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AIRCRAFT ENGINE OIL ANALYSIS BY NEUTRON ACTIVATION TECHNIQUES.(U)
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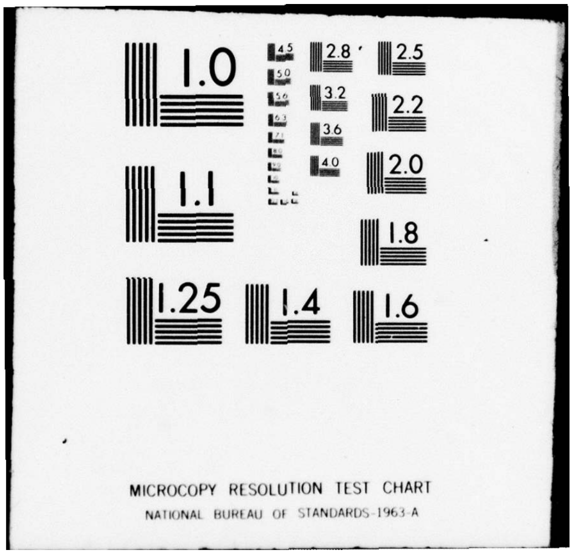
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FRANK J. SEILER RESEARCH LABORATORY

FJSRL TECHNICAL REPORT -78-0016
DECEMBER 1978

AIRCRAFT ENGINE OIL ANALYSIS BY NEUTRON ACTIVATION TECHNIQUES

THOMAS A. MENARD

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PROJECT 2303

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

FJSRL-TR-78-0016

This document was prepared by the Faculty Research Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F1-32, Aircraft Engine Oil Analysis by Neutron Activation Techniques. Captain Thomas A. Menard was the Project Scientist in charge of the work.

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This report has been reviewed by the Chief Scientist and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

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AIRCRAFT ENGINE OIL ANALYSIS BY NEUTRON ACTIVATION TECHNIQUES

By

Captain Thomas A. Menard

December 1978

Department of Physics
United States Air Force Academy, CO

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER ⑭ FJSRL-TR-78-0016

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) ⑥ Aircraft Engine Oil Analysis by Neutron Activation Techniques.

5. TYPE OF REPORT & PERIOD COVERED ⑨ Summary Rep~~or~~t.,

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) ⑩ Thomas A. Menard, ~~Captain, USAF~~

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Department of Physics
DFP
USAF Academy, Colorado 80840

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

PE61102F
⑯ 2303-F1-32 ⑰ F1

11. CONTROLLING OFFICE NAME AND ADDRESS

Frank J. Seiler Research Laboratory
AFSC
USAF Academy, Colorado 80840

12. ~~REPORT DATE~~ ⑪ Dec~~ember~~ 1978

~~13. NUMBER OF PAGES~~

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) ⑫ 60 p.

15. SECURITY CLASS. (of this report) Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Neutron Activation
Aircraft Engine Oils
Wear Metal Analysis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

→ At the present time all three military services use the Spectrometric Oil Analysis Program (SOAP) for the routine analysis of engine oil samples. The purpose of this program is to continually monitor the amounts of wear metal contaminants found in engine oil as an indicator of engine wear and possible engine failure. Use of such a program results in large savings by extending the time between oil changes and, more importantly, by indicating when engines should be taken out of service for preventive maintenance. The current →

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program uses either atomic emission or atomic absorption for the analysis. The problems associated with the current methods are twofold. First, the instruments require a laboratory environment and thus can not necessarily be located near the equipment being sampled. In some cases, the results from a particular sample may take days to return to the user. Under these conditions an engine might be operated to failure before notification ~~can be received~~ of a failed oil sample. Secondly, the instruments are fairly expensive. This report summarizes the research which was done using Californium-252 as a neutron source in order to determine the feasibility of using such a source for analyzing USAF aircraft engine oil samples by neutron activation techniques. The desired solution would be an inexpensive facility which could be located on every flightline and provide the individual concentration of 13 different elements in each oil sample prior to the aircraft being flown again.

PREFACE

The author would like to thank all of the people who participated in this project, especially Major Anthony K. Hyder who first suggested the project and who designed the californium container, and Captain Virgil H. Webb who conducted the feasibility study. All of the work described in this report was sponsored by the Frank J. Seiler Research Laboratory (Air Force Systems Command). Special thanks go to the Savannah River Operations Office (Energy Research and Development Administration) for their cooperation in providing the californium sources on loan to the U.S. Air Force Academy for this study.

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INTRODUCTION

At the present time all three military services use the Spectrometric Oil Analysis Program (SOAP) for the routine analysis of engine oil samples. The purpose of this program is to continually monitor the amounts of wear metal contaminants found in engine oil as an indicator of engine wear and possible engine failure. Use of such a program results in large savings by extending the time between oil changes and, more importantly, by indicating when engines should be taken out of service for preventive maintenance.

The current program uses either atomic emission or atomic absorption for the analysis. The problems associated with the current methods are two-fold. First, the instruments require a laboratory environment and thus can not necessarily be located near the equipment being sampled. In some cases, the results from a particular sample may take days to return to the user. Under these conditions an engine might be operated to failure before notification can be received of a failed oil sample. Secondly, the instruments are fairly expensive.

This report summarizes the research which was done using californium-252 as a neutron source in order to determine the feasibility of using such a source for analyzing USAF aircraft engine oil samples by neutron activation techniques. The desired solution would be an inexpensive facility which could be located on every flightline and provide the individual concentration of 13 different elements in each oil sample prior to the aircraft being flown again.

CURRENT USAF PROGRAM

The U.S. Air Force currently runs a program of sampling for all aircraft engines and some ground equipment at 10 hour or less intervals. Each sample is checked for those elements of interest, the amounts of which depend upon the wear condition of the engine, time since last oil change, and the amount of impurities present due to dust, dirt, and cleaning agents.

Not only is the absolute amount of interest, but records are kept in order to show trends for each engine. The limits which have been placed upon the oil samples give a direct indication of the sensitivities which are desirable for a neutron activation technique.

The elements of interest are listed below with the primary wearmetals underlined.

Na, <u>Mg</u>, <u>Al</u>, Si, Ti, <u>Cr</u>, <u>Fe</u>, Ni, <u>Cu</u>, <u>Ag</u>, Sn, Mo, Pb

The presence of any single element or combination of elements not only indicates that a problem may exist but also where the problem may be. Table 1 shows the sample limits for the six major elements for the T56-7/9/15 engine used on the C-130. (1:2-56).

The following maintenance requirements are mandatory for the appropriate oil sample results:

1. If any wearmetal (except Al) reaches a "T" code value, then an engine teardown inspection must be accomplished.

2. If aluminum reaches a "T" code value, then a gearbox teardown inspection is necessary.

3. If iron increased by 5 PPM or more in any ten hours of operating, then an engine teardown inspection is necessary.

TABLE 1. SOAP Limits for the T56-7/9/15 Engine and A/E35U-3 Spectrometer

	Fe	Ag	Al	Cr	Cu	Mg
A	0-38	0-6	0-8	0-6	0-11	0-35
D	39-40	7	9	7	12	36
K	41-44	8-9	10-11	8-9	13-14	37-39
T	45+	10+	12+	10+	15+	40+

CODES:

A - Continue routine sampling.

D - Do not change oil, submit redtagged sample after each flight.

K - Submit redtagged sample as soon as possible. Suspect possible discrepancy due to increasing wearmetal trends, recommend maintenance inspection. If aircraft has flown since last sample, ground unit until results of this sample are known.

T - Ground unit, examine for suspected discrepancy. Advise laboratory of findings.

The narrative below (1:2-57) and Figure 1 (1:3-39) show how combinations of elements indicate the location of the engine parts with excess wear.

T56-7/9/15 (C-130)

Caution must be exercised when evaluating this system since the power section and reduction gearbox are lubricated with the same oil supply. Major problem area detected by SOAP is the reduction gearbox lube pump.

High Cu by itself usually results from newly depot-overhauled pumps due to flaking or wearing of bronze spray coating in pump cavities. Reduction gearbox lube pump failures are usually indicated when Fe, Cu and Mg increase in combination or at near the same rate. When Fe increase is more than Cu increase, accompanied by moderate increase in Mg and small amount of Cr and Ag, discrepancy is usually with the reduction gearbox pinion bearing. When increase in Fe and Mg occur, accompanied by moderate increase in Cu with small amount of Cr and Ag, the discrepancy is usually in one of three components: power section side gear bearing, accessory case bearing, or reduction gearbox oil pump drive gear bearing. A significant increase in Fe in absence of other wearmetals may indicate discrepancy in reduction gear train and/or rear turbine scavenge pump assembly. Bronze metalizing repair procedure on oil pumps is discontinued and will reduce Cu content.

<u>Fe</u>	Main bearing balls/rollers and races Reduction gear assembly gears Accessory drive gears, shafts and splines
<u>Fe Cu</u> & Si	Accessory diffuser scavenge pump
<u>Fe Cu</u> & Si Mg	Accessory turbine scavenge pump
<u>Fe Mg</u>	Accessory drive housing
<u>Mg</u>	Reduction gear assembly housing
<u>Cu Mg</u>	Reduction gear assembly oil pump
<u>Cu Ag</u> & Fe Si	Main bearing cages Reduction gear assembly bearings

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From this example, it can be seen that analytical sensitivities on the order of 5 PPM or less are necessary in order to implement the program as

