/g of parent radionuclide. The decay with time of some contaminants has been observed. A few measurements were also made on a number of other materials.

MESURES DE LA RADIOACTIVITE A NIVEAU INFERIEUR SUR L'ALUMINIUM, L'ACIER ET LE CUIVRE

On a mesuré les niveaux de contamination radioactive dans des échantillons d'aluminium, d'acier et de cuivre que nous ont fournis un nombre de producteurs de ces matériaux et les activités ont été apportées à des radio-éléments naturels possibles. On trouva ces activités dans la gamme de 0,02 à 0,6 pCi/g de la radionucléide parente. On a observé la déchéance avec le temps de quelques contaminants. Aussi a-t-on fait quelques mesures sur un nombre d'autres matériaux.

РАДИОМЕТРИЧЕСКИЕ ИЗМЕРЕНИЯ С НИЗКИМ УРОВНЕМ АКТИВНОСТИ ПРИ АЛЮМИНИИ, СТАЛИ, МЕДИ

Измерены уровия радиоактивиого загрязиенин во образцах алюминии, стали и меди, снабженных рядом изготовителей, приписаиы определенные активиости к возможиым естествеиным радиоактивным элементам. Устаиовлено, что эти активиости находятсн в интервале исходного радиоизотопа от 0,02 к 0,6 pCi/г. Замечен распад некоторых загрязняющих веществ в ходе времени. Производятся несколько измерений и на некоторых других материалах.

RADIOAKTIVITÄTSMESSUNGEN AUF NIEDRIGEM NIVEAU AN ALUMINIUM, STAHL UND KUPFER

Die radioaktiven Verseuchungsniveaus in Proben von Aluminium, Stahl und Kupfer, die von mehreren Herstellern dieser Werkstoffe geliefert wurden, sind gemessen worden und Aktivitäten sind möglichen natürlichen Radioelementen zugeordnet worden. Man fand, dass diese Aktivitäten im Bereich von 0,02 bis 0,6 pCi/g des Ausgangsnuklides lagen. Der Zerfall einiger Verseuchungsmittel wurde als Funktion der Zeit beobachtet. Messungen wurden auch an einigen anderen Werkstoffen unternommen.

INTRODUCTION

When there appeared to be some danger of radioactive contamination due to fall-out from atmospheric nuclear-bomb tests in the late 1950's, a program was started at the National Bureau of Standards to measure the levels

* This investigation was supported by the U.S. Atomic Energy Commission.

† The data presented in this paper were acquired between 1964 and 1969 by the first four authors, who also computed the average values of activity and standard error for all samples, which are also characterized by year of production and age at measurement. The two senior authors left the project in 1969, and the final preparation of this paper and analysis of the data, by the methods illustrated in Figs. 4–14, were carried out by the last three authors.

TABLE 1. Contributors of low-level sample materials

The Algoma Steel Corporation
Allegheny Ludlum Steel Corporation
Aluminum Company of America (ALCOA)
Aluminum Laboratories Ltd. (ALCAN)
Anaconda Aluminum Company
The Anaconda Company
Apex Smelting Company
Armco Steel Corporation
Atlantic Coast Line Railroad Company
The Baltimore and Ohio Railroad Company
Bangor and Aroostook Railroad Company
Bessemer and Lake Erie Railroad Company
Bethlehem Steel Corporation
Canadian Pacific Railroad
Chicago and Eastern Illinois Railroad
Chicago and North Western Railway Company
Chicago, Milwaukee, St. Paul and Pacific Railroad
Crucible Steel Company of America
Dominion Steel and Coal Corporation Ltd.
Fagersta Steels, Inc.
Harvey Aluminum, Inc.
Inland Steel Company
Jones and Laughlin Steel Corporation
Joslyn Stainless Steels
Kennecott Copper Corporation
Latrobe Steel Company
The New Haven Copper Company
Republic Steel Corporation
Sociedad Mixta Siderurgia Argentina (SOMISA)
Southern Railway System
United States Steel Corporation
White Pine Copper Company
Youngstown Sheet and Tube Company

of such contamination in materials that might be used for the construction of nuclear-radiation detectors, and in reagent chemicals that might commonly be used in radioanalytical chemistry. Although the Nuclear Test Ban Treaty intervened to minimize this danger, the low-level measurements, which had already been started, were continued in order to establish the natural environmental contamination levels of the 1960's. It is the purpose of this paper to report briefly on a significantly large number of low-level radioactivity measurements that were made on samples of aluminum, steel, and copper, kindly provided by the producers listed in Table 1, samples being taken from different production batches, produced in some 30 plants in North America and one in Argentina. The results of these measurements all lay in a range of radioactivity that is of interest today in the problems that are associated with the levels of radioactivity in the environment from natural sources and the normal peace-time applications of nuclear energy. A few results of measurements of activity in other materials are also reported, and some approximate values of half-lives determined.

MEASURING EQUIPMENT

Three types of radiation detectors have been used to make these measurements, namely (i) a number of zinc sulphide scintillation detectors for alpha particles, (ii) a hemispherical 2π thin-window gas-flow Geiger–Müller counter, incorporating a built-in anti-coincidence shield, with an automatic 50-sample changer, for beta particles; and (iii) a 5 × 4-in. sodium iodide (Tl) well crystal, enclosed in a mercury shield lined with lead, cadmium and copper, for gamma rays; a 3 × 3-in. sodium iodide (Tl) crystal in a mercury shield. Detection efficiencies for the alpha-particle, beta-particle and 5 × 4-in. sodium iodide detector systems are given in Table 2.

The choice of aluminum, steel and copper for assay resulted from a survey of 20 manufacturers of nuclear radiation detectors to determine which materials were of greatest interest to them from the point of manufacturing radiation detectors with low backgrounds. In order

TABLE 2. Efficiencies of the detecting systems

Detection system	Radiation source ^{210}Po (α)	^{90}Sr–^{90}Y (β)	^{60}Co (γ)
α	51%	<0·1%	<0·1%
β	50%	45%	0·9%
γ 5 × 4 in. NaI(Tl)	<0·001%	1·8%	24%

of importance the materials of interest were: copper, steel, aluminum, lead, gold, beryllium, tungsten, tin, silver, nickel, titanium, molybdenum, and platinum. Of these, the radioactive contamination of lead was already being studied.[1]

On receipt from the manufacturers, the aluminum, steel and copper samples were machined into discs, 22 mm in diameter and 3 mm thick, for alpha-particle and beta-particle counting, and into cylinders 2 cm in diameter and 5 cm long, which were placed in plastic vials in the 5 × 4-in. sodium iodide well crystal for gamma-ray assay.

The steel samples were given a hardness test and annealed, when necessary, before machining. The machining was carried out using newly sharpened tools to avoid the transfer of radioactive contamination between samples, and the machined surfaces were cleaned by washing in alcohol.

In most cases dates of production of the samples were supplied by the manufacturers. In the case of steel a useful source of dated material came from sections of railroad rails, on each of which the vintage is normally stamped. In addition to samples from producers in North America, 10 samples of steel were obtained from Argentina where, being in the southern hemisphere, the fallout was 5–10 times less than in the northern hemisphere.

BACKGROUND MEASUREMENTS, GENERAL CONSIDERATIONS

The major part of the background count of most radiation detectors is comprised of responses to extraneous sources such as cosmic radiation and radioactive contamination present in the construction materials used in building the laboratory or building the radiation detector and its shield. This external component, the cosmic part of which has temporal variation, can be largely reduced by using various shielding materials such as lead, cadmium, copper and plastics and also by the use of electronic anticoincidence shielding. Temporal fluctuations, due to changes in the sources or in atmospheric pressure, are normally monitored by adequately frequent background measurements.

There is also another component of the background that is due to the proximity of the sample itself to the detector. Normally for higher levels of radioactivity, this component is too small to be considered and the background reading is simply obtained by measuring the count-rate response of the detector in the absence of any sample. In the case of low-level measurements, however, the presence of the sample may either increase the count rate by scattering radiation into the detector, or decrease it by acting as an additional material shield.

