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X-RAY FLUORESCENCE SURFACE CONTAMINANT ANALYZER
A FEASIBILITY STUDY

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ABSTRACT

The bonding of liner material to the inner metal surfaces of solid rocket booster cases is adversely affected by minute amounts of impurities on the metal surface. Suitable non destructive methods currently used for detecting these surface contaminants do not provide the means of identifying their elemental composition. This report investigates the feasibility of using isotopic source excited energy dispersive x-ray fluorescence as a possible technique for elemental analysis of such contaminants.

A survey is made of the elemental compositions of both D6-ac steel, a common construction material for the booster cases, and Conoco HD-2 grease, a common surface contaminant. Source and detector choices that maximize signal to noise ratio in a "Recessed Source Geometry" are made. A Monte Carlo simulation is then made of the optimized device incorporating the latest available x-ray constants at the energy of the chosen source to determine the device's response to a D-6ac steel surface contaminated with Conoco HD-2 grease. An examination of the response for a grease layer of 100 angstroms, this is 1 milligram per square foot if the grease is spread uniformly over the square foot, should produce a count rate of about 1 count per second for a 1 curie iron 55 exciting source (0.82×10^{10} photons per second).

As a result of this optimization calculation, an iron 55 radioactive isotopic source excited x-ray fluorescence spectrometer that would mount on the existing robotic arm used for remote scanning of the inside of the large booster tank is proposed. It could operate in conjunction with the presently used contaminant detection devices. The resultant size and weight restrictions favor a cooled lithium drifted silicon semiconductor x-ray detector, and isotopic source. These same restrictions favor a Peltier cooling unit over the more common liquid nitrogen filled dewar.

Since calcium was chosen as an indicator for the grease, it is recommended that, prior to constructing the analyzer, spectra be accumulated from samples of D-6ac steel using conventional x-ray fluorescence equipment available at MSFC within the Chemistry Laboratories to ascertain the absence or presence of calcium in the steel.

ACKNOWLEDGMENTS

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INTRODUCTION

X-ray fluorescence spectroscopy is a technique for quantitative elemental determinations wherein the characteristic x-rays emitted by the excited atoms of various elements within the sample are analyzed as to energy and intensity. The energy of an emitted x-ray is related to the atomic number of the excited atom, hence the atomic species (Mosley's Law); while, the intensity of the emitted x-rays at a given energy is proportional to the number of atoms of a given species residing within the illuminated volume of the sample. There are a number of different methods of exciting the atomic species in a sample but the one that generally gives the most economical, most compact, and least weight assembly is the isotopic source.

In the isotopic source method of excitation, one uses a radioactive source that provides either x-rays or low energy gamma rays. To perform the analysis, one merely illuminates the sample with the photons from the source and then collects the fluorescent x-rays emitted by the sample with a suitable detector that will disperse these x-rays in energy. The spectra will in general be complicated by elastic and inelastic scattering of the incident x-rays by the sample as well as the fluorescent x-rays from the atomic species within the sample that are not of interest to the analysis.

By a judicious choice of the radioactive source used for excitation, one may limit the analysis to a selected range of the atomic species present. A detector may also be chosen that is most sensitive to a selected range of x-ray energy to futher eliminate the contributions of the undesirable x-rays. Finally filters may be inserted in the incident beam, the scattered beam, or in both to reduce the background.

The availability of high resolution high efficiency solid state x-ray detectors, fast pulse processing electronics, and personal computers with adequate speed and memory capacity has provided the means to perform a complete elemental analysis of certain specimen. The technique's exploitation is limited by the availibity of exciting sources of suitable energy and adequate intensity, interference by elements in the sample that are not of interest, and the count rate limits of the pulse handling electronics. With currently available components, analyses are routinely made in a matter of minutes to detection limits of 1 microgram (Rachetti and Wegscheider, 1986).

THE ANALYTE: CONOCO HD-2 GREASE

Conoco HD-2 Grease is composed (Law, 1987) principally of a light paraffin oil (70%), the calcium soap of mixed aliphatic sulfonic acids and alkylaryl sulfonic acids (15%), and the calcium soap of mixed aliphatic carboxylic acids (8%). It also contains inorganic calcium bases (~5%), calcium carbonate (2%), and diphenyl amine (0.3%). Based on the above mentioned work of Law, the elemental composition of HD-2 Grease as calculated for this work is shown in Table 1.

TABLE 1 - Elemental Composition of Conoco HD-2 Grease

Element	Weight Fraction
CALCIUM	.0067
CARBON	.00306
HYDROGEN	.00022
SULPHUR	.00002
SODIUM	.00008
CHLORINE	.0032
NITROGEN	.00004
SILICON	.000028
MANGANESE	.000008
IRON	.000054
MAGNESIUM	.000028
ALUMINUM	.000028
COPPER	.00002
ZINC	.000002

THE SUB-STRATA: D-6ac STEEL

Ladish D-6ac is quite similar in composition to AISI/SAE 4340 a member of the family of medium carbon low alloy ultrahigh-strength steels (Philip, 1980). Since the actual concentrations of the additives in D-6ac are not given, those for 4340 will be used with the following modifications: (1) the upper limit for each element's concentration will be used, (2) vanadium will be added at the same rate as nickel (3) the amount of nickel will be the same as 4340. With these modifications, the pertinent properties of the elements in D-6ac steel are presented in Table 2.

TABLE 2 - Elements In D-6ac Steel used in Background Calculation

Element	Weight Fraction	Molecular Weight	Atom Fraction	Density grams/cm^3
Carbon	.0043	12.01	.02	2.25
Manganese	.0080	54.94	.008	7.3
Silicon	.0035	28.09	.007	2.24
Chromium	.0090	52.01	.01	6.93
Nickel	.0200	58.71	.02	8.8
Molybdenum	.0030	95.95	.002	9.0
Iron	.9322	55.85	.9322	7.86
Vanadium	.0200	50.95	.02	5.6

ANALYSIS TECHNIQUE

Elements in the grease that were not also present in the steel could be used as an indicator of the presence of grease on the steel surface. In addition, if the concentration of the element was consistent within the grease, a quantitative measurement of the amount of that element could also be a quantitative measure of the amount of grease. Upon examination of Table 3, the "----" means that a concentration for that element was not reported, and the elements in it with regard to their x-ray characteristics, one finds that carbon, silicon, iron, and manganese which are in the grease are also in the steel. The energy of the K alpha line from the elements hydrogen, sulfur, sodium, chlorine, magnesium, nitrogen, and aluminum is so low that they would not be effectively detected if the system was operated in the atmosphere using a detector with a standard entrance window. For the application proposed in this study, the system would be operated in just that environment. Under such operating conditions, these x-rays would be severely absorbed within the intervening medium between sample and detector sensitive volume. The elements copper, and zinc have a K alpha excitation energy greater than iron. This means that, if a source were chosen with a high enough energy to excite these elements, this source would also excite the iron in the steel sub-strata. The fluorescent x-rays from the iron, because of the large amount of iron present, would interfere with the the detection of the much smaller amounts of these elements in the grease layer. The element calcium is left as the best possible candidate to serve as an indicator of the presence of the grease on the steel.