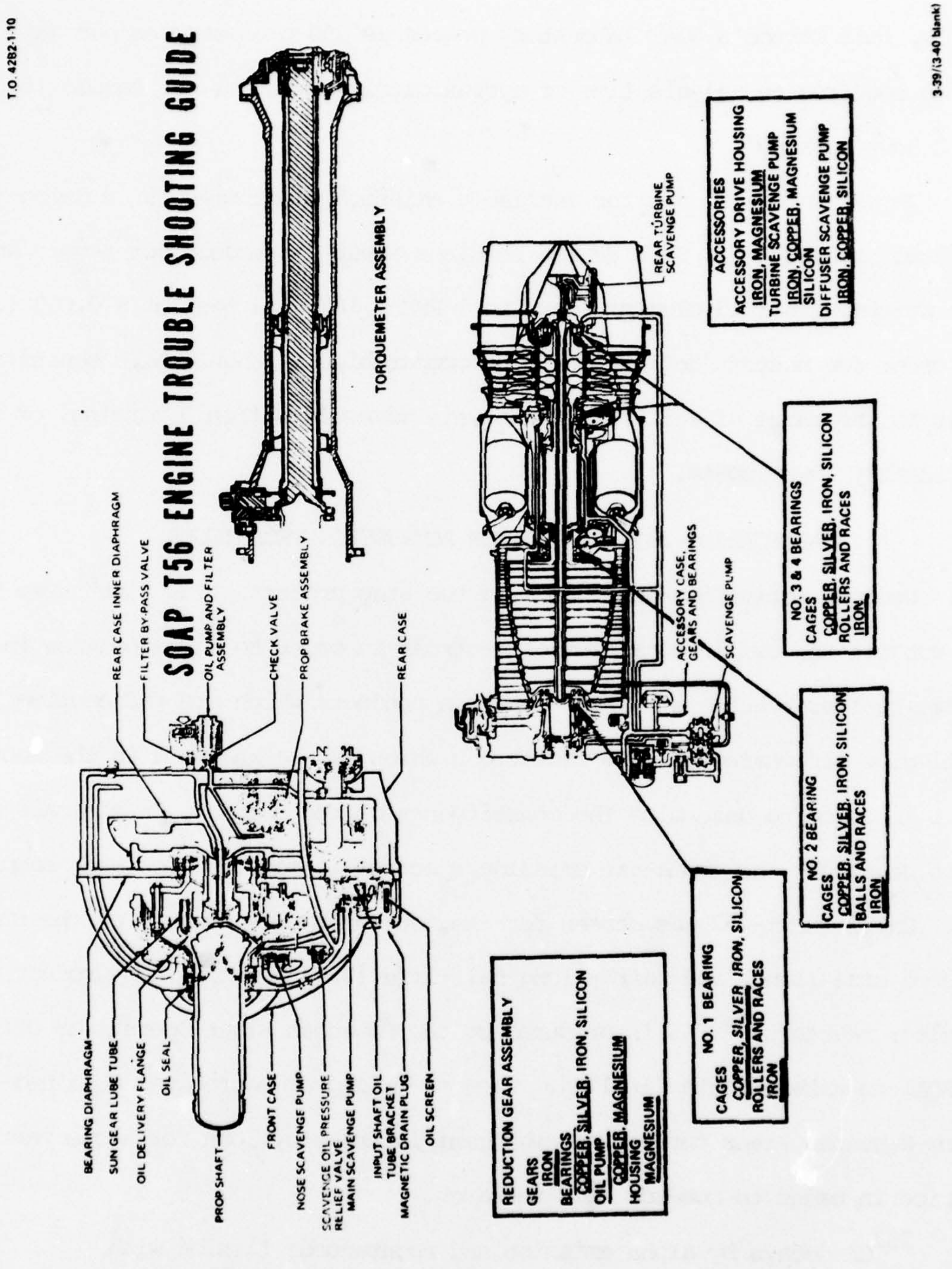

Figure 1. SOAP T56 Trouble Shooting Guide -- Shows the engine cross section and the elements associated with the major points of wear. (1:3-59)

it exists. In addition to the sensitivity requirements, there is a time requirement since some bases generate large numbers of samples. For example, Fort Carson's SOAP laboratory processes 200-plus samples per day which requires an anlysis time of approximately 3 minutes per sample (for a 12 hour workday).

The state of the art for available emission spectrometers is demonstrated by A/E35U-3. This device requires about 45 seconds per sample and can determine all 13 elements down to 1 PPM ± 10% at a cost of $70,000 (3). In order for neutron activation to be comparable, it should have senitivities in the range of 1-5 PPM and analysis times less than 3 minutes, or significantly lower costs.

CALIFORNIUM-252 AND NEUTRON ACTIVATION TECHNIQUES

Neutron activation analysis is a two step process. The first step is to subject the sample to a flux of neutrons in order to cause neutron induced nuclear reactions. Those reaction products which are radioactive will give off characteristic radiations which can be analyzed in the second step in order to determine the constituents of the sample. In the case of this research the gamma-ray emission spectrum is measured for each sample.

Californium-252 was chosen for the neutron source because of the small source size (1 mg) and fairly long half-life (2.63 years). A byproduct of nuclear reactors, ^{252}Cf is produced by the Savannah River Operations Office (ERDA) in Aiken, South Carolina. The one milligram source was obtained from Savannah River through a government interagency loan for a one year period in order to conduct this research.

^{252}CF decays by alpha emission and spontaneous fission with an effective half-life of 2.65 years. The neutron yield per milligrams is 2.34×10^9 neutrons per second. Figure 2 shows a diagram of the neutron fission spectrum from one milligram of ^{252}Cf.

The one milligram of ^{252}Cf was divided into four source capsules (Type SR-CF-100). The sources were stored in the lead container shown in Figure 3. The four sources were arranged at 90° intervals around the sample irradiation point at approximately 3/4" from the sample center. Previous work done by Eastman Kodak (4:41) indicated that this source to sample distance would provide essentially the fission spectrum at the sample position. Between the sources and sample there was 3/8" of "Lucite". The samples were lowered into position through a plexiglass tube running up to the surface of the water. Samples were sealed in disposible 5 ml polystyrene culture tubes. The source shielding container, shown in Figure 3, consisted of 3" of water, 6" of paraffin, 9" of borated paraffin, and 31" of concrete blocks in the horizontal direction. The entire container rested in the corner of a room shielded by 16" of reinforced concrete.

The thermal neutron flux at the position of the sample was measured using gold and indium 1/2" diameter foils. The results were:

$$\text{Flux} = 2.2 \times 10^6 \ \frac{\text{neutrons}}{\text{cm}^2\text{-sec}} \ \text{with a cadmium ratio of } 4.5$$

The neutrons provided by this facility were used to induce a variety of nuclear reactions. Whenever a neutron is absorbed by a nucleus causing a nuclear reaction, it results in another particle being emitted. The shorthand notation for this is (n,γ) in the case of gamma-ray emission. Other possibilities are (n,p), (n,α), $(n,2n)$ and others. The (n,γ) reaction is exoergic and thus can take place with thermal or low energy neutrons.

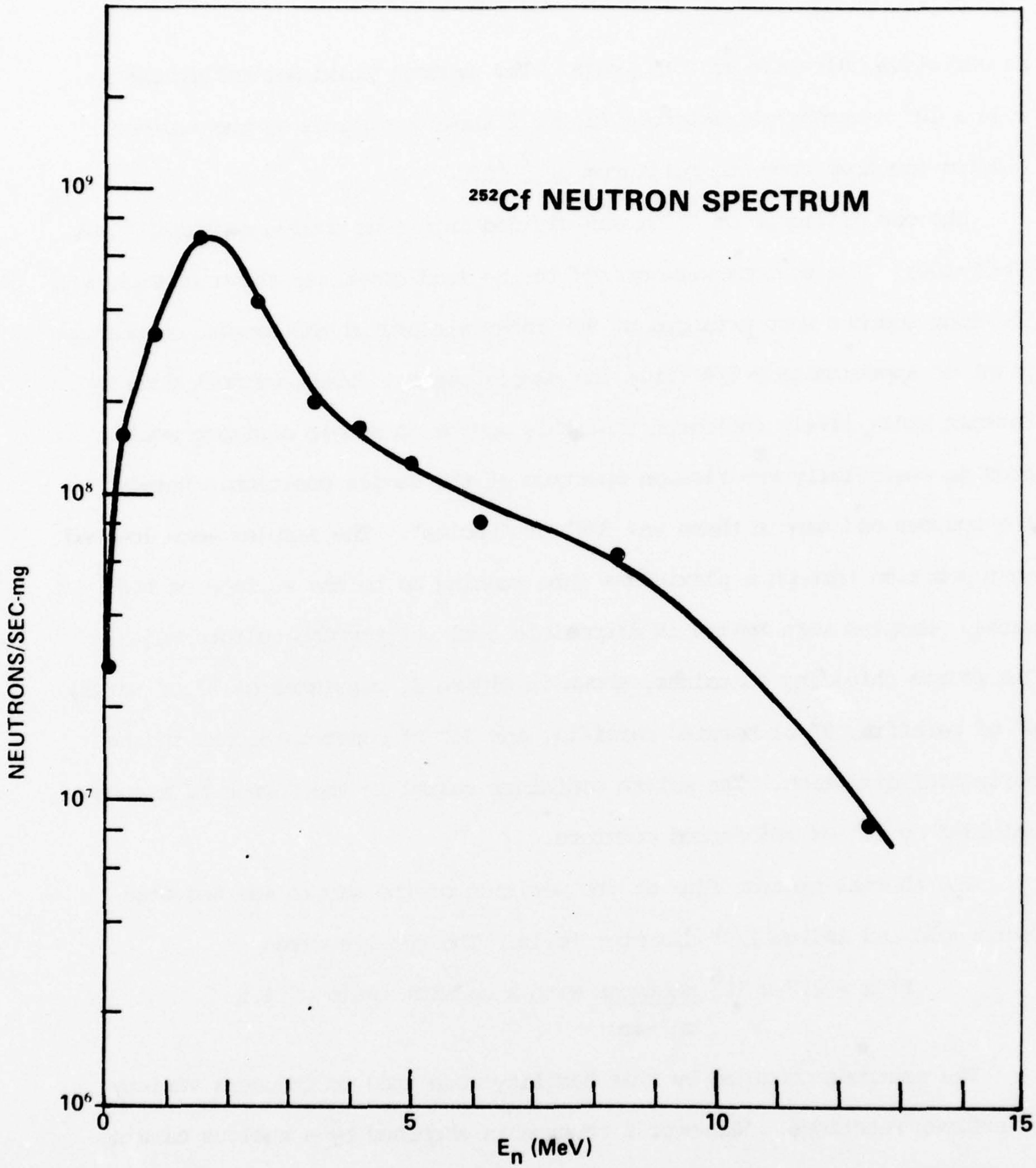

FIGURE 2. NEUTRON SPECTRUM FROM SPONTANEOUS FISSION FOR 1 mg OF ^{252}Cf.