The three types of detector used in the present investigation differed widely in their kind of background response characteristics. The alpha-particle detectors with their thin layer of zinc sulphide phosphor were very specifically sensitive only to alpha particles and had a background count rate of only about 1 count per hour, without any kind of shielding as they are quite insensitive to external radiation. The sodium iodide crystal was, however, very responsive to the cosmic-ray component, having no anti-coincidence shield, while the Geiger–Müller 2π proportional counter, with its built-in anti-coincidence shield, lay somewhere in

TABLE 3. Operating characteristics of the four detection systems

Detector	Radiation measured	Shielding	Typical energy range	Background rate, B	Maximum sample size
ZnS (activated scintillator) phototube	α	None	3·5–8 MeV	30·0 d^{-1}	2·5 cm diameter
2π gas-flow, thin window Geiger counter	$\beta(\gamma)$	Anticoincidence and lead	5 keV–3 MeV	520 d^{-1}	5·1 cm diameter
5 in. × 4 in. NaI(Tl) well crystal	γ	Mercury, copper, cadmium and plastic	90 keV–3 MeV	235 min^{-1}	28 ml
3 in. × 3 in. NaI(Tl) (Marinelli beaker)	γ	Mercury	90 keV–3 MeV	240 min^{-1}	1000 ml

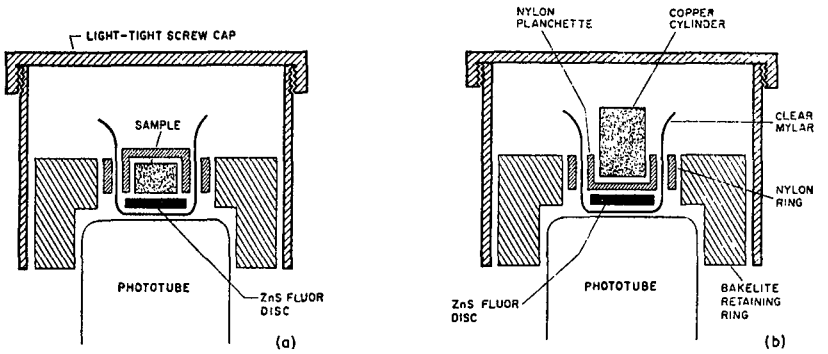

FIG. 1. Schematic diagram of the zinc sulphide scintillator with phototube for the detection of alpha particles. (a) shows the sample "package" in a nylon planchette in contact with the zinc sulphide fluor deposited on a plastic disc and sealed by means of 0·0005 in. thick Mylar film and placed on the end window of the phototube. (b) illustrates the configuration used for background measurements.

between. The treatment of background is thus specific to each of the three detector systems used, and it is therefore appropriate to consider them separately. As, in low-level counting, the activities to be measured are of the same order as the background count rate, or less, it is essential that the parameters involved in the background measurements shall be clearly understood. Typical background data for each system are shown in Table 3.

ALPHA-PARTICLE DETECTOR BACKGROUND

The alpha-particle detectors closely follow the system designed by the U.S. Atomic Energy Commission's Health and Safety Laboratory.[2] The sample is mounted, together with the zinc sulphide phosphor, inside a nylon planchette and the whole is placed upon a phototube in the manner indicated in Fig. 1(a). Background readings were taken with the sample removed from the planchette but with a copper cylinder, supplied by the manufacturer, *outside* the planchette in the manner indicated in Fig. 1(b). The purpose of the copper cylinder is to keep the planchette assembly reproducibly in contact with the phototube. That the base of the nylon planchette is thick enough to absorb all alpha-particles has been demonstrated with an ^{241}Am source replacing the copper cylinder in Fig. 1(b). High intensity beta-particle and gamma-ray sources, in contact with the zinc sulphide phosphor, have also been used to demonstrate that there is no significant response to these radiations.

Twelve different scintillation counters were available for the alpha-particle measurements which were initially carried out for 15 h overnight, but latterly for periods up to 100 h, for both sample and background measurements. The routine for each counter was to take two or three background counts, two sample counts on different samples, two or three background counts, and so on. The background counts, which were carried out with the copper cylinder as described above, now had to be related to a background count carried out with blank, or non-radioactive, disc-shaped samples of aluminum, steel and copper. These blank samples had to be chosen subsequent to most of the measurements, using the criterion of apparent freedom from radioactive contamination.

Three such samples, one each of aluminum, steel and copper, were found which, upon insertion into the planchette next to the zinc sulphide phosphor, actually *decreased* the alpha-particle count rates *below* the background rate. It is therefore to be surmised that these samples were shielding the zinc sulphide scintillator from alpha-particles possibly arising in the nylon planchette from (n, α) reactions. At this low level of activity, it is impossible to say whether the blank samples also had a residual alpha-particle activity which was masked by their shielding of the nylon. All

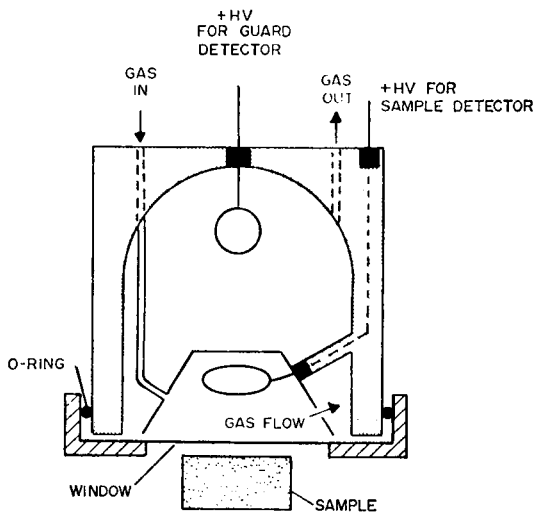

FIG. 2. The Geiger–Müller detection system showing the disposition of the guard detector around the 2π-proportional gas-flow detector. The window is 5 cm in diameter and less than 125 mg/cm^2 thick.

that can be said is that all results are relative to these three samples which had the lowest measured alpha-particle contamination, and were therefore assumed to give the background count rate. The average negative count rates, relative to the background rate, were $3{\cdot}78 \pm 0{\cdot}91$ d^{-1} cm^{-2} for aluminum, $5{\cdot}36 \pm 0{\cdot}97$ d^{-1} cm^{-2} for steel, and $3{\cdot}49 \pm 0{\cdot}84$ d^{-1} cm^{-2} for copper, the errors shown being standard errors. At these low levels, it is almost pointless to try to differentiate between the apparent shielding effects of the samples of aluminum, steel or copper, and accordingly we have chosen to use the weighted mean of all three samples namely $4{\cdot}12 \pm 0{\cdot}55$ d^{-1} cm^{-2} as the effective background count rate.

GEIGER–MÜLLER DETECTOR BACKGROUND

The Geiger–Müller detector system (Fig. 2) is also sensitive to alpha particles, which therefore constitute a component of background. In general, however, alpha-particle emission, or count rates are over 10 times less than the beta-particle levels so that we have not considered the alpha-particle contribution to the beta-particle detector's background count rate of somewhat over 500 d^{-1} (Table 2). Because of the possibility of the Geiger–Müller counter detecting alpha particles, its response is referred to as "β" or "beta" (in quotation marks) in the rest of this paper.

The beta-particle counting times for the 50 positions in the automatic sample changer were either 100 or 300 min for each position. A background count was interspersed between every two sample counts, so that there were, in the full cycle, 18 background counts, 31 sample counts, and 1 count of a ^{36}Cl control sample to monitor the long-term stability of the system. As there were not 18 background blanks available, the background counts were taken with empty sample holders and the change in background due to insertion of a blank was subsequently determined.

As in the case of the alpha-particle detectors, insertion of the lowest acting blanks available gave a *decrease* in count rate amounting to $0{\cdot}49 \pm 0{\cdot}18$ h^{-1} cm^{-2} for aluminum, $0{\cdot}68 \pm 0{\cdot}27$ h^{-1} cm^{-2} for steel, and $0{\cdot}94 \pm 0{\cdot}22$ h^{-1} cm^{-2} for copper. These count rates must therefore be added to the respective net count rates based on the background count rates obtained with empty sample holders.

GAMMA-RAY DETECTOR BACKGROUND

The 5×4-in. sodium iodide crystal has material shielding (Fig. 3(a)), but no anti-coincidence shield. It is therefore very exposed to cosmic-ray interactions and the background count rate is greater than 200 min^{-1} (Table 2), which is subject to both temporal and atmospheric-pressure changes. A sensitive-recording barograph was therefore used to record average pressures during all counts.

The gamma-ray count rates for aluminum, steel and copper were around 150, 20 and 0 per day per gram, respectively. The background count rates, taken with an empty plastic vial in the well, were of the order of $3{\cdot}4 \times 10^5$ per day, with a standard deviation of about 0·25 per cent. Sample and background readings were taken for 8 h (in the day), 14 h (overnight), and approximately 60 h (weekends).