TABLE 3 - WEIGHT FRACTIONS OF ELEMENTS IN HD-2 GREASE AND D-6ac STEEL

ELEMENT	D6-ac STEEL	HD-2 GREASE
CARBON	.0043	.00306
MANGANESE	.0080	.000008
SILICON	.0035	.000028
CHROMIUM	.0090	.------
NICKEL	.0200	.------
MOLYBDENUM	.0030	.------
IRON	.9322	.000054
VANADIUM	.0200	.------
CALCIUM	.----	.0067
HYDROGEN	.----	.00022
SULPHUR	.----	.00002
SODIUM	.----	.00008
CHLORINE	.----	.0032
NITROGEN	.----	.00004
MAGNESIUM	.----	.000028
ALUMINUM	.----	.000028
COPPER	.----	.000002
ZINC	.----	.000002

The above discussion has also fixed the radioactive source that could best serve in the analyzer as iron 55. This isotope decays by electron capture to manganese 55 which then emits its characteristic x-rays as the electron cloud around the nucleus rearranges to accommodate the daughter nucleus. Of the resultant electromagnetic decays, 25 percent are radiative with 22.1 percent being at an energy of 5.9 kilo electron volts (KeV) and 2.9 percent being at an energy of 6.5 KeV. These x-rays are too low in energy to appreciably excite the iron in the steel and low enough to effectively excite the calcium in the grease. The K alpha excitation edge for calcium is 4.09 KeV.

There are a variety of designs for the geometrical arrangement of the source, sample, and detector to perform a x-ray fluorescence type of analysis. It is generally accepted that the "Recessed Source Geometry" provides the greater detection efficiency (Conde and dos Santos, 1985) for a proportional type counter and this geometry will be applied in this study for the Si(Li) detector. The geometrical arrangement for the recessed source geometry is shown in Figure 1. The radioactive face of the

SOURCE: Fe^{55}
DETECTOR: $Si(Li)$

SOURCE
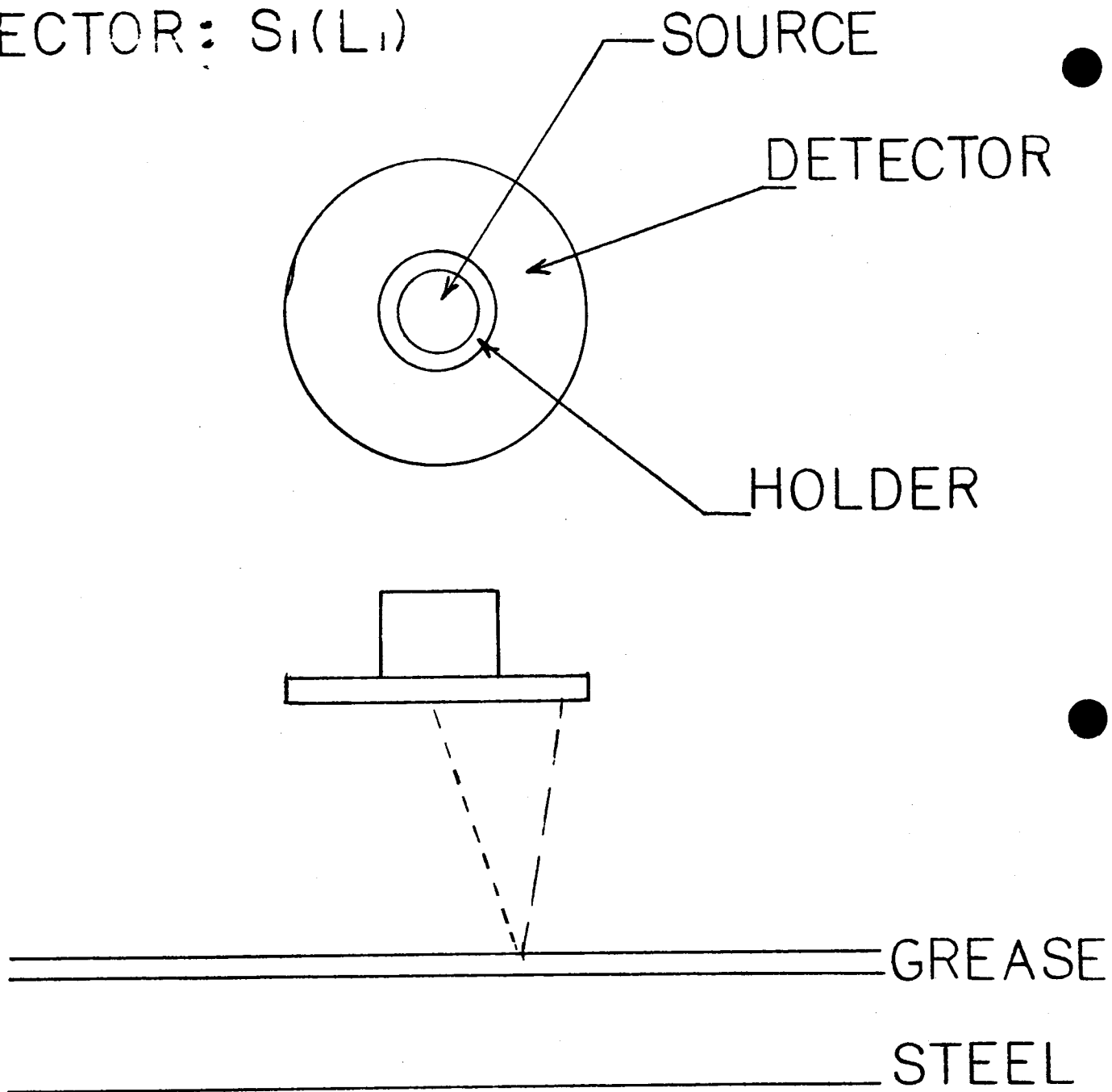
DETECTOR

HOLDER

GREASE

STEEL

FIGURE I
X-RAY FLUORESCENCE
SURFACE CONTAMINANT
ANALYZER

X-6

source is flush to the face of and coaxial with its holder assembly whose diameter on that face is 4 mm greater than the source diameter. The source, with its holder, is then mounted flush to the face and coaxial at the center of the silicon wafer that is the sensitive volume of the x-ray detector. The radioactive face of the source is on the same side as the entrance face of the detector. An x-ray emitted from the iron 55 source that causes a calcium atom in the grease layer to fluoresce and the resultant fluorescent x-ray from the excited calcium atom is then absorbed within the detector's sensitive volume would provide the mechanism by which the device responded to the presence of grease on the steel. There would also be fluorescent x-rays impinging upon the detector from other atoms excited in both the grease layer and the underlying steel strata. These other fluorescent x-rays from the steel would be background and would serve to only degrade the signal to noise ratio for the experiment and prescribe the degree of energy resolution and pulse processing rate that the detector and ancillary electronics must have. Any other elements that were present could provide an additional measurement of the amount of grease present. It is possible that contaminants other than grease could be quantitatively measured on the surface, simultaneously, provided adequate energy resolution and counting rate capabilities were present in the detection system.