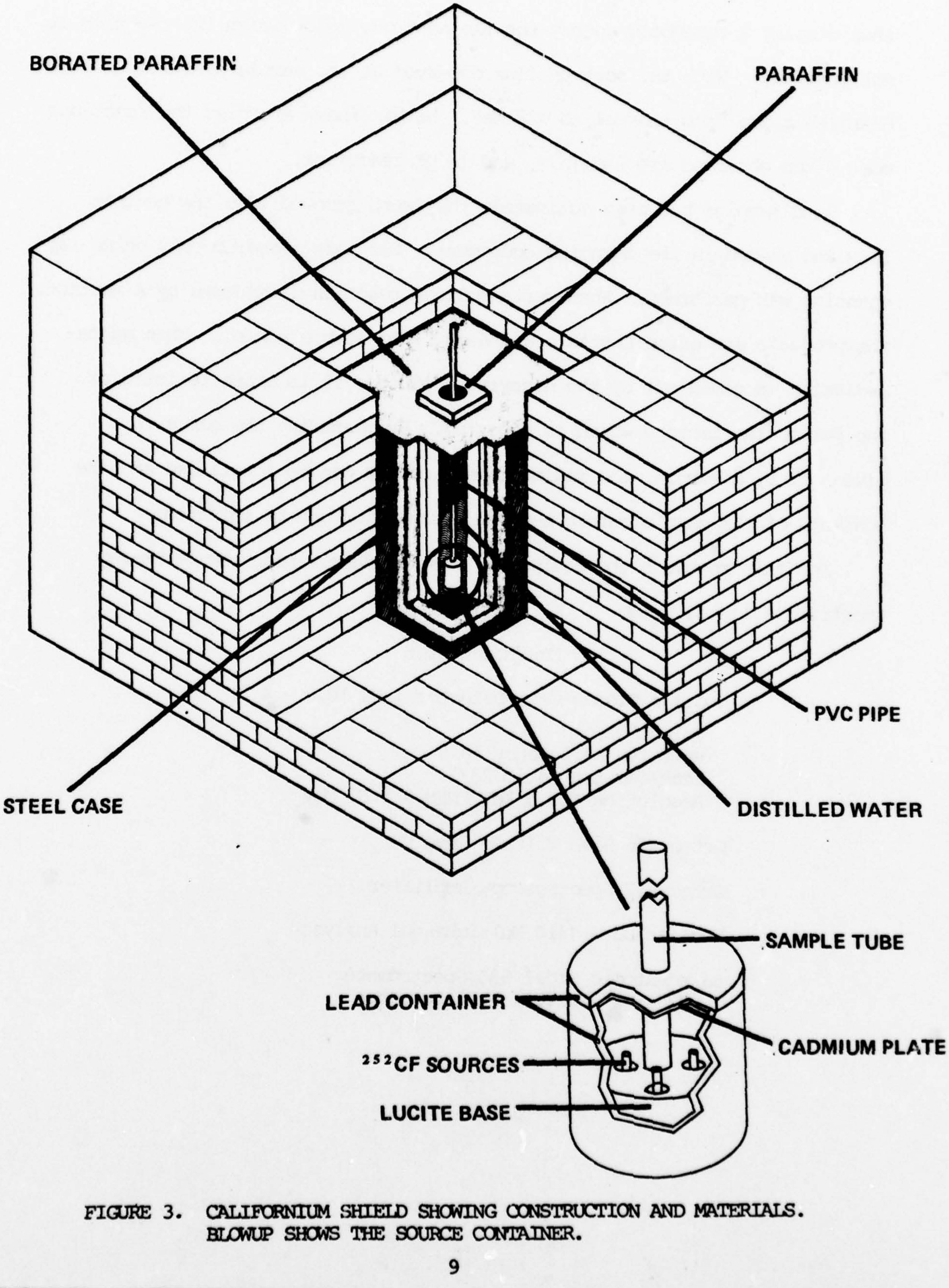

FIGURE 3. CALIFORNIUM SHIELD SHOWING CONSTRUCTION AND MATERIALS. BLOWUP SHOWS THE SOURCE CONTAINER.

(Thermal refers to the fact that the neutron is in kinetic equilibrium with its surroundings). The other reactions, however, are usually endoergic and thus display a threshold energy for the neutron, below which the reaction is not possible. With the neutron flux observed at the sample position, neutron energies range from thermal to ∿ 8 MeV. Within these energies the reactions most often observed are the (n,γ) and (n,p) reactions.

Once samples had been activated, they were removed from the neutron flux and placed in the counting equipment. For this research only gamma-ray counting was performed. Whenever a nuclear reaction is induced by a neutron, the products are often unstable and decay into stable nuclei. When gamma-radiation is given off by the decaying products, it is characteristic of the particular isotope which is decaying. By measuring the gamma-rays given off by a sample, the radioactive isotopes can be identified and the contents of the sample before neutron irradiation can be inferred.

For this research the equipment used for determining the gamma-ray spectrum is listed below.

Equipment List

Nuclear Diodes GeLi Detector (LGC 10.0 - 4.0)
  Volume 62 cm^3
  Relative Efficiency 10.6%
  Peak/Compton Ratio 23/1
  Resolution ∿ 3.5 KeV FWHM @ 1.33 MeV

Ortec 456 High Voltage Supply

Ortec 452 Spectroscopy Amplifier

Nuclear Data 4410 Multichannel Analyzer

Baird-Atomic Model 530 Spectrometer
  w/2" x 2" NaI(Tl) Well Detector

The data from the gamma dectectors were stored in 1024 channels of memory and then permanently stored on digital cassettes. Data reduction was accomplished by first performing a five point least squares smoothing routine to compensate for poor statistics. The data was then searched for gamma-ray peaks and when found, a least squares Gaussian fit was performed. The output indicated the energy of each gamma-ray peak and the total counts under each peak.

NEUTRON ACTIVATION RESULTS

The experimental procedure used in this research was the preparation of calibration standards for each of the 13 elements. These standard samples were activated and counted using the GeLi detector in order to determine the counts/milligram for particular gamma-ray peaks. From these results, a table of overall sensitivities was determined which shows the minimum amount of each element which can be detected by neutron activation techniques.

A. Individual Elements

Each sample was prepared in various concentrations in solution form. Solutions were used in order to keep the sample element evenly distributed within the sample tube during irradiation and counting. From these samples, calibration curves were drawn showing counts vs milligrams for each element for the most prominent gamma-ray peak observed. In most cases the samples were in aqueous solutions. Previous work (5:31) has shown that distilled water causes very little flux depression and thus yields accurate calibration curves. In addition, water has a similar effect on the flux as pure oils so that these calibrations were applicable to later oil sample activations. As long as the compounds used in the sample preparation did not contain matrix elements with high neutron absorption properties, the calibrations were accurate.

A second technique is also shown in the following sections. Samples were activated and counted in a NaI(Tl) well detector and the gross counts for all gamma-rays between 100 KeV and 2.5 MeV were used to derive calibration curves. The purpose here was to determine if the gamma activity of a sample could be used as a direct indicator of wearmetal content.

For each element below, the sample preparation technique, observed nuclear reactions, and calibrations results are given. The irradiation/wait/counting times were 60/1/60 minutes for the peak calibration method and 40/1/30 minutes for the gross gamma calibration method.

Sodium

The samples were prepared using $NaNO_2$ dissolved in distilled water. The observed reactions are shown in Table 2 along with the observed gamma-rays (*indicates the most prominent gamma) and the product half-life.

TABLE 2. Observed Reaction with Sodium

Reaction	E_γ (KeV)	$T_{1/2}$
$^{23}Na(n,\gamma)^{24}Na$	1368*, 2754	15.02 hrs

Figure A1 shows the calibration curve for the 1368 KeV Gamma peak (114 ± 2 counts/mg) and Figure B1 shows the gross gamma calibration curve (1470 ± 20 counts/mg).

Magnesium

The samples were prepared by dissolving magnesium powder in nitric acid.

TABLE 3. Observed Reactions with Magnesium

Reaction	E_γ (KeV)	$T_{½}$
$^{26}\mathrm{Mg}(n,\gamma)^{27}\mathrm{Mg}$	824*, 1014	9.45 min
$^{24}\mathrm{Mg}(n,p)^{24}\mathrm{Na}$	1368*, 2754	15.02 hrs

Figure A2 shows the 1368 KeV curve (0.83 ± .06 counts/mg) and Figure A3 the 842 KeV curve (4.8 ± .1 counts/mg). Figure B2 shows the gross gamma curve (109 ± 1 counts/mg). Note that the presence of magnesium produces ^{24}Na so that if magnesium and sodium occur together in the same sample, the analysis is complicated by the common 1368 KeV gamma.

Aluminum

The samples were prepared from $Al(NO_3)_3 \cdot 9H_2O$ in distilled water.

TABLE 4. Observed Reactions with Aluminum

Reaction	E_γ (KeV)	$T_{½}$
$^{27}\mathrm{Al}(n,\gamma)^{28}\mathrm{Al}$	1780*	2.24 min
$^{27}\mathrm{Al}(n,p)^{27}\mathrm{Mg}$	842*, 1014	9.45 min

Figure A4 shows the 1780 KeV curve (33.9 ± .7 counts/mg) and Figure A5 the 842 KeV curve (14 ± 1 counts/mg). Figure B3 shows the gross gamma counting curve (1670 ± counts/mg). Note that when aluminum and magnesium occur together the analysis is complicated by the common 842 KeV gamma.

Silicon

The samples used for the peak search method were prepared by dissolving

$Na_2SiO_3 \cdot 9H_2O$ in distilled water. The presence of the sodium does cause some flux depression to an unknown degree. The gross gamma count samples were prepared by suspending SiS in a mixture of glycerol and distilled water. The effect of the sulfer was accounted for.

TABLE 5. Observed Reaction with Silicon

Reaction	E_γ (KeV)	T½
$^{28}Si(n,p)^{28}Al$	1780*	2.24 min

Figure A6 shows the 1780 KeV curve (2.15 ± .09 counts/mg) and Figure B4 the gross gamma curve (388 ± 3 counts/mg) for silicon. Note that the only gamma-ray observed is the same as for aluminum. When silicon and aluminum occur together the analysis is complicated by the common 1780 KeV gamma.

Titanium

The samples used for the peak search method were prepared by dissolving $TiCl_3$ in ethyl alcohol. The chlorine produced an unknown amount of flux depression. The gross gamma samples were prepared by suspending TiS_2 in glycerol and alcohol.