From a long series of measurements of background count rates with "inactive" aluminum (Al-71) and copper (Cu-27) samples and with,

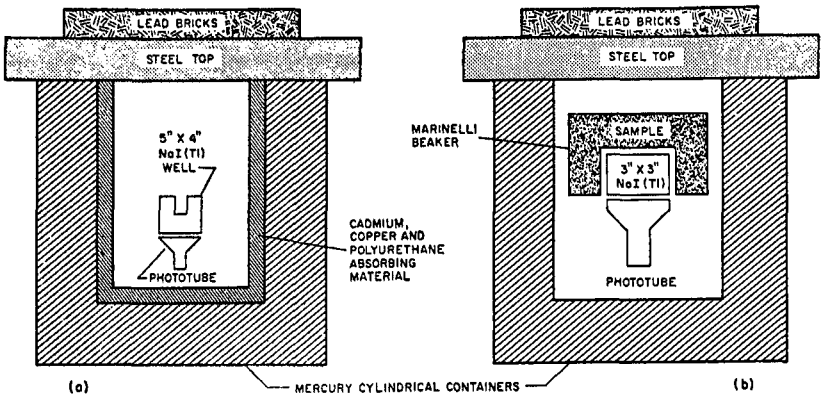

FIG. 3. Cross-sectional drawing of the shielding arrangements for the 5 × 4-in. and 3 × 3-in. sodium iodide (Tl) crystals.

in the majority of cases, an empty plastic vial in the well of the crystal, a pressure coefficient was computed by least squares, assuming a linear dependence of background on the pressure. The value of this coefficient was of the order of -5 counts min^{-1} in^{-1} of mercury pressure, the standard pressure being taken as 29·80 in. of mercury. Thus at 30 in. of mercury there would be a pressure correction of 1 count min^{-1}, amounting to somewhat less than 0·5 per cent in the background. Sample count rates grouped around the background count rate of about 235 min^{-1} (Table 3), up to a maximum of about 275 min^{-1}. As the measurements progressed the pressure coefficient was frequently recalculated using new data, and maximum and minimum values were $-7{\cdot}21$ and $-1{\cdot}10$. The higher background count rates of the sodium iodide detector allow of an approximate assessment of the pressure variation coefficient, which was not possible with the zinc sulphide and Geiger–Müller systems.

Two or three background measurements were made every week in order to allow for changes in cosmic-ray intensity.

The shielding effect due to the sample was measured using the low-level aluminum sample, Al-71. This sample consisted of a number of discs cut from a single sample of aluminum which could be placed in various numbers in a plastic vial to make cylinders of various length and mass. A mass coefficient was determined, using least-squares analysis, assuming a linear dependence of shielding effect on mass. This coefficient was found to be $-0{\cdot}0180$ counts min^{-1} g^{-1}, so that a 10-g sample of aluminum would decrease the background count rate by 0·18 min^{-1}, or less than 0·1 per cent of background. As this correction is small, the same coefficient (per unit mass) was assumed to hold for steel and copper, as well as for aluminum. The basis for this assumption is that the shielding provided by the same volume of aluminum, steel, and copper will be proportional to the number of electrons in this volume, which is also approximately proportional to the respective masses of this volume of aluminum, steel, and copper.

Similar desiderata were applied in the case of the 3 × 3-in. sodium iodide (Tl) crystal that was generally used in conjunction with plastic Marinelli beakers (Fig. 3(b)).

RESULTS

The presentation of the results has constituted something of a problem in that, whereas many of the data were obtained from readings of the same duration and around background count rate, some measurements were made over longer periods of time. Thus, while the normal routine was to count during the night and to collect data and then process it and prepare new samples during the day, there was always an urge to use the weekends to collect more data on both backgrounds and low-level samples. Counting periods therefore

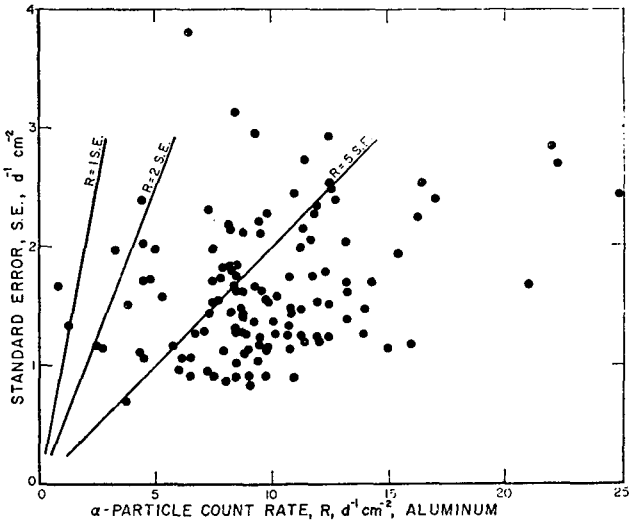

FIG. 4(a). Standard error vs. mean alpha-particle count-rate per square-centimeter for aluminum samples. Areas for R between 1 and 2 standard errors and 2 and 3 standard errors are indicated. The concentration of count rates around 8–9 d^{-1} cm^{-2} is quite apparent.

tended to group into durations of either 15 h or 72 h but, on occasions when counting systems were not required, counting periods of up to 10 days occurred. In addition, repetitive measurements on samples were carried out different numbers of times.

The problem of presentation that therefore arose was, how to show in a concise manner data having widely different counting statistics? Histographic count-rate presentation was tried and gave some indication as to "peaking" at certain levels of radioactivity. But the distributions obtained were invalid in that the contributions of some samples far exceeded those of others.

The method ultimately chosen to present the data was to take the average value (R) of all results for the count rate of any given sample together with the weighted standard deviation of this average (S.E.), based on the total number of sample and background counts taken. The weighted standard error taken in each case was the larger of either $(1/\Sigma w_i)^{1/2}$ or $\{(\Sigma w_i(R_i - R)^2)/(n-1)\,\Sigma w_i\}^{1/2}$, where w_i are the weighting factors taken as the reciprocals of the variances.

The results were then shown graphically by plotting the weighted standard error of the average activity of each sample against the activity, as shown in Fig. 4(a). The average activity and standard error of every individual sample is thus shown and, in the presentation of Fig. 4(a), a concentration of alpha-particle activity, for aluminum, is shown quite dramatically around 9 d^{-1} cm^{-2}. The final presentation adopted for all the data was as shown in Fig. 5, for aluminum, where some attempt was made also to differentiate between freshly and less recently produced samples. In this figure the open circles refer to samples measured less than 1000 days after production and the solid circles those that were older than 1000 days when measured. In this and some of the subsequent figures there is a tendency for the higher activities to be favored by the younger samples. In Figs. 5–13, lines have been drawn relating average count rate (R) with estimated standard error, S.E., for R = 1S.E. Depending upon the criterion chosen for the detection limit, one may ignore all results below that level. An interesting modification to the method chosen consists of plotting R/S.E. against R, and is shown for the alpha-particle activity of aluminum in Fig. 4(b). Here the desired detection limit is chosen merely by selecting values above a horizontal line corresponding to the desired value of R/S.E. The method of plotting S.E. against R was felt,

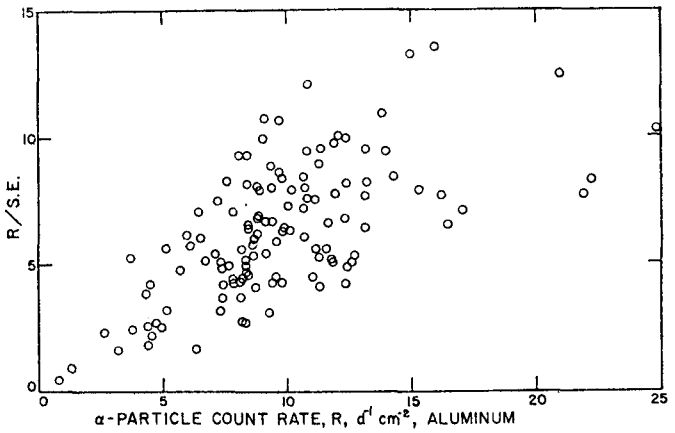

FIG. 4(b). Mean count rate divided by standard error vs. mean alpha-particle count-rate per square-centimeter for aluminum samples. Here the "signal-to-noise" ratio can be chosen by considering only those values above the appropriate value of R/S.E. For activities which are less than background the standard error should be approximately constant, which accounts for the rather well-exhibited positive slope about which the points tend to cluster. The background count rate is of the order of 24 d^{-1} cm^{-2}. The spread in slope is accounted for in part by the differences in the times of measurement and numbers of measurement (i.e. total counts) for different samples. Here again the concentration of count rates per unit area around 8–9 d^{-1} cm^{-2} is apparent.

however, to be slightly preferable as it gives, by simple inspection, not only the values above detection limits, say, R = 1S.E., but also R and S.E. for every sample measured.