SIMULATION OF THE ANALYZER

The straightforward calculation of the response of the
device shown schematically in Figure 1 involves the solution of a
multidimensional integral equation wherein the integrand is not a
simple function (Jenkins, Gould, and Gedcke, 1981). What is
frequently done, instead of analytically solving the equation
representing the response of the device, which of course would be
generally preferred, is to compromise by performing a "Monte
Carlo" or stochastic simulation of the process (Kalos and
Whitlock, 1986), (Rubinstein, 1981), and (Hammersley and
Handscomb, 1967). The first step in the simulation consists of
dividing the physical process into a number of sequential events
whose outcomes are governed by known probability distribution
functions. The outcomes of these events are then determined by
properly choosing from these probability distribution functions.
The individual histories of the objects under study, in this case
x-ray photons, are then compiled. These historical compilations
are the desired solution which, in this case is, the response of
the instrument in Figure 1.

For the particular case under study, the sequence of events
starts with an circular area which emits photons of a definite
energy in a random direction. The position that a photon is
emitted from the surface is chosen from a distribution that is
uniform, or constant, over the circular area and zero everywhere
else. Once the position is chosen, the direction of emission is
chosen from a distribution that is uniform in the polar angle
over the region 0 to 90 degrees and uniform in the azimuthal
angle from 0 to 360 degrees. Actually a photon emitted at a polar
angle of 90 degrees would never reach the parallel surface of the
sample, so a small "cut off" angle is introduced. This
introduction has its attendant compromise to the accuracy but is
necessary in a practical calculation. The net result is that
photons of polar angles very near 90 degrees are discarded as
failures at that point in their histories.

Once the position and direction of the emitted photon is
decided, a path length or distance that it will travel before
interacting with the medium is picked from the proper
distribution. There are parameters in the distribution function
of path lengths and the values of these parameters are determined
by the nature of the medium and the energy of the photon.

At the interaction site, the type of atom that the photon
interacts with is chosen. The probability of interacting with a

particular atom species is just the fractional number of that species in the sample. What type of interaction that occurs at that site is then chosen. From the interaction site, the original photon could emerge at a different direction, a different energy, or both. The original photon could also disappear and a different photon emerge. Each type of event would be picked in a random fashion from its proper distribution function.

In general, each photon would be traced on through the sample until it was absorbed or impacted the sensitive volume of the detector. The number of a particular energy photons that struck the detector's sensitive volume would be the response of the device to a given element for a certain source strength. When the history of a photon ends, another photon is started out from the source and its subsequent history is chronicled. After a very large number of these histories are compiled, in theory there should be an infinite number, the ratio of the number of a particular energy photon that strike the sensitive volume of the detector to the total number of photons that left the source, is the efficiency of the device for detecting a particular element in the sample.

RANDOM NUMBER GENERATOR

Central to the Monte Carlo method of solving integral equations is the availability of a sequence of truly random numbers. It is postulated that a Monte Carlo simulation will be an accurate representation of a physical process if the number sequence used in the simulation is truly random. However, to have a truly random sequence not only must the sequence be of infinite length but also each number must have an infinite number of digits. Finite amounts of time alloted a mortal and finite sized computer registers rule out the use of a truly random sequence in the solution of most practical problems. One must therefore compromise the accuracy by using a sequence of numbers of finite length, each of which have a finite number of digits. This so called pseudo random sequence approaches the ideal random sequence as both its length and the number of digits in the individual members becomes infinite.

A sequence of random numbers used in this simulation were generated using the GW-BASIC function RND(1). The function, RND called with the argument (1), started the sequence with the same member each time the program was run. To test the randomness of the number sequence generated by RND(1), a program was written to generate the sequence and then determine the frequency distribution of the numbers within the sequence. The frequency with which numbers, whose values lay within the interval, occurred for ten uniform intervals between 0 and 1 is shown in Table 4, for a sequence of numbers with 5,000 members. The percent deviation from the average for the frequency is as high as 10%. The data in Table 4 imply that a sequence with 5000 members is not an adequate representation of an infinite sequence.

TABLE 4 - Frequency of distribution of random numbers
in 5,000 member sequence; GW-BASIC RND(1)

Interval	Frequency	Deviation	Percent
0 - .1	447	-53	10.6
.1 - .2	496	-04	00.8
.2 - .3	503	+03	00.6
.3 - .4	514	+14	02.8
.4 - .5	524	+24	04.8
.5 - .6	515	+15	03.0
.6 - .7	470	-30	06.0
.7 - .8	498	-02	00.4
.8 - .9	531	+31	06.2
.9 - 1.0	502	+02	00.4

Table 5 shows the frequency distribution for a sequence of 50,000 members. The maximum percent deviation from the average for this sequence is about one tenth of Table 4 indicating that that this sequence is a much better approximation to the ideal random sequence. As a compromise between accuracy and computing time, the sequences used in this simulation were greater than 250,000 members in length. The effect of computer word size on the randomness of the sequence was not explored.

TABLE 5 - Frequency of distribution of random numbers in 50,000 member sequence; GW-BASIC RND(1)

Interval	Frequency	Deviation	Percent
0 - .1	5025	+25	00.5
.1 - .2	5026	+26	00.5
.2 - .3	5053	+53	01.0
.3 - .4	5025	+25	00.5
.4 - .5	5057	+57	01.1
.5 - .6	5082	+82	01.6
.6 - .7	4989	+11	00.2
.7 - .8	4964	-36	00.7
.8 - .9	4948	-52	01.1
.9 - 1.0	4931	-69	01.4

UNIFORM SOURCE

To check the part of the simulation program that generates a circular surface that emitts photons uniformly from its surface, a test was made of a source of radius 2 mm. A cartesian coordinate system was chosen with the origin at the center of the circular source. Each coordinate, X and Y, was divided into 10 equal intervals over the range -2 to +2. The frequency of occurrence of the coordinates (X,Y) of the point of emission of a photon lying within the area bounded by a given interval in X and Y was then computed. One quarter of the circular source is shown in Figure 2 where the source is superposed on an X,Y grid of the area intervals. For a square which lies wholly within the boundary defined by the circle, the relative frequency of a photon being emitted from this area is just the area of the square divided by the total area of the circle.