TABLE 6. Observed Reactions with Titanium

Reaction	E_γ (KeV)	T½
$^{50}Ti(n,\gamma)^{51}Ti$	320*, 608, 929	5.76 min
$^{48}Ti(n,p)^{48}Sc$	983, 1037, 936	43.7 hrs

Figure A7 shows the 320 KeV curve (10.8 ± .4 counts/mg) and Figure B5 shows the gross gamma curve (304 ± 2 counts/mg).

Chromium

Samples were prepared using $Cr(NO_3)_3 \cdot 9H_2O$ dissolved in distilled water.

TABLE 7. Observed Reactions with Chromium

Reaction	E_γ (KeV)	T½
$^{50}Cr(n,\gamma)^{51}Cr$	320*	27.71 days
$^{52}Cr(n,p)^{52}V$	1434	3.755 min

Figure A8 shows the 320 KeV curve (0.824 ± .008 counts/mg) and Figure B6 shows the gross gamma curve (43 ± 1 counts/mg).

Iron

Samples were prepared using $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in distilled water.

TABLE 8. Observed Reaction with Iron

Reaction	E_γ(KeV)	T½
$^{56}Fe(n,p)^{56}Mn$	847*, 1811, 2113 2522, 2657, 2962	2.582 hrs

Figure A9 shows the 847 KeV curve (3.4 ± .1 counts/mg) and Figure B7 shows the gross gamma curve (34 ± 1 counts/mg).

Nickel

Samples were prepared by dissolving nickel powder in nitric acid.

TABLE 9. Observed Reactions with Nickel

Reaction	E_γ (KeV)	$T\frac{1}{2}$
$^{64}Ni(n,\gamma)^{65}Ni$	367, 1115 1480*, 1725	2.52 hrs
$^{58}Ni(n,p)^{58}Co$	511, 810	71.3 days

Figure A10 shows the 1480 KeV curve (1.28 ± 02 counts/mg) and Figure B8 shows the gross gamma curve (39.2 ± .4 counts/mg). In addition a curve was determined for the 511 KeV gamma (0.25 ± .1 counts/mg) so that a correction can be made for nickel when it occurs in a sample with copper.

Copper

Samples were prepared using $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in distilled water.

TABLE 10. Observed Reactions with Copper

Reaction	E_γ (KeV)	$T\frac{1}{2}$
$^{63}Cu(n,\gamma)^{64}Cu$	511*, 1346	12.74 hrs
$^{65}Cu(n,\gamma)^{66}Cu$	1039	5.10 min

Figure A11 shows the 511 KeV curve (384 ± 8 counts/mg) and Figure B9 shows the gross gamma curve (3370 ± 30 counts/mg).

Silver

Samples were prepared using $AgNO_3$ dissolved in distilled water.

TABLE 11. Observed Reactions with Silver

Reaction	E_γ (KeV)	$T_{1/2}$
$^{107}Ag(n,\gamma)^{108}Ag$	434, 511, 616, 633*	2.41 min
$^{109}Ag(n,\gamma)^{110}Ag$	658, 818	24.6 sec
$^{109}Ag(n,\gamma)^{110m}Ag$	658, 885, 937	252 days

Figure A12 shows the 633 KeV curve (39 ± 1 counts/mg) and Figure B10 shows the gross gamma curve (6000 ± 20 counts/mg). In addition a calibration was determined for the 511 KeV gamma as a correction for when silver and copper occur in the same sample.

Tin

Samples were prepared by dissolving tin powder in sulfuric acid.

TABLE 12. Observed Reactions with Tin

Reaction	E_γ (KeV)	$T_{1/2}$
$^{122}Sn(n,\gamma)^{123m}Sn$	160*	40.0 min
$^{124}Sn(n,\gamma)^{125m}Sn$	332, 589, 643, 1403	9.2 min
$^{112}Sn(n,\gamma)^{113}Sn$	392	115 day

Figure A13 shows the 160 KeV curve (37 ± 1 counts/mg) and Figure B11 shows the gross gamma curve (468 ± 5 counts/mg). The 332 KeV gamma can also be used and yields similar results to the 160 KeV gamma (34 ± 1 counts/mg).

Molybdenum

Samples were prepared using MoO_3 dissolved in NH_4OH.

TABLE 13. Observed Reactions with Molybdenum

Reaction	E (KeV)	$T_{1/2}$
$^{98}Mo(n,\gamma)^{99}Mo$	141, 181, 740, 778, 881	66.02 hrs
$^{100}Mo(n,\gamma)^{101}Mo$	128, 192, 307* 545, 591, 1012	14.6 min

NOTE: 23 other gamma peaks were identified as coming from ^{101}Mo but not listed. Figure A14 shows the 307 KeV curve (161 ± 5 counts/mg) and Figure B12 shows the gross gamma curve (1880 ± 20 counts/mg). In addition a calibration curve was computed for the 510 KeV gamma from ^{101}Mo in order to correct for the 511 KeV count when copper and molybdenum are present in the same sample.

Lead

Samples were prepared using $Pb(NO_3)_2$ dissolved in distilled water.

TABLE 14. Observed Reaction with Lead

Reaction	E (KeV)	$T_{1/2}$
$^{204}Pb(n,n')^{204m}Pb$	373*, 899, 912	66.9 min

Figure A15 shows the 373 KeV curve (0.69 ± .04 counts/mg) and Figure B13 shows the gross gamma curve (5.3 ± .2 counts/mg).

B. Overall Results

When evaluating neutron activation techniques for the 13 elements of interest, the first problem which arises is the interference which has already been noted between certain elements. Listed below are those elements which have common or very closely spaced gamma-ray peaks.

sodium - magnesium	1368 KeV
magnesium - aluminum	842 KeV
aluminum - silicon	1780 KeV
titanium - chromium	320 KeV
copper - silver - tin - nickel - molybdenum - background	511 KeV

If the elements sodium, magnesium, aluminum, and silicon are present in the same sample, it is impossible to determine the quantity of each without performing a separate activation with entirely thermal neutrons thus eliminating the (n,p) reactions.

The elements titanium and chromium have major gamma-ray peaks which are less than 1 KeV apart and cannot be resolved. These two elements can be determined uniquely by again activating with thermal neutrons thus eliminating the chromium peak or by using chromium's less abundant 1434 KeV gamma peak which halves the sensitivity for chromium.

The analysis of copper is complicated by the fact that silver, tin, nickel and molybdenum result in 511 KeV gammas or peaks which are very close to that. In addition a natural background peak always occurs at 511 KeV. All of these effects must be subtracted in order to arrive at an accurate value for copper.

The interference effects that have been noted above are not difficult to overcome, but in order to arrive at an accurate determination of all 13 elements together, additional chemical or neutron activation techniques will be needed. The following section presents the results of the peak analysis method with the above interferences neglected.

Peak Search Analysis

Table 15 shows the detection limits in parts per million by weight for the 13 elements of interest using the GeLi detector, multichannel analyzer and peak search/fit routines. All data has been normalized to 60 minute irradiation/1 minute wait/60 minute count and to one milligram of ^{252}CF.

TABLE 15. Detection Limits* for 1 mg of ^{252}Cf

Element	Detection Limit (PPM)	Gamma (KeV)	$T_{1/2}$	Type Reaction
Sodium	71 ± 1	1369	15.0 hrs	thermal
Magnesium	1620 ± 40	842	9.45 min	thermal
Aluminum	237 ± 5	1780	2.24 min	thermal
Silicon	3580 ± 140	1780	2.24 min	fast
Titanium	695 ± 30	320	5.76 min	thermal
Chromium	9700 ± 90	320	27.7 days	fast
Iron	2280 ± 60	847	2.58 hrs	fast
Nickel	5990 ± 100	1480	2.52 hrs	thermal
Copper	21.3 ± .4	511	12.74 hrs	thermal
Silver	20.4 ± 5	633	2.41 min	thermal
Tin	206 ± 8	160	40.0 min	thermal
Molybdenum	47 ± 1	307	14.6 min	thermal
Lead	11500 ± 600	373	66.9 min	thermal

*Detectable Limit set at 100 counts above background
Sample size 10 grams
Irradiation 60 minutes/Wait 1 minute/Count 60 minutes.

The most important elements are underlined in Table 15. The half-life of the radioactive isotope being counted is the determining factor for optimum irradiation/counting times. For irradiation times of three times the isotope's half-life, 87% of the maximum activation is achieved. Four times the half-life yields 94%. It is desired to use minimum times between three and four half-lives for irradiation and counting if optimum utilization of the technique is to be achieved. For Table 15 only six of the 13 elements are being irradiated/counted for more than four half-lives. Thus for optimum performance of the neutron activation technique, times in excess of 60 minutes are desirable for more than half the elements. A good example is iron which should have irradiation/counting times of ∿ 10 hours. For sample process times of only several minutes the listed detection limits for all 13 elements would be seriously degraded.

Calibration oil samples were obtained from the SOAP laboratory at Peterson AFB and activated in order to show a verification of the detection capability. In contrast to Table 15 the sample tubes used in this research contained only 5 grams of oil so the detection limits are doubled. Figure 4 shows the gamma-ray spectrum obtained by a 300 PPM standard oil sample with the GeLi detector. Figure 5 shows a similar sample spectrum counted with a NaI(Tl) detector. The second spectrum was added as a contrast to show the capabilities of the NaI in relation to the GeLi detector. The NaI, which is less expensive and has a higher absolute efficiency, shows a much poorer resolution (∿ 100 KeV) than the GeLi detector. These two types of detectors will be discussed later in terms of costs vs detection limits. Table 16 shows the results of the activation shown in Figure 4.

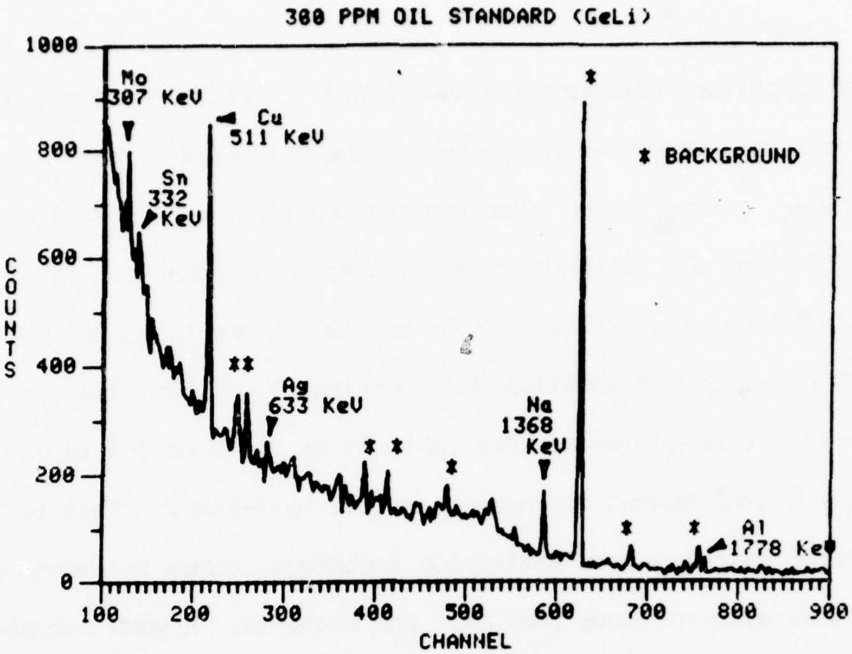

FIGURE 4. GAMMA SPECTRUM FOR A 300 PPM OIL STANDARD USING A GeLi DETECTOR.