It was suggested by J. E. Leiss that an integral curve (number of samples against activity) would show whether, for samples in the various categories (Fig. 5–13), there were any tendency for there to be one or more probable levels of activity (peaks), or none.

The complete results for the average activities, and corresponding weighted standard deviations, for all aluminum, steel and copper samples measured are shown in the upper portions of Figs. 5–13. The integral curves giving the number of samples as a function of their average count rates are also shown.

In the lower parts of Figs. 5–13 the weighted average of the radioactivities of all samples are shown as a function of the time of production; as so many days from production date for "fresh" samples, and as year of production for samples with an age of more than 360 days between the date of production and the date of measurement. In the case of the "fresh" samples, average activities were obtained for 60-day intervals of age, which intervals are characterized in the figures by the mid-point of the interval, ranging from 30 to 330 days. These results therefore cover the interval of up to nearly 1 yr, and the measurements on older samples are grouped and averaged by year of production.

Two aluminum average beta-particle results, for samples Al-49 and Al-53, were considerably higher than the range of results for other samples, and these have been omitted from the aluminum results shown in Fig. 6. The results of the Geiger–Müller counter measurements on sample Al-53, as a function of time, are shown in Fig. 14. The abscissa shows the age of the sample, in days, from its date of production and there is evidence of a relatively short-lived component of activity. Average alpha-particle results shown at 212 and 1171 days from production show no decay, so that the short-lived component is presumed to be due to beta-particle activity.

A number of different materials, in a variety of forms in Marinelli beakers, were also measured for gamma-ray using the 3 × 3-in. crystal. The geometrical-efficiency is not very well

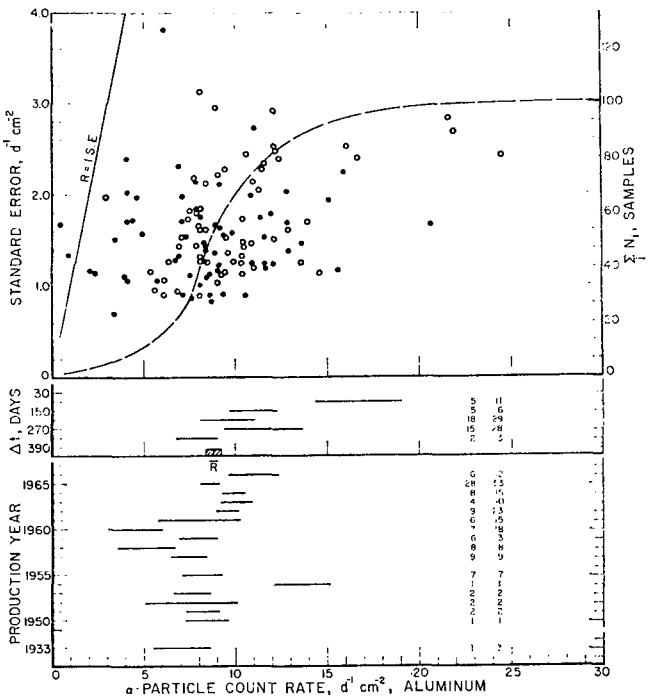

FIG. 5. (Upper section) Diagrams of standard error vs. average values of α-particle count rate for 127 samples of aluminum, and integral curve of ΣN_i in numbers of samples. The more gradual negative rate of change of slope of the integral curve is indicative of a short-lived component of radioactivity. The following high-activity values have not been plotted: 38·74 ± 1·81, 45·44 ± 2·46, and 69·35 ± 22·46. Open circles are for samples less than 1000 days old, solid dots for samples greater than 1000 days old. (Middle section) Mid-date interval in days vs. average values of α-particle count rates for 60-day intervals from date of production. An activity having a half-life of 33 ± 21 d is apparent (see Table 6). (Lower section) Production year vs. average α-particle count rate, showing a long-lived residual activity with a weighted average value of $\overline{R}$ with the standard error shown. The columns of figures on the right-hand side of the lower section indicate the number of samples from each year of production and the number of measurements made on samples from that year of production, respectively.

defined and the results are therefore somewhat qualitative, but they are summarized in Table 4. Apart from the results for nickelous oxide and one sample of tungsten, none shows significantly high count rates.

DISCUSSION

While the overwhelming majority of aluminum, steel and copper samples was obtained from domestic producers in various localities of North America, a small group of samples of steel was obtained from Argentina. This was of interest because for many years the fall-out level has been smaller, by a factor of from 5 to 10, in the southern hemisphere than that in the north. The plant selected is also located in an area of low natural radioactivity.

The methods used for refining and producing the samples can vary widely.

Practically all aluminum is produced by the electric-furnace, or Hall-electrolytic, process. Two broad types of aluminum are produced, namely alloyed and unalloyed, which differ in the proportions of minor components. The majority of manufacturing plants which produced the samples tested are located in two regions (i) north-east United States and south-east Canada, and (ii) north-west United States and south-west Canada.

There are three major manufacturing processes

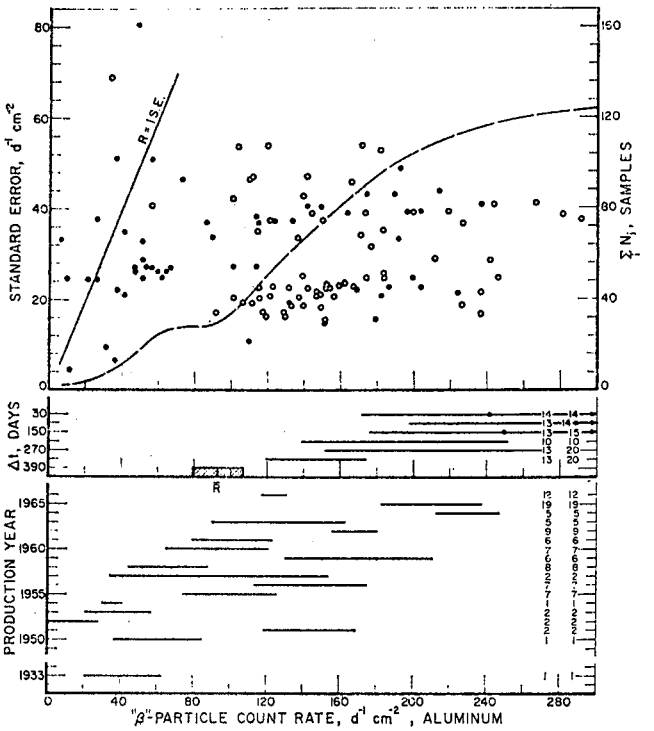

FIG. 6. (Upper section) Diagrams of standard error vs. "β"-particle count rate for 123 aluminum samples, and integral curve of $\Sigma_t N_t$ in numbers of samples. The three points of inflection in the integral curve are the result of the combination of a short-lived component and measurements being made at two "preferred" times after production. Open circles are for samples less than 1000 days from date of production, solid dots for samples greater than 1000 days old. Middle section and lower section. As in Fig. 5, but for "β" radiation. The middle section indicates a very uncertain half-life of 17 $\pm$ 22 d; the lower section, a half life of 15·3 $\pm$ 3·9 yr (see Table 6). $\bar{R}$ is the average activity for the lower section with standard error as shown. The columns of figures on the right-hand side of the lower section indicate the number of samples from each year of production and the number of measurements made on samples from that year of production, respectively. The following high-activity values have not been plotted in the upper section: 302·86 $\pm$ 13·44, 317·14 $\pm$ 25·90, 318·43 $\pm$ 19·66, 312·48 $\pm$ 24·72, 442·18 $\pm$ 13·82, 1217·90 $\pm$ 43·94 and 1355·04 $\pm$ 42·46. (The 30-, 90- and 150-day points are plotted because the positive limits of the standard errors lie off the graph.)

for steel, namely the open-hearth, electric-furnace and basic-oxygen processes, and a number of processes of smaller output, such as the acid-Bessemer-converter and duplex-open-hearth processes. Manufactured steel can be divided into three major types, carbon steels, alloy steels and stainless steels, which again differ in the proportions of minor components. The plants manufacturing the samples surveyed, while being located throughout the United States, are predominantly in Pennsylvania, New York, Ohio, northern Illinois and northern Indiana (around Chicago), and Alabama.