As an example, consider the small square bounded by 1.2 < Y < 1.6 and 0 < X < 0.4. the area of the square is (0.4) x (0.4) or .16 square millimeters. The area of the whole circle, whose radius is 2 mm., is 12.566... square millimeters. The ratio of the two, the fractional number of photons emitted from that area on the source is 0.0127... . Consider now a square that lies wholly outside the area of the circle. No photons should be emitted from this area since it is outside the source area so the frequency of occurrence of coordinates for the emission point of a photon should be 0. For the squares that lie partially inside and partially outside the circle, in Figure 2, the relative number of photons being emitted from a point with coordinates within the square, is just the area of the square that is within the circle divided by the total area of the circle. This number may be calculated exactly from the expression:

$$\frac{1}{4\pi} \int_{1.2}^{1.6} \int_{1.2}^{\sqrt{4-x^2}} dx\, dy$$

for the particular square defined by 1.2 < Y < 1.6 and 1.2 < X < 1.6.

Table 6 is a compilation of the two dimensional frequency distribution in X and Y for the discrete areas shown bounded by

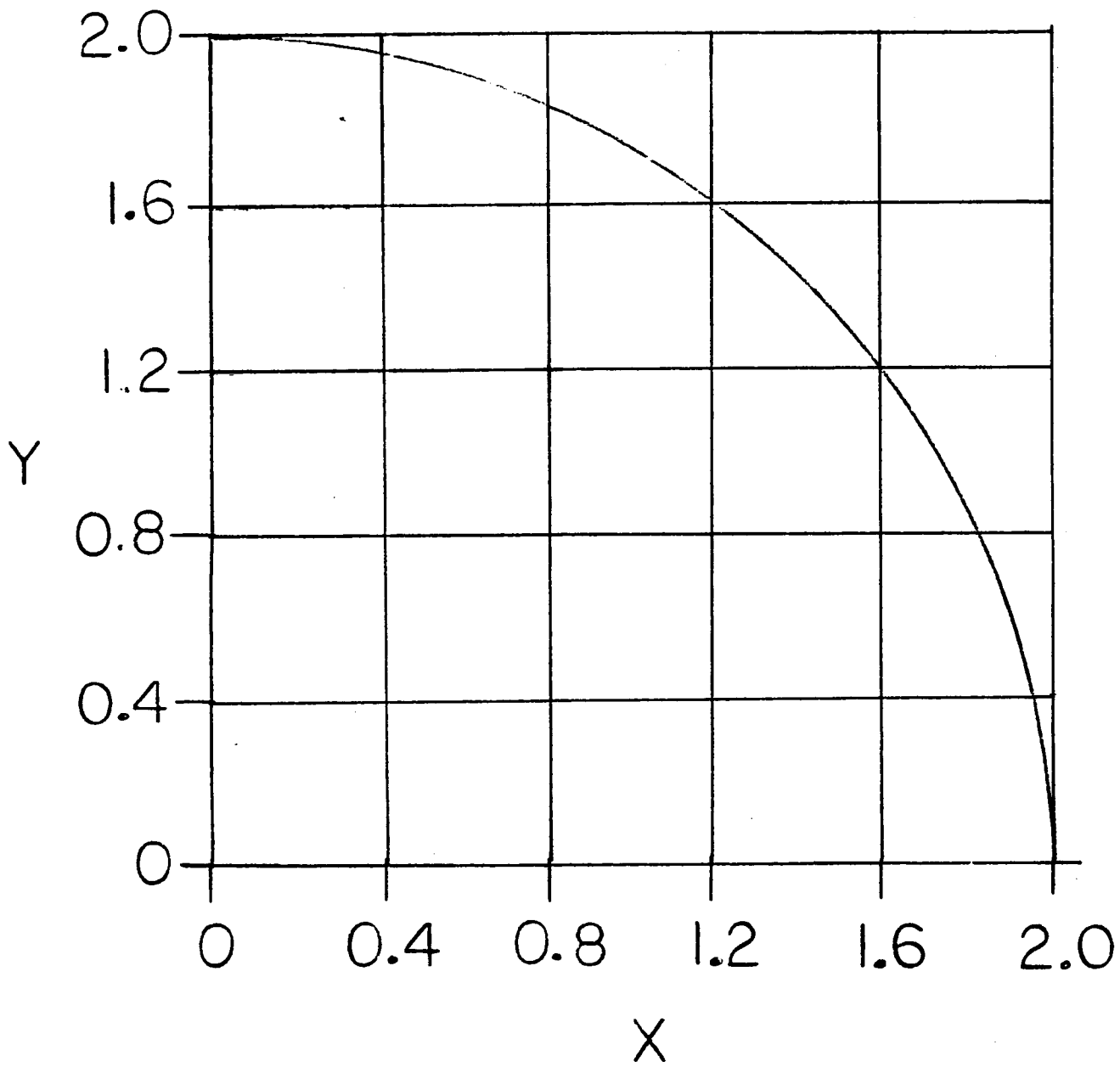FIG. 2 PHOTON SOURCE
UNIFORMITY TEST

X—14

the Y intervals (vertically) and the X intervals (horizontally).
By symmetry, a study of any one quarter of the circle is
sufficient, actually there is also symmetry along a 45 degree
line in the X,Y plane. The calculated frequencies, enclosed
within parenthesis, are placed under the "MONTE CARLO" determined
frequencies for comparison. Table 6 demonstrates that the
simulated source shows the desired uniformity of emission over
its area.

TABLE 6 - SOURCE UNIFORMITY TEST MONTE CARLO
(CALCULATED)
294,232 HISTORIES

	INTERVAL		RELATIVE FREQUENCY			
	2.0-1.6	.012307	.009632	.003861	.000000	.000000
		(.012513)	(.009948)	(.004138)		
	1.6-1.2	.013031	.012725	.012517	.006947	.000000
					(.006950)	
Y	1.2-0.8	.012891	.012256	.012990	.012888	.004051
		(.012733)				(.004138)
	0.8-0.4	.012738	.012847	.012901	.013051	.009435
						(.009948)
	0.0-0.4	.012915	.012854	.012579	.012677	.012528
						(.012513)
	INTERVAL	0.0-0.4	0.4-0.8	0.8-1.2	1.2-1.6	1.6-2.0

X

THE GEOMETRIC EFFICIENCY

At this stage in the simulation, we choose the area of the source and the height to operate the source from the sample surface that will give the optimum efficiency. The maximum size of the outer detector diameter is choosen as 30 millimeters by economic and resolution considerations. The wall thickness of the source holder was taken as 2 millimeters, a thickness that will be sufficient to protect the sensitive volume of the detector from direct illumination of the primary beam and still maximize the sensitive area of the detector available. This thickness is depicted, not to scale, in Figure 1 and labeled "HOLDER".