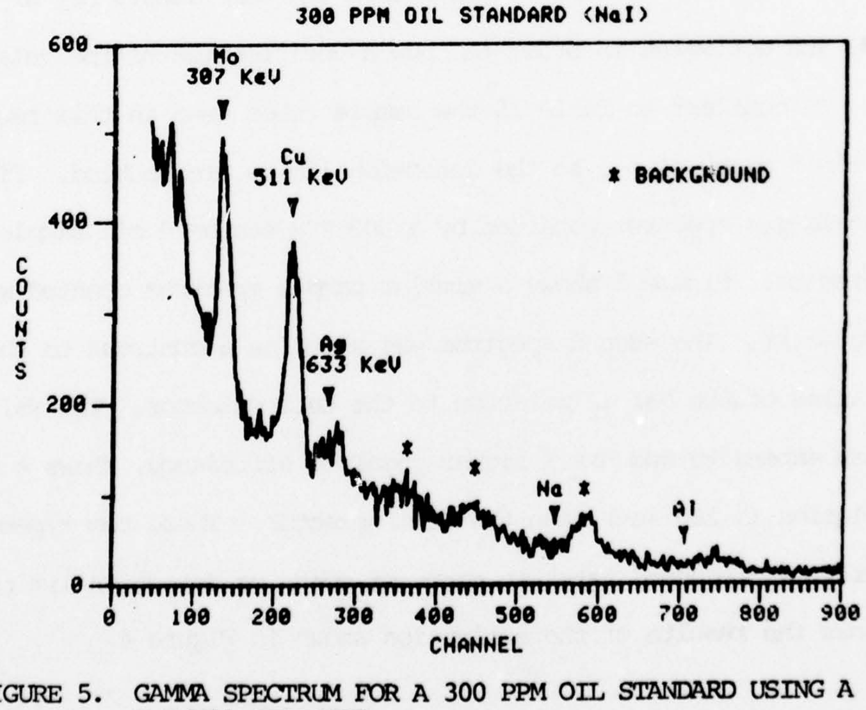

FIGURE 5. GAMMA SPECTRUM FOR A 300 PPM OIL STANDARD USING A NaI(Tl) DETECTOR.

TABLE 16. Elements Detected in a 5 Gram Standard Oil Sample

Element Detected	Computed Content (PPM)	Actual Content	Error (%)
Na	427 ± 82	300	42
Al	355 ± 69	300	18
Cu	321 ± 61	300	7
Mo	377 ± 95	300	26

Only four of the 13 elements were detected with sufficient reliability to allow calculations. The errors noted are a direct reflection of the poor statistics involved with these peaks. Better numerical analysis and thicker shielding around the detector would improve the errors and also improve the number of elements detected.

Gross Gamma Analysis

This method of analysis was performed in order to determine if total gamma counts could be used as a determination of oil contamination. The advantage of this method is the use of low cost detectors with high efficiencies and low cost electronics. In the case of this research, a 2" x 2" NaI(Tl) well detector was used with scalar counters. The upper and lower level discriminators were set so that gamma photons in the range of 100 KeV to 2.5 MeV were counted. The total absolute efficiency for this detector is ∿ 19% at 1.33 MeV (the total absolute efficiency of the GeLi detector used previously was ∿ 2% at 1.33 MeV). The disadvantage of this method is that it allows no determination of the quantity of each element, only an indication of the total activity of the activated samples. Table 16 shows the detection limits for all 13 elements in parts per million by weight.

All data has been normalized to 40 minutes irradiation/1 minute wait/30 minutes count and to one milligram of ^{252}Cf.

TABLE 17. Detection Limits* for 1 mg of ^{252}Cf

Element	Detection Limit (PPM)
Sodium	5.17 ± .06
Magnesium	69.5 ± .6
Aluminum	4.53 ± .04
Silicon	19.4 ± .1
Titanium	20.3 ± .1
Chromium	177 ± 5
Iron	225 ± 7
Nickel	193 ± 2
Copper	2.24 ± .02
Silver	1.256 ± .003
Tin	16.1 ± .2
Molybdenum	4.02 ± .04
Lead	1410 ± 50

*Detectable Limit Set at 100 counts above background
Sample Size 10 grams
Irradiation time 40 minutes
Wait time 1 minute
Count time 30 minutes

The most important elements are underlined above. The detection limits shown above are much improved over those listed in Table 15 for the peak analysis method. This method is a more sensitive technique for sensing the presence of metals but the lack of element determination is a definite disadvantage. An example is a sample containing aluminum and iron. If 100 counts above background results from the activation then this could either mean an aluminum content of 4.5 PPM, an acceptible level, or an iron content of 225 PPM, well above the level requiring a teardown inspection.

CONCLUSIONS

Peak Analysis Method

The results of the peak analysis method were not satisfactory for oil analysis in terms of the source and equipment used here. Listed below are the detection limits observed for the five major elements with a two hour sample analysis time.

magnesium	1620 PPM
aluminum	237 PPM
chromium	9700 PPM
iron	2280 PPM
copper	21 PPM
silver	20 PPM

Of the above, only copper and silver have sufficiently low detection limits to allow analysis of a normal oil sample. Even then, the uncertainty in the answer would probably approach 30-50%. The only way that these limits can be brought down is to increase the efficiency of the detector or increase the size of the neutron source.

Listed on the next page is a price list for a state of the art, self-contained analysis system. (Prices quoted are from current price lists of a leading manufacturer). This system would combine the highest efficiency GeLi detectors available with a computing system capable of performing the analysis.

Equipment	Price
2 each Hyperpure Germanium Detectors. 19% relative efficiency 2.3 KeV FWHM	$17,500 each
Shield and Stand 4" Pb graded	4,500 each
Amplifier	740
Warning Monitor	390
High Voltage Supply	475
Pulser	460
NIM Bin and Power Supply	560
	$42,125 Total
Computerized Disk-Based Multichannel Analyzer System	22,200
	$64,125 Total

If the neutron source were increased to 10 mg (the maximum which would probably be allowable in a flightline environment) then the cost list on the next page shows what could reasonably be expected. The cost listed for the ^{252}CF itself might be highly flexible due to the interagency relationship of ERDA and the military services

If the first delivery of californium was made up of three capsules of 4 mg each and each year thereafter one source capsule was removed and replaced by a 4 mg source capsule, then the constant level of the entire source would remain in the range of approximately 9 to 11 mg.

Equipment	Price	
Shield	$ 6,900	
Automatic Transfer System	14,000	
^{252}Cf (Initial)	120,000	
Encapsulation	8,178	
	$ 149,078	Total
^{252}Cf	40,000	
Encapsulation	2,726	
	$ 42,726	Total

This totals up to a cost of $191,203 initially and $42,726 per annum. The shield price quoted above is the cost of a shipping container large enough to hold 10 mg of ^{252}Cf, but it should be representative of the engineering costs of a permanent container. The automatic transfer system is a programable model with a rotating irradition table and 30′ of transfer tubes. The ^{252}Cf cost is the currently available cost of $10/µg (6:1). The encapsulation fee is the value quoted for the sources used in this research.

For the equipment quoted above, Table 18 shows the approximate detection limits for each element. Comparing this with Table 1 it is seen that at a cost of $191,000 this technique still cannot determine iron, chromium and magnesium at the levels required for teardown inspection.

Another alternative which can be looked at is the use of NaI(Tl) detectors because of their higher efficiency and lower cost. Figure 16 and Figure 15 show the spectrums which result from a NaI and GeLi detectors. This author did not have, nor was he able to locate any computer programs which are capable of resolving the gamma peaks resulting from 13 elements

TABLE 18. Detection Limits* for 10 mg of ^{252}Cf (GeLi)

ELEMENT	Detection Limit (PPM)
Sodium	2
Magnesium	47
Aluminum	7
Silicon	104
Titanium	20
Chromium	280
Iron	66
Nickel	170
Copper	.6
Silver	.6
Tin	6
Molybdenum	1
Lead	333

*Detectable Limit Set at 100 counts above background
10 gram sample
Irradiation 60 minutes
Wait 1 minute
Count 60 minutes

measured with a NaI detector. Assuming, however, that this can be done, the list below shows the appropriate costs.

Equipment	Cost
3" x 3" NaI(Tl) Well Detector	$ 1,240
4" Lead Shielding and Stand	4,500
Electronics	2,200
Multichannel Analyzer	6,610
Total	$14,550

The multichannel system quoted above is one which allows the data to be stored on disks and then fed into another computer for analysis. If this is again combined with the costs of the sources, the results are $163,700 initial costs ($120,000 of which is for the ^{252}Cf) and per annum costs of $42,700 ($40,000 of which is for the ^{252}Cf). Table 19 shows the approximate values for the new limits.

Of the five major elements only one (chromium) is still not detectable at sufficiently low levels. When these limits are compared to those provided by emission spectroscopy, however, the conclusion is drawn that at a cost of ∿ $44,000 initially (assuming the the ^{252}Cf were free), this method does not provide satisfactory results in terms of detection limits and sample analysis times in order to either supplement or take the place of the current oil analysis methods.

The gross gamma counting method which was described earlier is not a desirable option, either, because of the problem with greatly varying sensitivities among the elements. It would not be possible to set a gamma emission limit of any meaning when that limit might mean a small amount of silver is present or a large amount of iron.