Scrap material is always a valuable contribution to the manufacture of aluminum, steel, and copper, but only in the case of the steel samples surveyed, in the present investigation, was the information accompanying the samples sufficiently detailed to be useful. Most of the scrap comes from plant operations without ever having been used in the outside technological world. It cannot therefore be a source

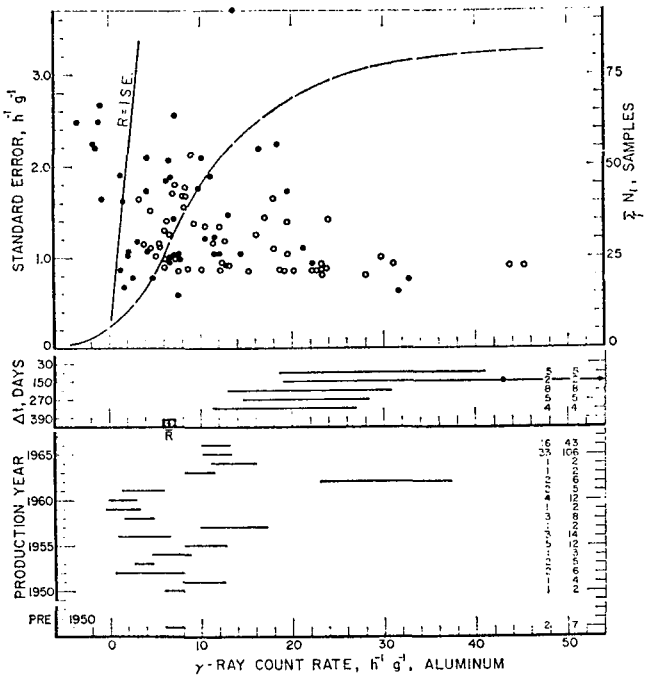

FIG. 7. Plots as shown in Figs. 5 and 6, for γ-ray contamination in 101 aluminum samples. A very uncertain half-life of 20 $\pm$ 22 d and a residual long-lived activity are indicated (see Table 6). The high-activity value, 67·83 $\pm$ 0·65, has not been plotted in the upper section. (The 150-day point is plotted because the positive limit of the standard error lies off the graph. Open circles are for samples less than 1000 d old.)

of radioactive contamination other than that normally occurring during the productino processes themselves. Some scrap discarded after an indeterminate life history outside the manufacturing industry, could however be contaminated and introduce radioactivity.

Commercial copper can be fire-refined or electrolytically refined, differing by the number and kind of refining stages involved. Electrolytically refined copper is purified twice, and is thus usually the purer of the two. Most of present-day copper being electrolytic, very few samples of fire-refined copper were received.

By inspection of the three parts of any one of the Figs. 5–13, it is possible to draw some conclusions as to whether there are any short-lived activities in the materials tested, or any residual probable level of activity remaining after the decay of any short-lived activity that may be present. If there is one long-lived activity present then, provided that there are sufficient numbers of measurements, there will be a symmetrical S-shaped curve (for a Poisson distribution) extending through a point of inflection corresponding to the average activity. Such an integral curve could well be represented by that shown in Fig. 13 for the γ-ray measurements on copper which show an average value of zero activity. In this case, however, no measurements were made on fresh samples because the 5 × 4-in. sodium iodide crystal was not immediately available and when it became available the rate of measuring individual samples was of necessity much smaller than that with which the α- and "β"-particle measurements could be handled with 12 α-particle counters and the Geiger–Müller counter with its 50-sample automatic changer. The symmetry of the integral curve for the copper γ-ray measurements is therefore to be expected, in the absence of any short-lived radioactive contamination.

A long-lived or stable daughter being fed by a shorter-lived parent will result in an integral curve that will rise to the point of inflection in the same manner as in Fig. 10, but will

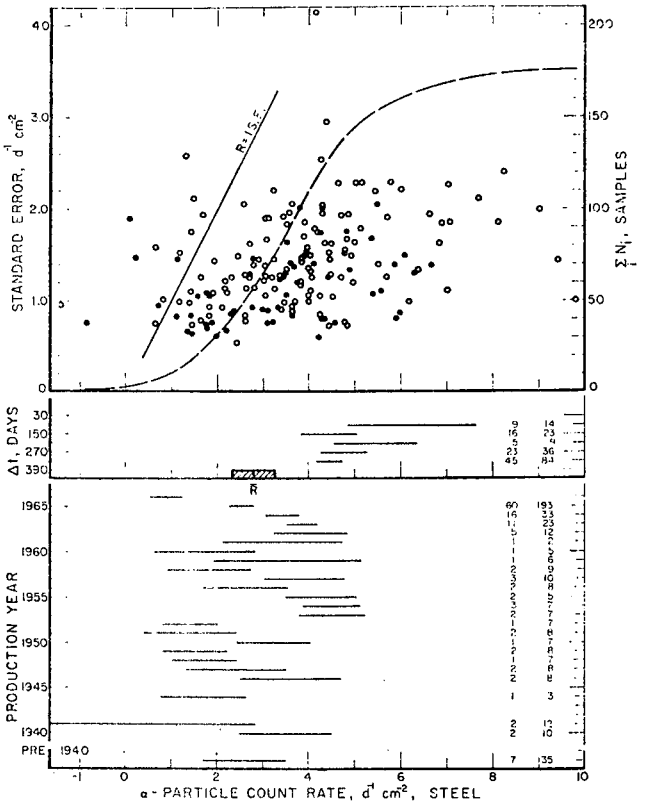

FIG. 8. Average activity plots for α-particle contamination in 186 steel samples. The 60-day interval samples indicate an activity with a half-life of 654 ± 129 d, and the lower section a long-lived residual activity (see Table 6). A majority of the values in the upper section lies in the area of R less than one standard error. (Open circles are for samples less than 1000 d old.)

then trail off asymmetrically with a larger negative rate of change of slope just after the point of inflection than the positive rate of change of slope just before. Such a situation is probably most clearly represented by the aluminum α-particle measurements shown in Fig. 5, but it is not too sure a criterion for pin-pointing a short-lived activity because of the uncertainties inherent in the integral curve. Another criterion, based on the average value of the aged samples, was therefore used to try to postulate the presence of a short-lived component of activity. For this purpose a weighted average value together with its standard deviation was calculated in each case for all aged samples. Those weighted averages are shown in Figs. 5–13 on the abscissae of the "fresh" samples. The criterion adopted was that there is a short-lived component of activity if the majority of the activities measured for the fresh samples was higher than the weighted average activity of the aged samples. This criterion indicates short-lived activities for the aluminum α, aluminum "β", aluminum γ, steel α and "β", and copper "β" results (Figs. 5–9 and 12). The aluminum and aluminum γ results (Figs. 6 and 7) also indicate a longer-lived decay (i.e. comparable with the span of the production years covered) in the aged samples. The presence of shorter- and longer-lived components is also indicated by inspection of the grouping of the open and filled data points indicating measurements respectively less than and more than 1000 days from the date of production. The criterion based on the weighted average of these years is still a valid one, however, for

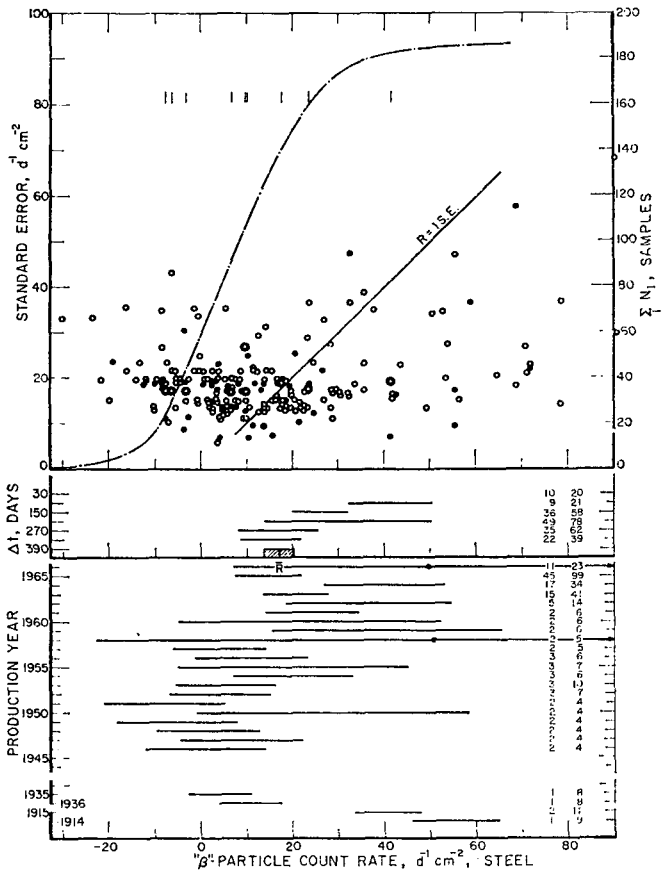

FIG. 9. Average activity plots "β"-particle contamination in 219 steel samples. The Argentinian samples are indicated by larger circles. As the points overlap with other data, the Argentinian data are also located by the series of short vertical lines at the top of the upper section. They are seen to bracket the most probable values of activity indicated by the integral curve. The following high-activity values have not been plotted in the upper section: 122·50 ± 13·61, 142·46 ± 14·81, 173·98 ± 21·77, 175·03 ± 20·02, 391·68 ± 36·10, 446·23 ± 15·79, 457·56 ± 18·84, 806·64 ± 17·88 and 811·75 ± 17·57. (The 1958 and 1966 points are plotted because the positive limits of the standard errors lie off the graph. Open circles are for samples less than 1000 d old.)

establishing a possible shorter-lived component.