To study how the geometric efficiency varies with the above parameters, a computer program was written using the random number sequence generator and the uniform circular source studied previously. In this program, photons emitted by the source were assumed to have an infinite "path length" in the air between the source and sample and a 0 "path length" in the grease layer on the surface. This means that the photons suffer no attenuation in the intervening air but are absorbed immediately when they strike the grease. They then excite an atom in the grease and the resultant fluorescent x-ray is remitted isotropically. All the probabilities involved in the physical process at the interaction are taken as 1 to increase the efficiency, hence decrease the computing time, in this part of the study. Of these remitted photons, those that come off with a polar angle greater than 90 degrees are traced and, if one should end up in the sensitive volume of the detector, a successful outcome of an event would have occurred. Such a photon is depicted in a highly schematic fashion in Figure 1. The shorter dashes on the broken line indicates the incident photon from the source, higher energy or shorter wavelength; while the longer dashes on the broken line indicate the fluorescent x-ray emitted by an atom in the grease that was excited by the incident photon. The fluorescent x-ray would have a lower energy, or longer wavelength, than the incident photon; hence, the dashes in the line representing its path are longer.

The results of the above study are shown in Figure 3. In this three dimensional plot, the height, in millimeters, of the source-detector assembly above the sample surface and the source diameter, in millimeters, are shown as the two perpendicular axes in the horizontal plane. The relative geometric efficiency of the device is plotted as the distance above that plane. The

GEOMETRIC EFFICIENCY

30 MM DETECTOR

FIGURE 3

EFFICIENCY (REL)

HEIGHT (MM)
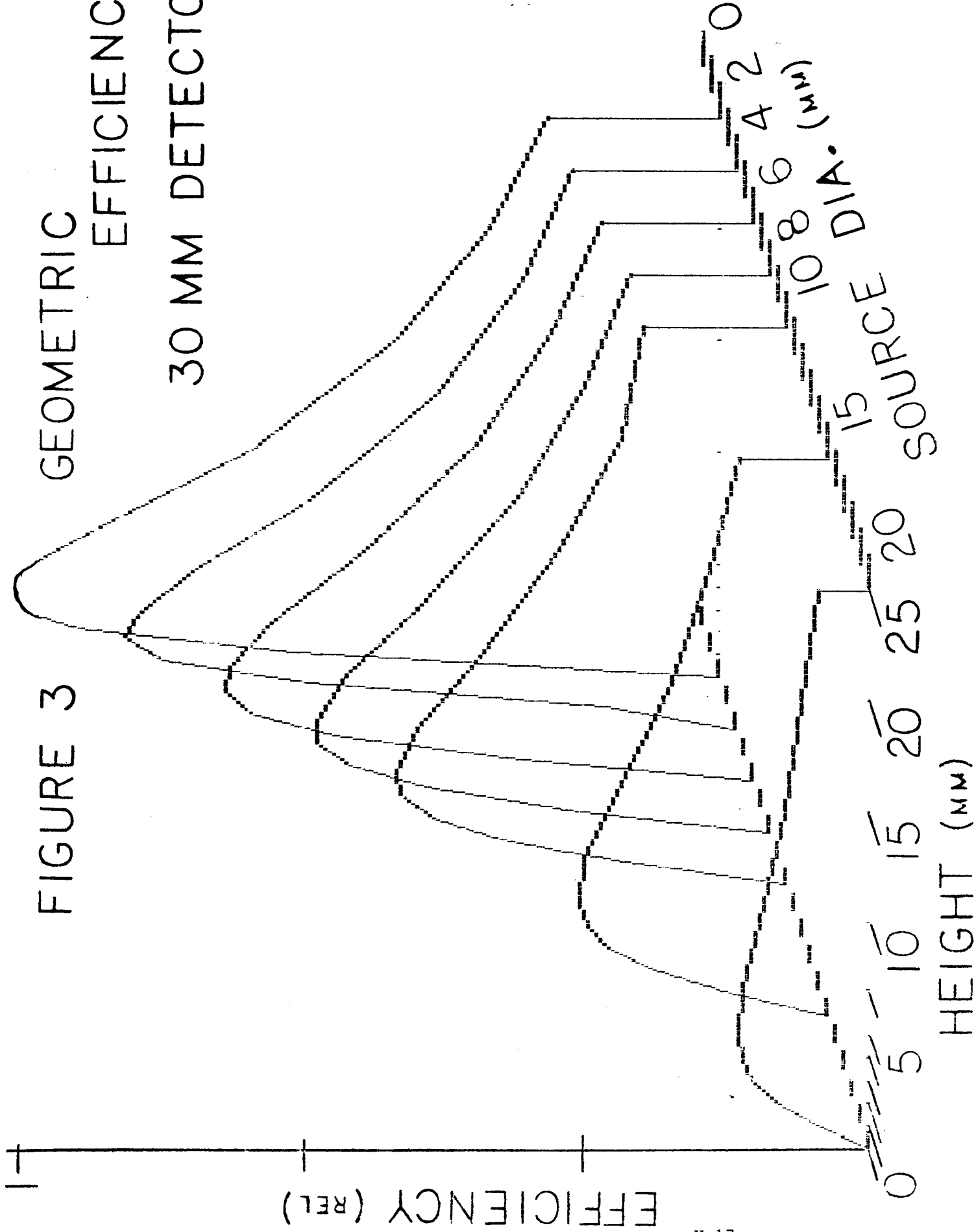
SOURCE DIA. (MM)

efficiency continues to increase as the source diameter is reduced, as would be expected, because the same radioactivity was assumed for the source regardless of its diameter. This situation is not physically realizable for the smallest source that can be constructed with a reasonable activity is about 4 millimeters in diameter. This size will be used in the rest of the study. At 4 mm source diameter, the geometric efficiency maximizes at a height above the sample surface of 4 mm so, in the rest of the study, the 4 mm diameter source will be placed 4 mm above the sample surface. The relative efficiency is shown in Figure 3. The magnitude of the efficiency, at the position of 4 mm above the surface for a 4 mm source, was 22.1%.

For the rest of the study, actual path length distribution functions will be used. Iron, however, will be substituted for D-6ac steel for purposes of path length calculation. The kind of atom impacted at each collision site will be selected according to the relative number of those kinds of atom per volume of the medium in which the collision occurred. The path length for the photons in air will, however, continue to be taken as infinite since such an approximation will introduce little error in the final results. In addition, second order collisions are neglected. This is reasonable at this stage since the flux available for second order collisions is about one millionth of the incident flux.