TABLE 19. Detection Limits* for 10 mg of ^{252}Cf (NaI)

Element	Detection Limit (PPM)
Sodium	.4
Magnesium	9
Aluminum	1
Silicon	20
Titanium	4
Chromium	53
Iron	12
Nickel	32
Copper	.1
Silver	.1
Tin	1
Molybdenum	.2
Lead	63

*Same conditions as Table 18.

RECOMMENDATIONS

As already stated in the conclusions, the use of californium as a neutron source for activation analysis of oil samples is not economically feasible. Even with the most optimistic cost estimates, the cost would be at least $44,000 initial costs (zero cost for the ^{252}Cf) for a system with poor detection limits on the 13 elements and even poorer time constraints on the analysis. No method was apparent to the author which would allow this technique to be used on normal oil samples within the context of the present requirements for time and accuracy. Only two possible alternatives were apparent.

1. If the oil were filtered aboard the aircraft so that the metallic contamination were concentrated, then neutron activation might become more feasible. It would require a concentration of between 100 and 1000 times, however, and a modification to all aircraft involved.

2. If a single tracer isotope were added to the metallic engine parts undergoing wear, it could be kept track of and when appropriate, the oil sample could be sent on for more accurate analysis. If the isotope were chosen for high sensitivity, the detector, electronics and sources, could be of much lower cost making the concept more feasible. For instance, if vanadium were used as a tracer, the samples (10 grams each) could be irradiated for four minutes and counted for four minutes with a detection limit of approximately 1 PPM. The appropriate costs are listed below:

Equipment	Price
3" x 3" NaI(Tl) Well Detector	$1240
Amplifier Single-Channel	555

Equipment	Price	
Timer-Counter, printing	$ 775	
High Voltage Supply	575	
Pulser	460	
NIM Bin and Power Supply	560	
	$ 4165	Total
Shield	$ 1100	
^{252}Cf (Initial)	2400	
Encapsulation	8178	
	$11678	Total
^{252}CF (Annual)	800	
Encapsulation	2726	
	$ 3526	Total

Thus the total initial cost would be about $15,800, with a per annum cost of $3,526. In this case, the amount of ^{252}Cf is only about 200 μg and the precautions for its handling and storage are much simpler than with 10 mg. This alternative would require, however, a modification to the manufacturing process of aircraft engine parts with unknown costs.

The end conclusion which is drawn from this research is that neutron activation analysis of oil samples is not today an economically viable alternative to the atomic emission methods already in use.

APPENDIX A

Appendix A is the collection of calibration curves which resulted from the peak search analysis of the 13 elements of interest. In some cases more than one curve is shown per element. The extra curves are necessary in order to overcome the problem of interfering reactions among adjacent elements. Each curve is normalized to 60 minutes irradiation/1 minute wait/60 minutes count and 1 mg ^{252}CF. Data was collected using a GeLi detector, multi-channel analyzer system and peak search/fit routines.

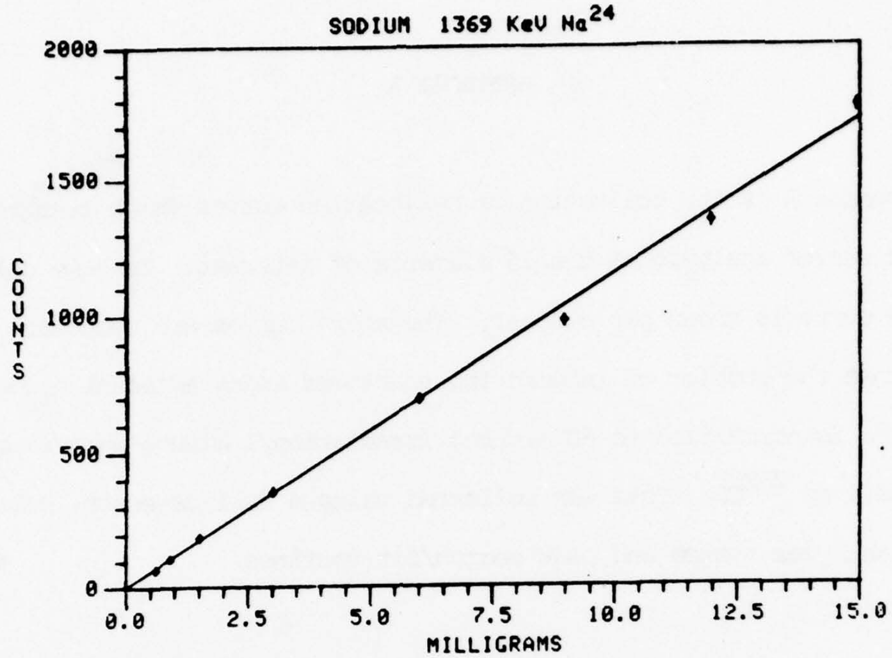

FIGURE A1. 1369 KeV CALIBRATION CURVE FOR SODIUM.

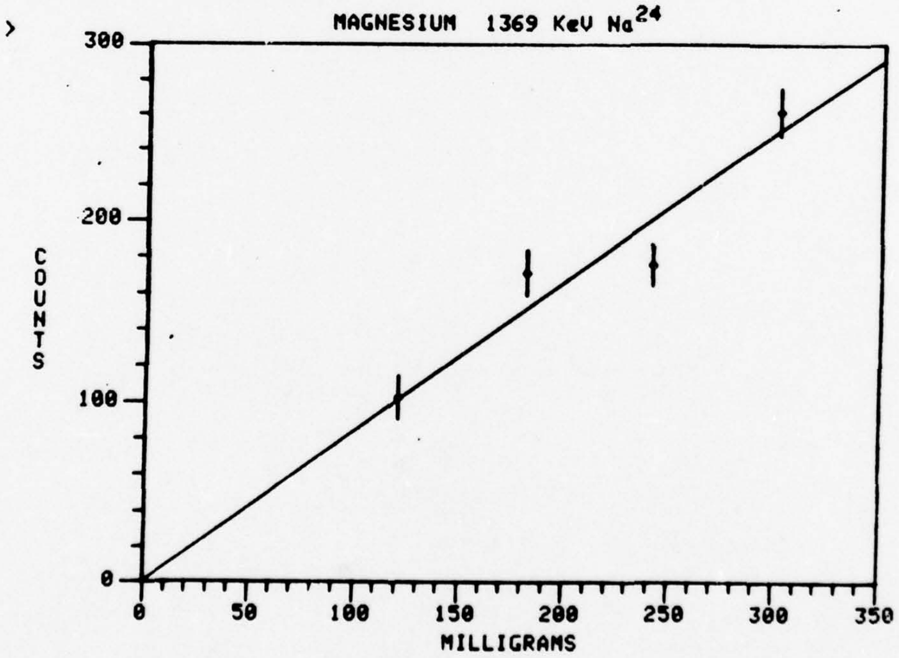

FIGURE A2. 1369 KeV CALIBRATION CURVE FOR MAGNESIUM.

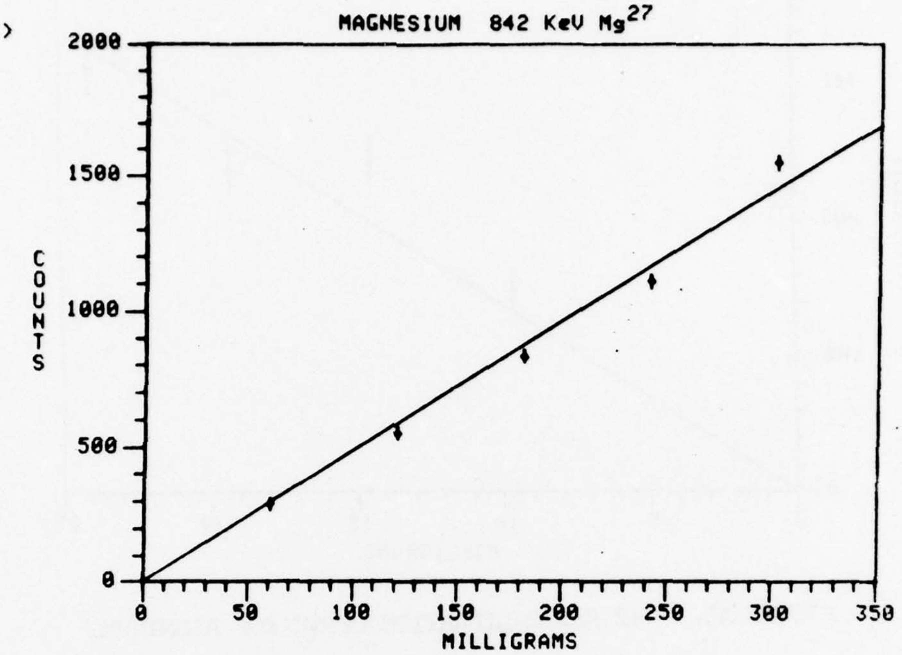

FIGURE A3. 842 KeV CALIBRATION CURVE FOR MAGNESIUM.

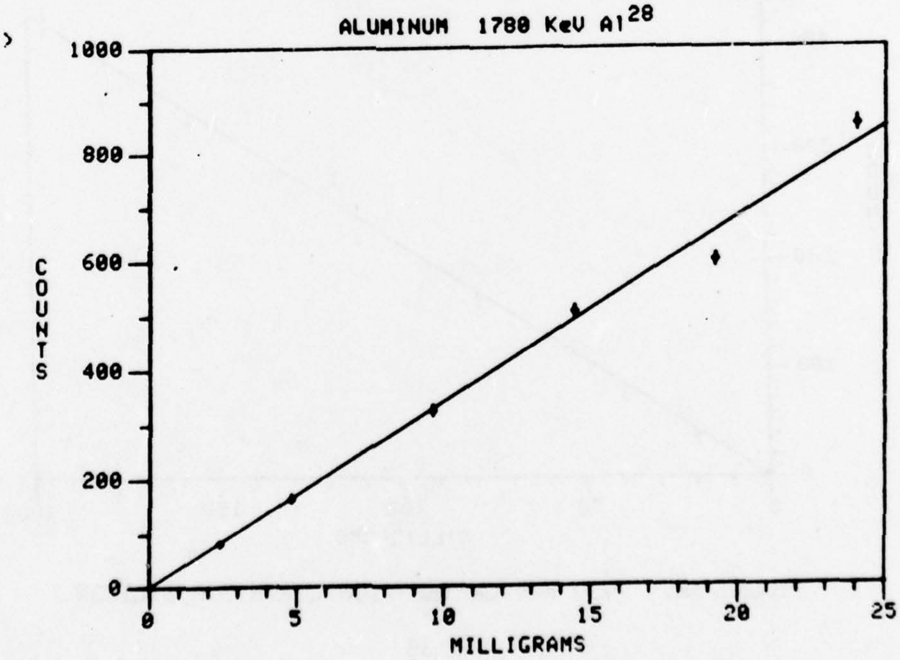

FIGURE A4. 1780 KeV CALIBRATION CURVE FOR ALUMINUM.