The integral curve for the aluminum-β results shows three points of inflection. These could arise from two possible causes, namely (i) the presence of two levels of activity, one in one group of samples and the other in the rest of the samples; or (ii) the measurement at two preferred times of samples with activities having a half-life comparable with the period of time covered by the measurements, with the activities of all samples approximately equal at the time of production. On inspecting the data, the latter hypothesis was found to fit the facts in that two groups of predominantly favored measurement times were found around 55 and 130 days.

In view of the fact that the samples of aluminum, steel and copper have been produced in various locations in the United States, the tendencies, as indicated by the integral curves, to cluster around fairly definite levels of activity is surprising, and would seem to indicate certain common sources of radioactive contamination. Even the samples from Argentina seem to

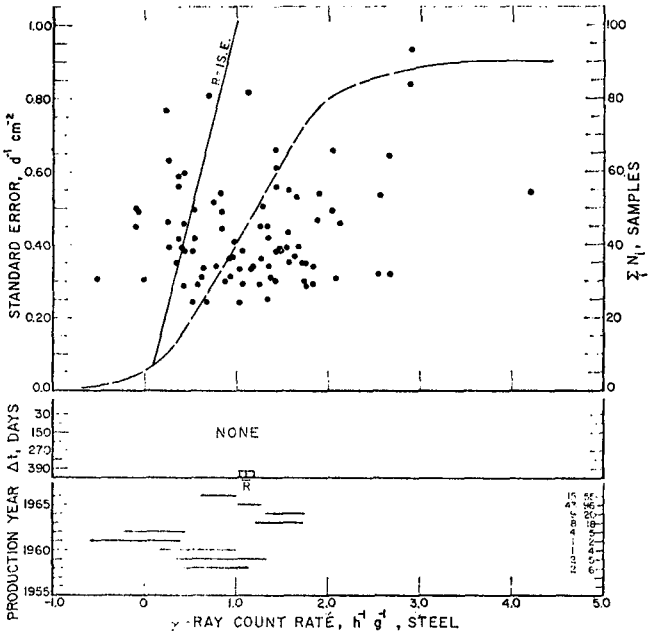

FIG. 10. Average activity plots for γ-ray contamination in 86 steel samples. No results were obtained for γ-ray contamination of samples less than 1 yr old. A residual long-lived activity is apparent in the lower section (see Table 6).

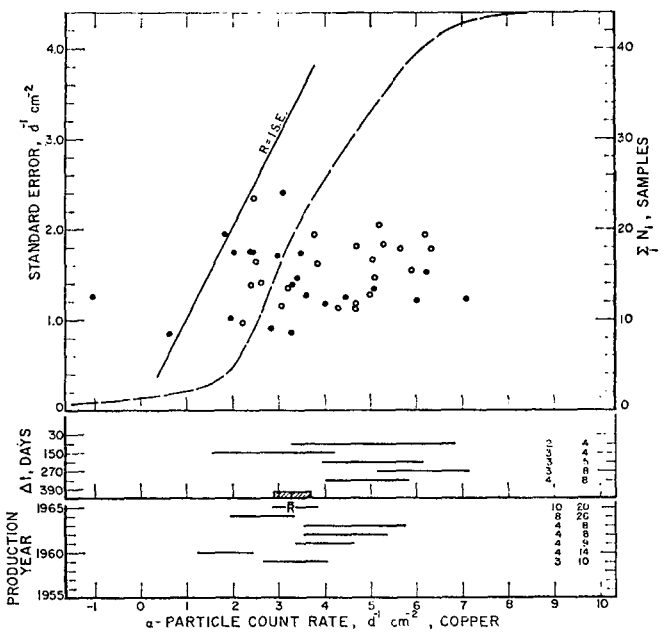

FIG. 11. Average activity plots for α-particle contamination in 43 copper samples. The great majority of points lie in the region of R greater than one standard error. No short-lived component is apparent and there are insufficient data to calculate the half-life of the residual long-lived component. (Open circles are for samples less than 1000 d old.)

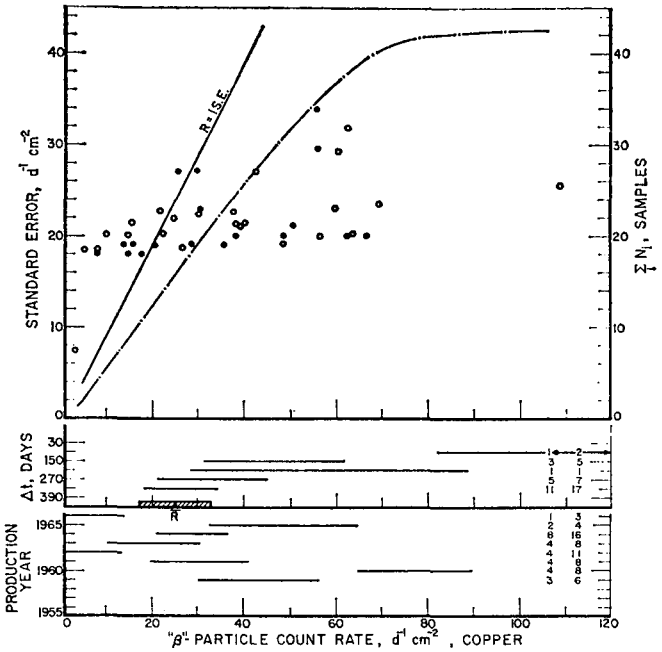

FIG. 12. Average activity plots for "β"-particle contamination in 43 copper samples. A short-lived activity of half-life equal to 40 $\pm$ 22 d appears to decay into a residual long-lived activity. (The 90-day point is plotted because the positive limit of the standard error lies off the graph. Open circles are for samples less than 1000 d old.)

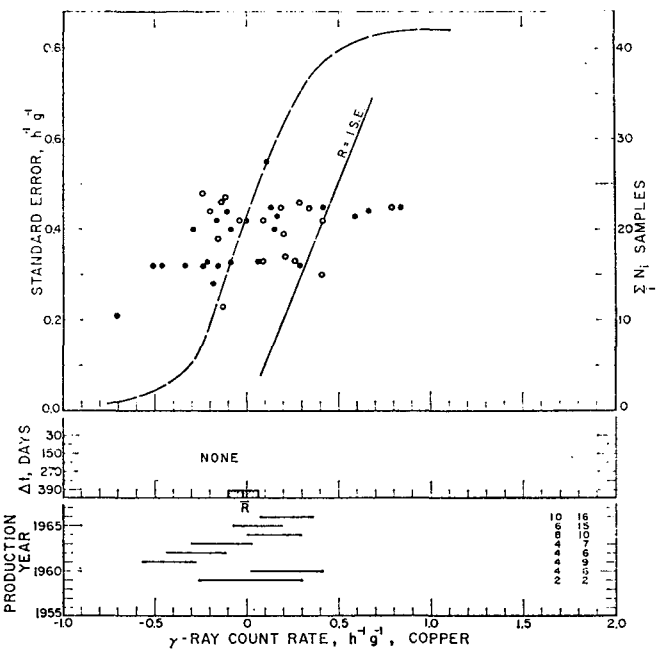

FIG. 13. Average activity plots for γ-ray contamination in 42 copper samples. No short-lived component data (less than 1 yr from date of production) have been obtained. There appears to be no long-lived activity present. (Open circles are for samples less than 1000 d old.)