These features were added to the program that was used to compute the geometric efficiency and this new program was run for a number of cases where the thickness of the grease layer on the steel SUB STRATA was varied. The program generated the number of calcium K alpha x-rays originating in the grease layer that subsequently ended up in the sensitive volume of the detector. The number of K alpha x-rays from the impurity atoms in the steel that, after excitation by the primary beam, made their way to the detector sensitive volume, were also tabulated by the program. These values would be a lower estimate of the background that would be expected when using this device.

PATH LENGTH DISTRIBUTION

A flux of photons transiting a medium characterized by a mass absorption coefficient μ and a density ρ is attenuated according to the formula (Jenkins, Gould, and Gedcke, 1981):

$$I(x) = I(0) \, e^{-\mu \rho x}$$

where:
    $I(x)$ = the flux of at position x
    $I(0)$ = the flux at x=0
    μ = mass attenuation coefficient
    ρ = density of the medium

If the number of photons that successfully transit the medium of thickness x, $I(x)$, is divided by the number of photons that started out into the medium, $I(0)$, the probability, to within an arbitrary constant, of a photon having a path length in that medium is obtained. This is to say that the number of successful outcomes of an event (a photon surviving the transit) divided by the successful plus the unsuccessful outcomes of an event (a photon being absorbed) defines the probability of a given photon surviving a distance x in the medium. We want the total probability that a photon has a path length between 0 and infinity to be 1, that is all photons are absorbed in an infinite medium, so, to normalize the distribution we divide by the factor:

$$\int_{0}^{\infty} e^{-\mu \rho x} \, dx$$

The expression for the probability of a randomly emitted photon having a path length x is:

$$P(x) = \mu \rho \, e^{-\mu \rho x}$$

The CONOCO HD-2 grease that serves as a contaminant on the steel is principally a hydrocarbon compound. For computing the path distribution for the 5.9 KeV photons in the grease we will

use the published value for paraffin like hydrocarbons, (Weast, 1987) value of 10 centimeters squared per gram and the actual value of the density of the grease, (Conoco, 1985) as 1 gram per centimeter cubed. Substituting these values in the probability distribution P(x), we obtain the expression for the path length distribution function for 5.9 KeV photons in HD-2 grease:

$$P(x) = e^{-x}$$

This expression must be solved for x, the path length, in terms of P, the probability of a particular x. This yields:

$$x = \ln\left[\frac{1}{P(x)}\right]$$

If P is now picked from a random distribution ranging from 0 through 1, x will be properly distributed.

To check these conjectures, 4,763,489 path lengths were generated with P in the above expression replaced with the random number generating function RND(1). The frequency with the path lengths occurred within specific intervals of length are shown in Table 7 and labeled "MONTE CARLO". They are to be compared with the frequencies labeled "EXACT". The calculated or exact value for the frequency of occurrence of path lengths within an interval of length bounded by the values a and b is given by:

$$\int_a^b e^{-x}\,dx$$

X-20

TABLE 7 - 5.9 KeV PHOTONS IN GREASE
PATH LENGTH DISTRIBUTION
4,763,489 HISTORIES

INTERVAL (in mm)	MONTE CARLO	EXACT
0 TO 1	.63222	.63212
1 TO 2	.23246	.23254
2 TO 3	.08557	.08548
3 TO 4	.03147	.03147
4 TO 5	.01159	.01158
5 TO 6	.00423	.00426
6 TO 7	.00154	.00157
7 TO 8	.00058	.00058
8 TO 9	.00021	.00021
9 TO 10	.00008	.00008
10 TO INFINITY	.00004	.00004

Since the expression for the path length probability distribution function gives the expected frequency distribution of paths, the same expression, with the parameters μ and ρ for grease replaced with those for iron, is used to pick the path length in the steel SUB STRATA.

THE INTERACTION SITES

After a photon left the source along a selected polar
direction, it suffers no attenuation until it contacts the grease
layer. There it either suffers an interaction in the grease layer
or not depending upon the random path length chosen for it and
the value of its previously chosen polar angle. If its path
length is less than the thickness of the grease layer divided by
the cosine of the polar angle, it suffers a collision in the
grease layer. If it suffers a collision in the grease layer, the
probability that that atom is a calcium atom is given by the
fractional number of atoms in the grease that are calcium.

Using the analysis of the grease discussed earlier (Law,
1987), the atom fraction of calcium is:

$$6.21 \times 10^{-5}.$$

The probability that a 5.9 KeV photon produces a K alpha x-
ray when it is absorbed by a calcium atom is given by:

$$F = \omega_k \left(\frac{r_k - 1}{r_k} \right) \frac{\tau}{\mu}$$

where: ω_k = K alpha x-ray fluorescence yield
          r_k = K edge jump factor
          μ = Total mass attenuation coefficient
          τ = mass photoelectric absorption coefficient

For the element calcium and at 5.9 KeV, using recent experimental
values for the physical quantities, (McMaster, Kerr Del Grande,
Mallett, and Hubbell), the above expression yields:

$$0.146.$$

The probability that both events occur is the product of the two
above probabilities:

$$(0.146) \times (6.21 \times 10^{-5}) = 9.067 \times 10^{-6}.$$

To make the program more efficient, with no sacrifice in
accuracy, we will assign the K alpha photon that comes from such
an encounter a "weight" of the above number.

If the photon transited the layer of grease without an interaction, it is restarted at the boundary between the grease and steel with the selection of a new path length using the same expression as was used for the grease but with the attenuation coefficient and density appropriate to iron, the major component of the steel.

At the end of the path length in the steel, a collision occurs in which the photon is absorbed. The type of atom in the steel that suffered the collision is selected by first generating a random number. The magnitude of the number determines the kind of atom that absorbed the photon according to Table 8.

TABLE 8 - METHOD OF CHOOSING KIND OF ATOM IN STEEL THAT ABSORBED
A 5.9 KeV PHOTON THAT PASSED THROUGH THE GREASE LAYER

Random Number Value	Kind Of Atom	Energy K alpha X-Ray(KeV)	Considered After Collision	Why Not ?
0.000-0.020	CARBON	0.26	NO	ENERGY TOO LOW
0.020-0.028	MANGANESE	5.89	YES	
0.028-0.035	SILICON	1.74	YES	
0.035-0.045	CHROMIUM	5.41	YES	
0.045-0.065	NICKEL	7.47	NO	NOT EXCITED
0.065-0.067	MOLYBDENUM	17.44	NO	NOT EXCITED
0.067-0.087	VANADIUM	4.95	YES	
0.087-1.000	IRON	6.4	NO	NOT EXCITED

The pertinent physical constants related to the atoms in the steel that are considered beyond their first collision in the background determination and calcium, considered in the grease, are shown in Table 9. The values were taken from a compilation of experimental results, where such data existed, and the rest were taken from published calculations and extrapolations, (Bambynek, Crasemann, Fink, Freund, Mark, Swift, Price, and Rao). Where the total mass absorption coefficient was not available, the total

photoelectric absorption coefficient was used. This procedure is quite accurate at these low x-ray energies. The column headings are defined earlier where the K alpha emission probability was discussed.