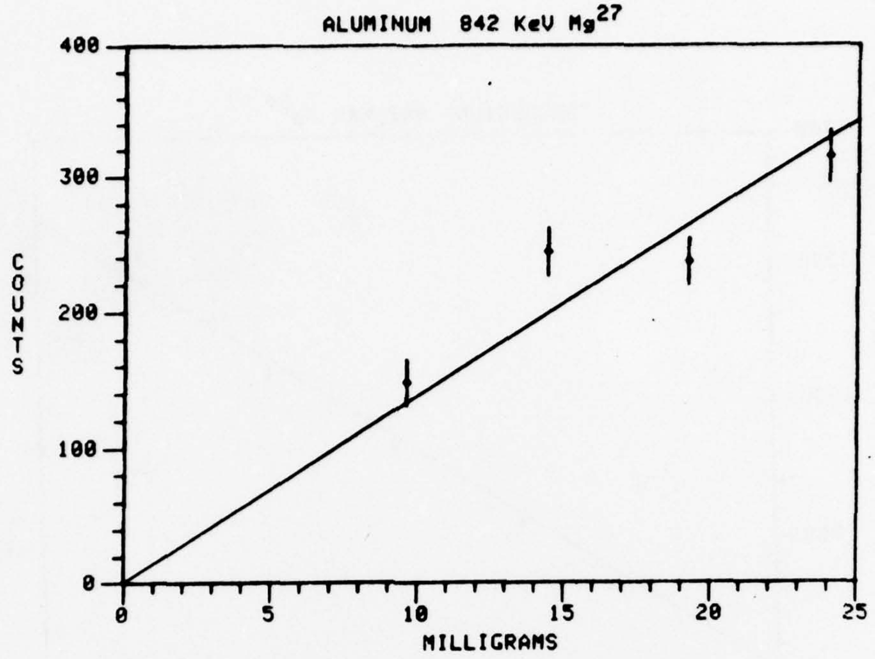

FIGURE A5. 842 KeV CALIBRATION CURVE FOR ALUMINUM.

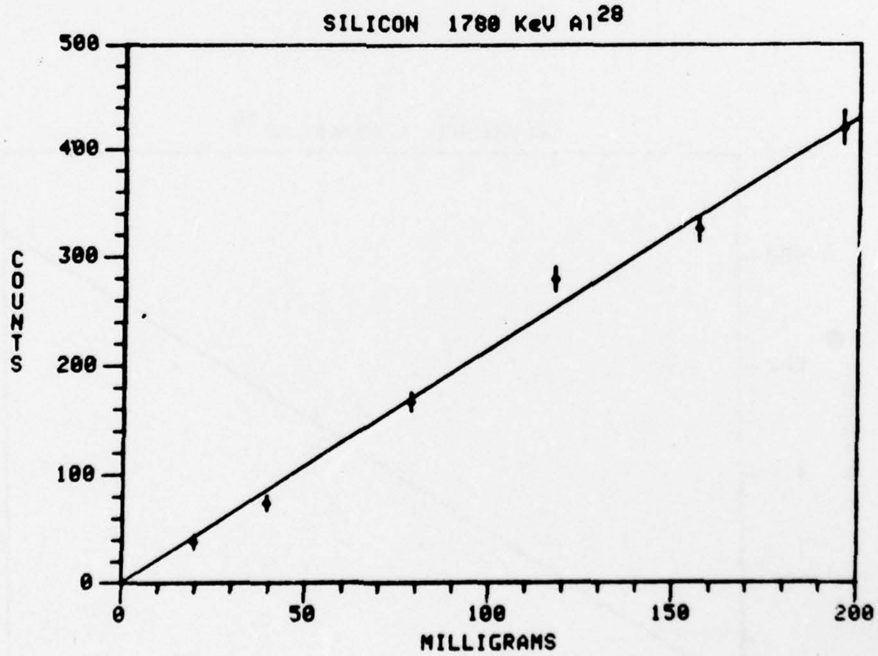

FIGURE A6. 1780 KeV CALIBRATION CURVE FOR SILICON.

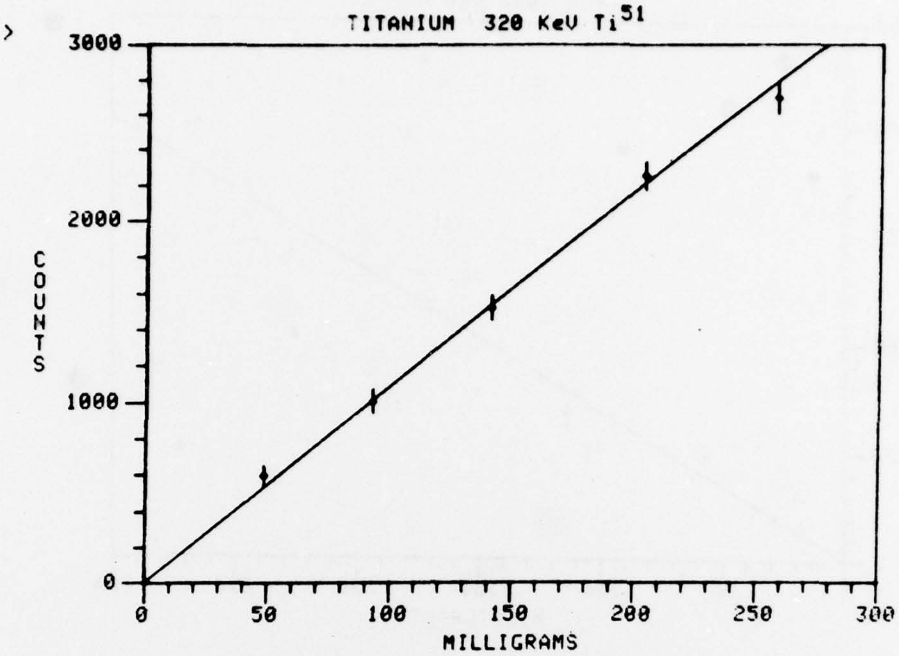

FIGURE A7. 320 KeV CALIBRATION CURVE FOR TITANIUM.

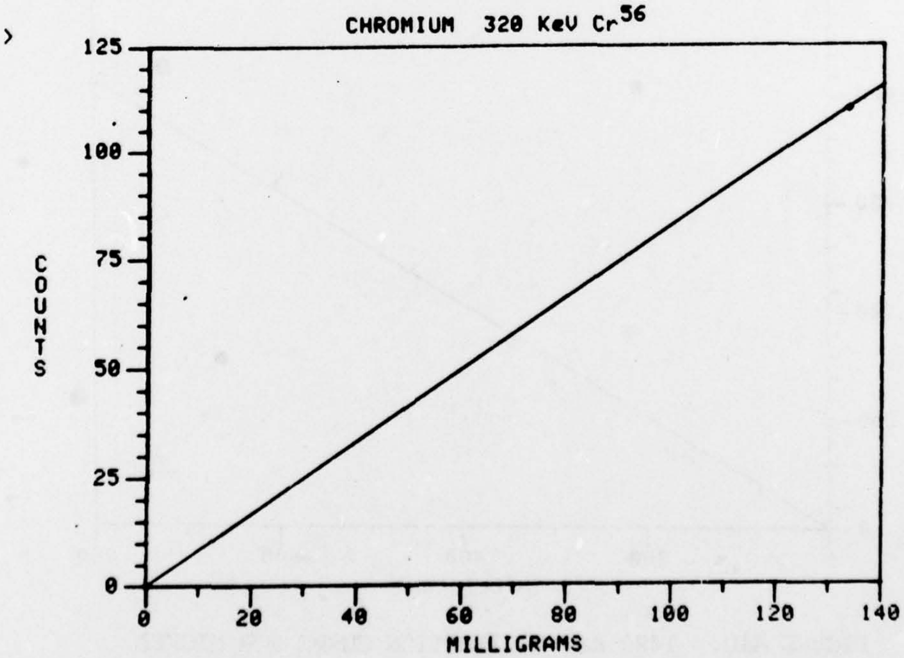

FIGURE A8. 320 KeV CALIBRATION CURVE FOR CHROMIUM.

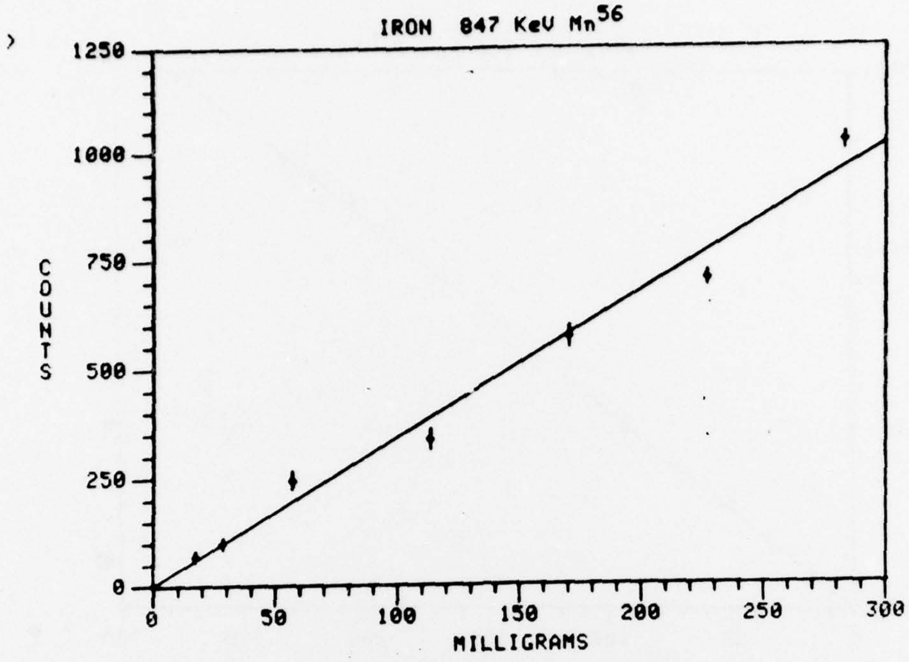

FIGURE A9. 847 KeV CALIBRATION CURVE FOR IRON.