TABLE 4. Count rate data for measurements made on the 3 in. × 3 in. NaI(Tl) system

Material	Physical form	Sample origin	Year of Prodn.	Mass of source	Net count rate per gram	Standard error (S.E.)
				g	cph/g	cph/g
Copper (refined)	Shot	Commercial	1968	6000	0·15	0·11
Copper (refined)	Shot	Commercial	1968	6000	0·01	0·08
Copper (refined)	Shot	Commercial	1969	6000	0·10	0·11
Copper (refined)	Shot	Commercial	1969	6000	0·05	0·08
Copper (unrefined anodes)	Shot	Commercial	1968	6000	0·25	0·11
Copper (unrefined anodes)	Shot	Commercial	1968	6000	0·17	0·11
Copper (unrefined anodes)	Shot	Commercial	1969	6000	0·20	0·11
Copper (unrefined anodes)	Shot	Commercial	1969	6000	0·24	0·11
Aluminum	Turnings	NBS standard	1959	1454	2·0	0·35
Aluminum	Foil	Commercial	1966	1422	4·1	0·36
Aluminum	Foil	Commercial	1965	(a)	2·7	0·29
Aluminum	Foil	Commercial	1965	1454	3·2	0·25
Aluminum	Foil	Commercial	1966	(a)	3·1	0·30
Aluminum	Small solid pieces	NBS, Metallurgy	1941	1951	2·4	0·13
Steel	Cut wire	Commercial	1966	6722	0·14	0·07
Steel	Cut wire	Commercial	1966	6218	0·36	0·08
Phosphor bronze	Turnings	NBS standard	1944	4333	0·06	0·12
Leaded tin bronze	Turnings	NBS standard	1957	3925	0·01	0·10
Zinc base alloy	Turnings	NBS standard	1955	4262	0·02	0·12
Lead–tin solder	Turnings	NBS standard	1942	3486	0·00	0·14
Copper–nickel–zinc alloy	Turnings	NBS standard	1958	656	0·08	0·78
Monel	Turnings	NBS standard	1949	3912	0·04	0·10
Manganese–aluminum bronze	Turnings	NBS standard	1951	2125	0·05	0·17
Nickelous oxide	Sintered powder	GSA stockpiles	1959	3972	4·1	0·13
Nickelous oxide	Sintered powder	GSA stockpiles	1959	(a)	4·3	0·10
Nickelous oxide	Sintered powder	GSA stockpiles	1959	(a)	3·7	0·10
Nickelous oxide	Sintered powder	GSA stockpiles	1959	3726	3·9	0·14
Nickelous oxide	Sintered powder	GSA stockpiles	1959	3802	4·3	0·13
Tungsten	Powder	GSA stockpiles	1952	5702	0·05	0·09
Tungsten	Powder	GSA stockpiles	1952	5702	0·03	0·09
Tungsten	Powder	GSA stockpiles	1952	5702	0·00	0·09
Tungsten	Powder	GSA stockpiles	1954	5702	5·5	0·07
Tungsten	Powder	GSA stockpiles	1951	5702	0·13	0·09
Titanium	"Sponge"	GSA stockpiles	1955	2058	0·61	0·25
Titanium	"Sponge"	GSA stockpiles	1955	2058	0·59	0·25
Titanium	"Sponge"	GSA stockpiles	1958	(a)	0·44	0·21
Titanium	"Sponge"	GSA stockpiles	1957	2100	0·41	0·24
Ferromolybdenum	Granular powder	GSA stockpiles	1946	2743	0·39	0·19
Ferromolybdenum	Granular powder	GSA stockpiles	1960	2648	0·83	0·14
Ferromolybdenum	Granular powder	GSA stockpiles	1961	2570	0·55	0·20
Ferromolybdenum	Granular powder	GSA stockpiles	1962	2742	1·9	0·13

TABLE 4 (*contd.*)

Material	Physical form	Sample origin	Year of prodn	Mass of source	Net count rate per gram	Standard error (S.E.)
				g	cph/g	cph/g
Ferromolybdenum	Granular powder	GSA stockpiles	1962	2900	1·12	0·17
Beryllium (refined)	Flakes	European	1946	798	2·6	0·64
Beryllium (unrefined)	Beads	Industrial	1966	1088·6	2·1	0·44
Graphite (nuclearly pure)	Small cubes	NBS, CRR	?	1088·6	0·22	0·33

(a) Measurements made on two samples of different mass.

TABLE 5. Average count rates for statistically different sets of samples

Material	Radiation measured	Sets compared	Respective average count rates and weighted standard errors (d^{-1} cm^{-2})	Level of significance
Steel	α	Carbon steel (open hearth) vs. stainless steel (electric furnace)	3·72 ± 0·35 vs. 4·67 ± 0·47	0·10
	"β"	Carbon steel (open hearth) vs. alloy steel (electric furnace)	14·2 ± 2·9 vs. 40·8 ± 7·2	0·01
Steel	"β"	Carbon steel (open hearth) vs. alloy steel (open hearth)	14·2 ± 2·9 vs. 24·7 ± 3·6	0·05
Steel	"β"	Carbon steel (open hearth) vs. stainless steel (electric furnace)	14·2 ± 2·9 vs. 43·4 ± 12·5	0·05
Steel	α	Alabama vs. Chicago area	3·40 ± 0·35 vs. 4·61 ± 0·40	0·02
Aluminum	α	Alloyed vs. unalloyed aluminum	9·36 ± 0·43 vs. 7·92 ± 0·43	0·02
Copper	"β"	Fire-refined vs. electrolytically refined copper	37·7 ± 7·7 vs. 16·8 ± 3·6	0·02

conform, for the few results available. One would therefore be tempted to suspect contamination from natural sources of radioactive contamination, either in the ores or in the raw materials used in the refining processes.

The average count rate data shown in Figs. 5–13 were also grouped into a number of sets according to method and place of production, and were compared to see whether any statistically significant differences could be observed. The only cases where a significant difference could be detected are shown in Table 5.

With reference to possible geographical influences, only one difference is significant: that between mean levels of alpha-particle radioactivity for Alabama and Chicago area; the corresponding difference for beta-particle activity is significant at 20 per cent statistical level; from both results it would appear that there are indications of a "cleaner" production at Alabama; all the samples from that area, however, correspond to carbon steel, significantly "cleaner" than the other kinds, and they were manufactured by the open hearth process, also seen to produce less contaminated steel. On the whole, therefore, it is concluded that no important geographical influences on radioactive contamination have been detected.

From an inspection of the data shown in Figs. 5–13 it can be seen that some of the contamination levels show a measurable decrease with elapsed time. With the exception of the aluminum-"β" results (Fig. 6) the annual results for years prior to about 1965 show only a long-lived low-level residual activity, showing little or no decay in the period covered by the measurements.

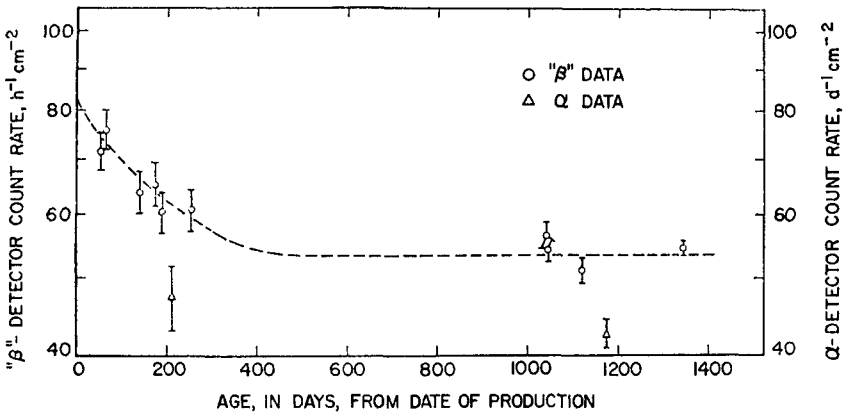

FIG. 14. Values of "β"-particle and α-particle activities vs. age in days for aluminum sample Al-53.

On the other hand, it must be remembered that the great majority of the results reported here are from measurements on individual samples, that could be expected to bear no relationship to each other, unless they have a common source of contamination and are subjected to a process or processes, of refinement that leave the level of contamination essentially unchanged. The general proximity of the points of inflection of the integral curves and the annual average activities, $\bar{R}$, indicates a degree of homogeneity in the residual activities after many years that must premise a like degree of homogeneity at the time of production. These annual averages remain homogeneous, within the limits of precision obtainable, without any dramatic discontinuity through the period in which fall-out was prevalent. We deduce, therefore, that the radioactive contamination is probably natural in origin. Two possible individual exceptions to this general conclusion have been noted, namely the two aluminum samples of high activity, the α- and "β"-particle activities of one of which is shown in Fig. 14. The initial "β"-particle decay of this sample, which was produced in 1965, has a half-life of approximately 100 days, and the activity could possibly be due to contamination by mixed fission products.