TABLE 9 - X-RAY CONSTANTS AT 5.9 KeV IN IRON
FOR SELECTED IMPURITY ATOMS

Atom Kind	$\tau\rho$ cm^{-1}	$\mu\rho$ cm^{-1}	ω_k	r_k	F	Atom fraction	K alpha Probab.
CALCIUM	615.42	617.52	.163	9.112	.146	6.21×10^{-5}	9.067×10^{-6}
CHROMIUM	479.61	484.82	.280	8.779	.245	.0100	.00245
MANGANESE	560.00	560.88	.314	8.612	.277	.0080	.00222
SILICON	372.64	372.64	.047	10.442	.042	.0025	.00029
VANADIUM	3221.2	3221.2	.253	8.770	.224	.0200	.00448

Once a K alpha x-ray had been emitted by one of the minor elements in the steel, a path length and direction was chosen for it in the iron which, of course, depended upon its energy. Table 10 gives the energy of the K alpha x-rays for each element considered and its mass absorption coefficient in iron. This x-ray could be absorbed in the iron, which ended its history, or it could proceed out into the grease layer. In the grease layer it might also be absorbed, which ended its history. It could also escape from the grease layer and, if it did, and happened to also hit the detector's sensitive volume, then a fraction of a background event was recorded. The fraction recorded is given in the last column of Table 9.

TABLE 10 - MASS ABSORPTION COEFFICIENTS FOR BACKGROUND ELEMENTS
IN D-6ac STEEL

Element	K alpha Energy	$\mu \rho$ cm^{-1}	Mean Path centimeters
Manganese	5.89	675.96	0.01479
Silicon	1.74	5545.49	0.00180
Chromium	5.41	806.72	0.01240
Vanadium	4.95	867.62	0.01153

RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

The final version of the GW-BASIC program that calculated the response of the device in Figure 1 to the calcium in the grease layer overlying a steel sub strata is listed as Appendix I. The program was run for several thickness' of the grease and the response for selected values of the grease layer thickness is tabulated in Table 11.

TABLE 11 - ANALYZER RESPONSE
TIMES 100,000
5.9 KeV PHOTONS
4mm DIA. SOURCE
30mm DIA. DETECTOR

	GREASE LAYER THICKNESS (A)		
ELEMENT	100	1000	10000
CALCIUM	.000015	.000047	.00037
MANGANESE	.326	.345	.306
SILICON	.0234	.0228	.0107
CHROMIUM	.477	.498	.445
VANADIUM	1.68	1.68	1.45

An examination of the response for a grease layer of 100 angstroms, this is 1 milligram per square foot if the grease is spread uniformly over the square foot, should produce a count rate of about 1 count per second in the calcium peak for a 1 curie iron 55 exciting source (0.82×10^{10} photons per second). This is a moderately intense source; however, 5.9 KeV photons can be attenuated quite easily so as not to present a health risk. An hours counting time would produce 3600 counts in the calcium peak for a precision, due to counting statistics, of 1.7%. It should be noted that the intensity of the calcium peak is not linearly related to the thickness of the grease layer.

The intensity of the background due to the trace elements in the steel are orders of magnitude greater than the calcium intensity. This should not present a problem in the operation of the device since Si(Li) detectors are available that provide an energy resolution of .15 KeV at an energy of 5.9 KeV.

As a result of this optimization calculation, an iron 55 radioactive isotopic source excited x-ray fluorescence spectrometer that would mount on the existing robotic arm used for remote scanning of the inside of the large booster tank is proposed. It could operate in conjunction with the presently used contaminant detection devices. The resultant size and weight restrictions favor a cooled lithium drifted silicon semiconductor x-ray detector, and isotopic source. These same restrictions favor a Peltier cooling unit over the more common liquid nitrogen filled dewar.

Electrical impulses, output from the detector, would be transported by coax cable from the detector to the modular electronics part of the spectrometer which could reside off the robotic arm in racks. There the impulses would be amplified and shaped by conventional components and fed into an analog to digital converter. The converters output would, in turn, be fed into a personal computer, such as an IBM PC. Both hardware and software, for a number of computers, are available to accumulate these electrical impulses into spectra and then provide analysis of resultant energy spectra of the x-rays impinging onto the detector.

It is also recommended that, prior to constructing an analyzer such as the one simulated in this study, spectra be accumulated from samples of D-6ac steel using conventional x-ray fluorescence equipment available at MSFC within the Chemistry Laboratories. These spectra should then be scanned for all peaks present and their relative intensities determined. The presence of calcium in this steel can then be determined and, if present above the limits of detection, the amount and consistency from sample to sample should be studied. The amount of calcium in the steel as well as its intra sample consistency, as compared to that of the grease, will indicate the feasibility of the application of x-ray fluorescence to this contaminant determination.

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APPENDIX I

GW-BASIC PROGRAM THAT SIMULATES AN X-RAY FLUORESCENCE SURFACE CONTAMINANT ANALYZER

```
100 REM COAXIAL SOURCE ANNULAR DETECTOR RESPONSE TO GREASE ON STEEL
110 DIM ELEMENT$(10),PROB(10),PATH(10),FLUX(10)
120 OPEN "A:ELEMENT.DAT" FOR INPUT AS #1
130 FOR I=1 TO 9:INPUT#1,ELEMENT$(I),PROB(I),PATH(I):NEXT I
140 CLOSE #1
150 CLS:LOCATE 5,10:INPUT"DIAMETER OF SOURCE (in millimeters)";S
160 R=S/2
170 LOCATE 7,10:INPUT"DIAMETER OF SOURCE CONTAINER (in millimeters)";C
180 C2=C/2
190 LOCATE 9,10:INPUT"DIAMETER OF SENSITIVE AREA OF DETECTOR (mm)";D
200 D2=D/2
210 LOCATE 11,10:INPUT"HEIGHT OF SOURCE-DETECTOR PLANE FROM SAMPLE
(mm)";H
220 LOCATE 13,10:INPUT"THICKNESS OF GREASE LAYER IN ANGSTROMS";T
230 T=T*.0000001   'CONVERT THICKNESS OF GREASE LAYER TO MILLIMETERS
250 J=1'LET THE SOURCE EMIT THE FIRST PHOTON
260 X=R*RND(1) 'POSSIBLE X COORDINATE SOURCE EMITTS PHOTON
270 Y=R*RND(1)' POSSIBLE Y COORDINATE SOURCE EMITTS PHOTON
280 IF(X^2+Y^2)>4 GOTO 260 'GOOD POSITION OF PHOTON EMISSION FROM
SOURCE??
290 SIGN=RND(1)' EQUAL LIKELYHOOD OF +,- FOR X
300 IF SIGN<.5 THEN X=-X
310 SIGN=RND(1)'  EQUAL LIKELYHOOD OF +,- FOR Y
320 IF SIGN<.5 THEN Y=-Y
330 TH=1.5707963#*RND(1) 'RANDOM THETA FOR DIRECTION OF EMITTED PHOTON
340 IF TH>1.5 GOTO 600 'EMITTED ALMOST PARALLEL TO SURFACE
350 PHI=6.2831853#*RND(1) 'RANDOM PHI FOR DIRECTION OF EMITTED PHOTON
360 L=H/COS(TH)'SAMPLE PLANE IS H(mm) ABOVE SOURCE SURFACE
370 X=X+L*SIN(TH)*COS(PHI)'X COORDINATE PHOTON STRIKES SAMPLE SURFACE
380 Y=Y+L*SIN(TH)*SIN(PHI)'Y COORDINATE PHOTON STRIKES SAMPLE SURFACE
385 K=1  'SET ELEMENT PARAMETERS FOR CALCIUM (IN THE GREASE)
390 LZ=RND(1) 'PICK RANDOM NUMBER FOR PATH LENGTH IN GREASE
400 IF LZ<.0000001 GOTO 600   'PATH TOO LONG; WILL CAUSE PROBLEMS; TOSS
410 PL=LOG(1/LZ)' PICK PATH LENGTH FROM PROPER DISTRIBUTION
420 IF PL>T/COS(TH) GOTO 700 'PHOTON PASSED THROUGH THE GREASE LAYER
430 X=X+PL*SIN(TH)*COS(PHI)
440 Y=Y+PL*SIN(TH)*SIN(PHI)
450 TH=3.1415927#*RND(1)'PHOTON INTERACTS IN TARGET ISOTROPIC SCATTER
460 IF TH<=1.6 GOTO 600 'MUST BE BACKSCATTERED TO HIT DETECTOR
470 PHI=6.2831853#*RND(1)'ALSO AZIMUTHAL ANGLE ISOTROPIC
```

```
480 L=-H/COS(TH)'DETECTOR IS H(mm) BELOW PLANE OF TARGET
490 X=X+L*SIN(TH)*COS(PHI)'X COORDINATE WHERE PHOTON HITS DETECTOR
500 Y=Y+L*SIN(TH)*SIN(PHI)'Y COORDINATE WHERE PHOTON HITS DETECTOR
510 IF(X^2+Y^2)<=C2^2 GOTO 600'PHOTON HITS SOURCE, CONTAINER INSTEAD OF
DETECTOR
520 IF(X^2+Y^2)>D2^2 GOTO 600 'PHOTON WIDE OF DETECTOR SENSITIVE VOLUME
530 FLUX(K)=FLUX(K)+PROB(K) 'ATOM FRACTION ELEMENT(K) * PROBABILITY Ka
X-RAY
600 A$=INKEY$
610 IF A$<>" " THEN J=J+1:GOTO 260
620 LPRINT S"(mm) ACTIVE DIAMETER SOURCE IN A";C;"(mm) DIAMETER
CONTAINER IN A";D;"(mm) DIAMETER DETECTOR";H;"(mm) ABOVE THE
SAMPLE";T;"(mm) OF GREASE"
630 LPRINT:LPRINT:LPRINT
640 LPRINT"NUMBER OF PHOTONS EMITTED";J:LPRINT:LPRINT
650 FOR I=1 TO 9
655 LPRINT ELEMENT$(I),PROB(I),PATH(I),FLUX(I)
660 NEXT I
695 END
700 K=9 'SET ELEMENT PARAMETERS FOR IRON
710 LZ=RND(1)  'RANDOM NUMBER FOR PATH LENGRH IN IRON
720 IF LZ<.0000001 GOTO 600  'IF TOO SMALL; CAUSES PROBLEM WITH LOG
FUNCTION
730 PI=PATH(K)*LOG(1/LZ)  'PATH LENGTH OF PHOTON IN IRON
740 Z=PI*COS(TH)+H+T  'UPDATE COORDINATES
750 X=X+PI*SIN(TH)*COS(PHI) 'POSITION FOR PHOTON THAT WENT THROUGH
GREASE
760 Y=Y+PI*SIN(TH)*SIN(PHI)
1000 ATOM=RND(1)'RANDOM NUMBER TO PICK TYPE OF ATOM HIT BY PHOTON IN
STEEL
1010 IF (ATOM>=0)*(ATOM<.02) THEN K=2:GOTO 600'HIT CARBON ATOM; DON'T
COUNT TOO LOW ENERGY
1020 IF (ATOM>=.02)*(ATOM<.028) THEN K=3:GOTO 1090'HIT A MANGANESE ATOM
1030 IF (ATOM>=.028)*(ATOM<.035) THEN K=4:GOTO 1090 'HIT A SILICON ATOM
1040 IF (ATOM>=.035)*(ATOM<.045) THEN K=5:GOTO 1090'HIT A CHROMIUM ATOM
1050 IF (ATOM>=.045)*(ATOM<.065) THEN K=6:GOTO 1090 'HIT A NICKEL ATOM
1060 IF (ATOM>=.065)*(ATOM<.067) THEN K=7:GOTO 1090 'HIT A MOLYBDENUM
ATOM
1070 IF (ATOM>=.067)*(ATOM<.087) THEN K=8:GOTO 1090'HIT A VANADIUM ATOM
1080 GOTO 600 'THESE ARE IRON INTERACTIONS; CAN'T EXCITE THE IRON Ka X-
RAYS
1090 TH=3.1415927#*RND(1) 'ISOTROPIC EMISSION OF Ka X-RAY
1100 IF TH<1.6 GOTO 600  'MUST BACKSCATTER TO HIT DETECTOR
1110 PHI=6.2831853#*RND(1)
1120 LZ=RND(1)
1130 IF LZ<.0000001 GOTO 1120
```

```
1140 PL=PATH(K)*LOG(1/LZ) 'PATH LENGTH IN IRON FOR Ka X-RAY OF Kth
ELEMENT
1150 Z=Z+PL*COS(TH)
1160 IF Z>H GOTO 600 'PHOTON DID NOT GET OUT OF IRON
1170 L=-Z/COS(TH)
1180 GOTO 490
1190 END
```