Wherever the plotted measurements, shown in Figs. 5–13, indicated a fairly definite decrease with elapsed time from the date of production, they have been treated as one group (i.e. assuming comparable levels of activity at the time of production) and subjected to least-squares analysis with a view to determining an approximate half-life. The results of these analyses are shown in Table 6, together with suggested radioactive contaminants and estimates of the levels of activity per gram of material. Plausible candidates for most of the contamination, based on compatibility with the approximate values of half-life shown in Table 6, appear to be the daughters of the two isotopes of uranium, ^{235}U and ^{238}U. The short half-lives that emerge from the analyses could be associated with a separation in refining of ^{227}Th ($T_{1/2} = 18{\cdot}2$ d) and its daughters, or possibly ^{210}Bi ($T_{1/2} = 5{\cdot}0$ d). A candidate for the approximately 2-yr activities in steel is possibly ^{228}Th ($T_{1/2} = 1{\cdot}9$ yr) and its daughters from the ^{232}Th series. The longer-lived activities can perhaps be identified with ^{226}Ra and its daughters, in equilibrium, and, in the case of copper, with a separation in refining, of ^{210}Pb ($T_{1/2} = 20$ yr) and its progeny, ^{210}Bi and ^{210}Po ($T_{1/2} = 138$ d). This assignment would be supported by the observation of no long-lived gamma-ray component of contamination in copper, the gamma-ray branching in the decay of ^{210}Po being completely negligible.

The approximate values of activity shown in Table 6 have been derived using the energies appropriate to the radiations from the postulated radionuclides, and then calculating the activities that would have to be present in various

TABLE 6. Suggested contamination activities in the three sample types

Source-radiation detected	Fig. No.	Short $T_{1/2}$	pCi/g of parent at production date	Possible activity	Long $T_{1/2}$	pCi/g of parent	Possible activity
Al-α	5	33 ± 21 d	1·0	^{227}Th+	long	0·1	^{226}Ra+*
Al-"β"	6	17 ± 22 d	0·3	^{227}Th+	15·3 ± 3·9 yr	0·6	^{210}Pb
					long	0·1	^{226}Ra
Al-γ	7	20 ± 22 d	0·6	^{227}Th+	long	0·08	^{226}Ra+
Steel-α	8	654 ± 129 d	0·08	^{228}Th	long	0·06	^{226}Ra+
Steel-"β"	9	73 ± 72 d	0·1	^{210}Bi	2·6 ± 3·7 yr	0·02	^{228}Th
					long	0·02	^{226}Ra
Steel-γ	10	—	—		long	0·02	^{226}Ra+
Cu-α	11	not apparent	—		long	0·4	^{210}Pb + ^{210}Bi + ^{210}Po
Cu-"β"	12	40 ± 22 d	0·3	^{210}Bi	long	0·1	^{210}Pb + ^{210}Bi
Cu-γ	13	—	—		not apparent		

* The + sign following a radionuclide signifies "+ daughters".

saturation thicknesses of the material to give rise to the observed external radioactivity.

Let us consider first the case of the aluminum-α observations. If we assume here that ^{227}Th has been separated in the refining process, then it will give rise, when in equilibrium with its daughters, to a sequence of five α-particle and two β-particle transitions before terminating in the stable state of ^{207}Pb. The longest-lived radionuclide in this chain after ^{227}Th is ^{223}Ra with a half-life of 11·4 d so that the 18·2 d ^{227}Th should be essentially in equilibrium with all its daughters in some 40–50 days. The energies of the α-particles range from about 5·7–7·4 MeV. The saturation thickness in copper for an energy of, say, 6·5 MeV is 6 mg/cm^2 and the contamination activity has been calculated on the basis of one-quarter of the α-particles in this layer leaving the surface of the aluminum disc and interacting with the zinc sulphide detector. The number of picocuries per gram is the α-particle activity of the presumed parent, ^{227}Th. Similar calculations have been carried out for the long-lived residual α-particle component in aluminum, assuming ^{226}Ra in equilibrium with its four daughter α-particle emitters, although, if ^{210}Pb were separated from ^{226}Ra in the refinement process the ^{210}Po α-particle activity would not have again reached equilibrium. In the case of copper, where the half-life of the α-particle activity seems to be of the order 20 yr, it has been postulated that the ^{210}Pb was indeed separated from its progenitors in refinement. The precision given by the least-square computation of half-life of the steel α-particle contamination is so good that one is reluctantly forced to conclude that is due to ^{228}Th, although this assignment to the thorium series is the only exception to assuming the ^{235}U and ^{238}U series. The α-particle activities have in all cases been calculated in the same manner as for aluminum.

It should be noted that a change in assumed energy of the alpha-particles of ± 1 MeV results in a change in range of about ± 35 per cent, which will change the estimated activity per gram in direct proportion.

In the case of the short-lived "β"-particle contamination of aluminum the assumed contaminants, ^{211}Pb and ^{207}Tl, in equilibrium with ^{227}Th give rise to β particles with maximum energies, respectively, of 1·36 and 1·44 MeV. For the purpose of calculating the order of magnitude level of contamination an average maximum energy of 1·4 MeV has been used. The range of 1·4 MeV electrons in aluminum is about 700 mg/cm^2. For the approximate calculation of contamination, the allowed β-ray spectrum was divided into four energy regions corresponding to 175 mg/cm^2 each. An estimate was then made of the number of β-particles originating in each of the four consecutive layers of aluminum, 175 mg/cm^2 in thickness, comprising the saturation thickness. Thus it

was assumed that β-particles from the whole energy range would escape from the top layer of 175 mg/cm^2, whereas only β-particles from the most energetic quarter region of the spectrum would escape from the fourth, or bottom 175 mg/cm^2, layer. It was also assumed that only one quarter of the β-particles would be escaping from the surface exposed to the Geiger–Müller detector. Similar calculations were made for the remaining levels of "β"-particle contamination shown in Table 6.

In the case of the aluminum-"β" results, the plot of activity vs. production year in Fig. 6 shows a component decaying with a half-life of 15·3 $\pm$ 3·9 yr. into a long-lived residual activity of about 40 d^{-1} cm^{-2}. The residual activity is not inconsistent with the long-lived residual activity in Fig. 5 of about 8 d^{-1} cm^{-2} which is due, we have assumed, to ^{226}Ra in equilibrium with its daughters, emitting in sequence five α-particles and three energetic β-particles ($\beta_{max} > 1$ MeV). The α-particle detectors are about 50 per cent efficient for α particles with negligible sensitivity to β particles (Table 1), while the β-particle detector is about equally efficient ($\sim$50 per cent) for α-particles and β-particles. Further, the saturation thickness in aluminum for β-particles is some 10 times greater than for α-particles. We might therefore expect that, for five α-particle emitters and three β-particle emitters in equilibrium, the ratio of the long-lived residual activity recorded by the β detector to that recorded by the α detector would be about 7:1. Within the limits of accuracy of the measurements made, and with the need to assume comparable levels of contamination at the time of production, the difference between 7:1 and the observed ratio of 5:1 is not unacceptable.

The aluminum "β"-particle activity of 15·3 $\pm$ 3·9 yr has been assumed to be due to an enhancement, in the production process, of ^{210}Pb ($T_{1/2} = 19{\cdot}4$ yr) to about double its equilibrium value with ^{226}Ra in the untreated ore. This should also show in the aluminum-α results shown in Fig. 5, due to the growth of ^{210}Po into equilibrium with the extra ^{210}Pb. This would, however, take nearly 2 yr to take place and the energy of the ^{210}Po α-particles is the lowest in the radium series. These are both mitigating parameters in an investigation where the activities are so low that an order-of-magnitude difference may be significant but a factor of 2 is not. Nevertheless, on examining the production-year section of Fig. 5, it is observed that four of the five values for the later production years 1962–1966 are all higher than the average value of activity, $\bar{R}$. In a least-squares analysis this observation would have carried little weight and it is only in retrospect, armed with the aluminum-"β" data, that one can perhaps attach significance to the higher aluminum-α results for the years 1962–1966.

It should be noted that a change in assumed energy of the alpha-particles of $\pm$1 MeV results in a change in range of about $\pm$35 per cent, which will change the estimated activity per gram in direct proportion.

The gamma-ray activities were all computed using an average Compton scattering coefficient between 0·4 and 1·5 MeV.

Acknowledgements—The authors wish to acknowledge with thanks very helpful discussions with J. E. Leiss, and the cooperation of F. J. Schima in running the least-squares half-life computations. We are also grateful to the many manufacturers in North and South America, listed in Table 1, who cooperated in making samples available for the radioactivity measurements.

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