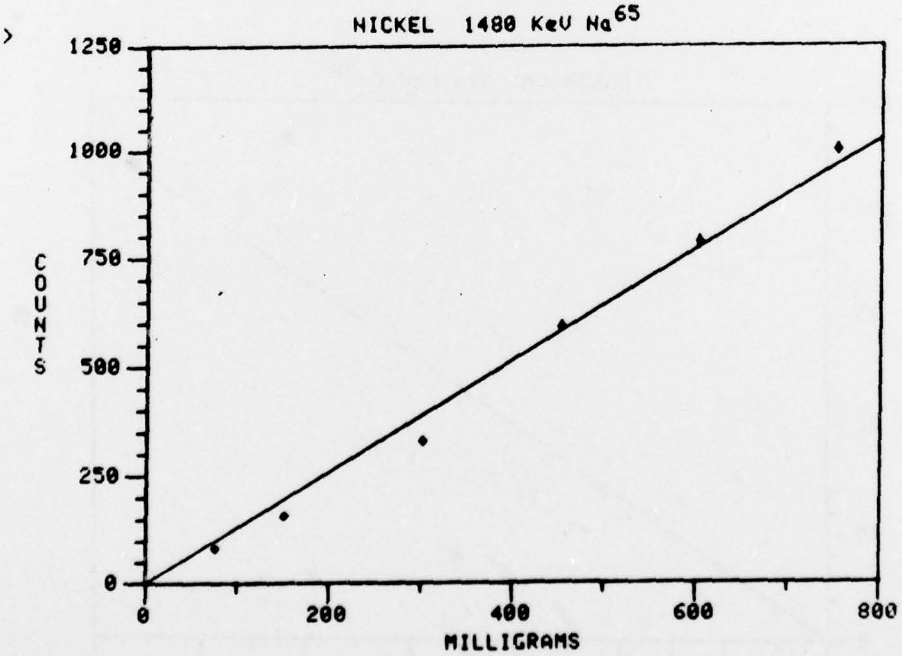

FIGURE A10. 1480 KeV CALIBRATION CURVE FOR NICKEL.

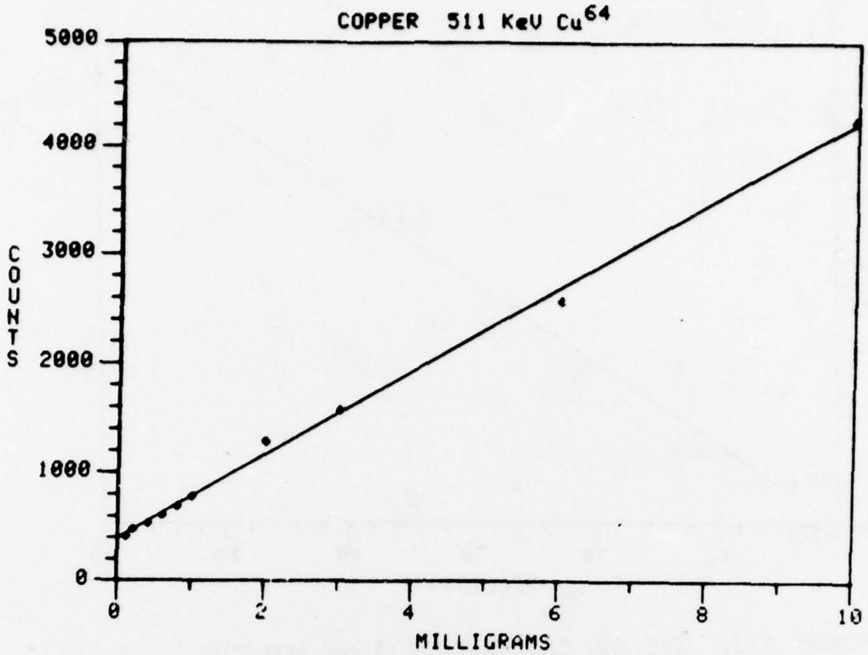

FIGURE A11. 511 KeV CALIBRATION CURVE FOR COPPER.

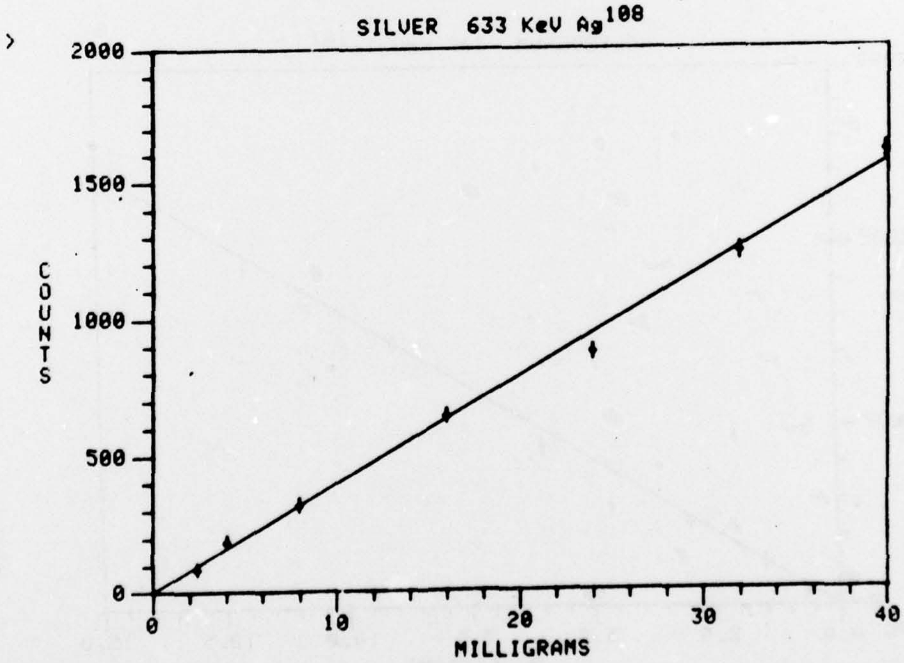

FIGURE A12. 633 KeV CALIBRATION CURVE FOR SILVER.

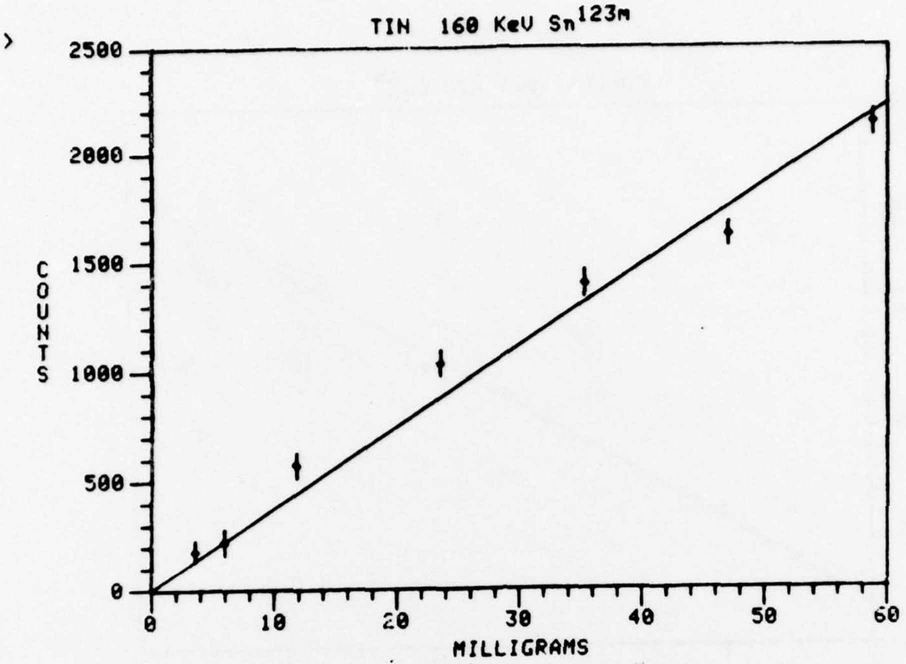

FIGURE A13. 160 KeV CALIBRATION CURVE FOR TIN.

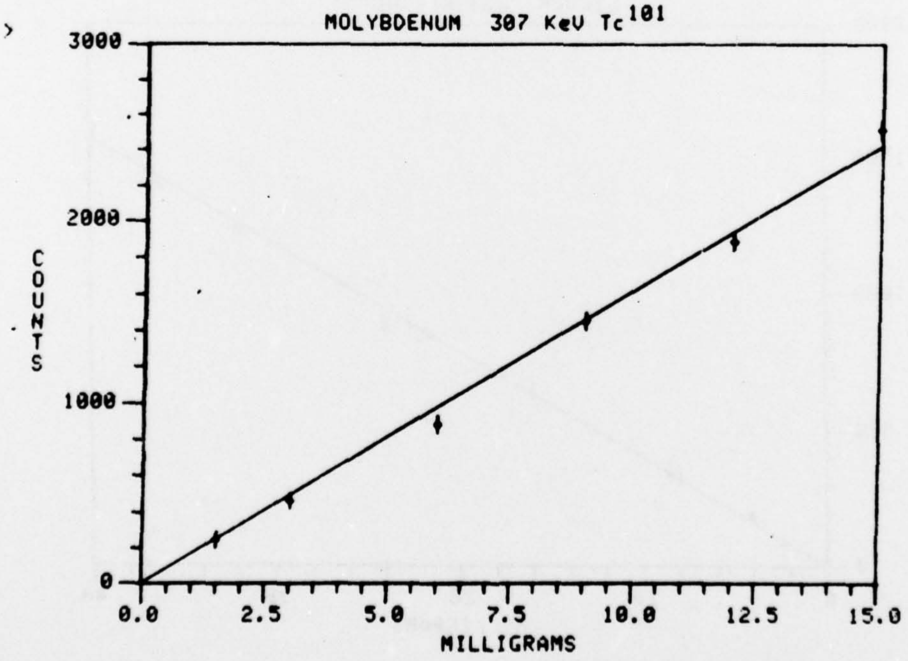

FIGURE A14. 307 KeV CALIBRATION CURVE FOR MOLYBDENUM.

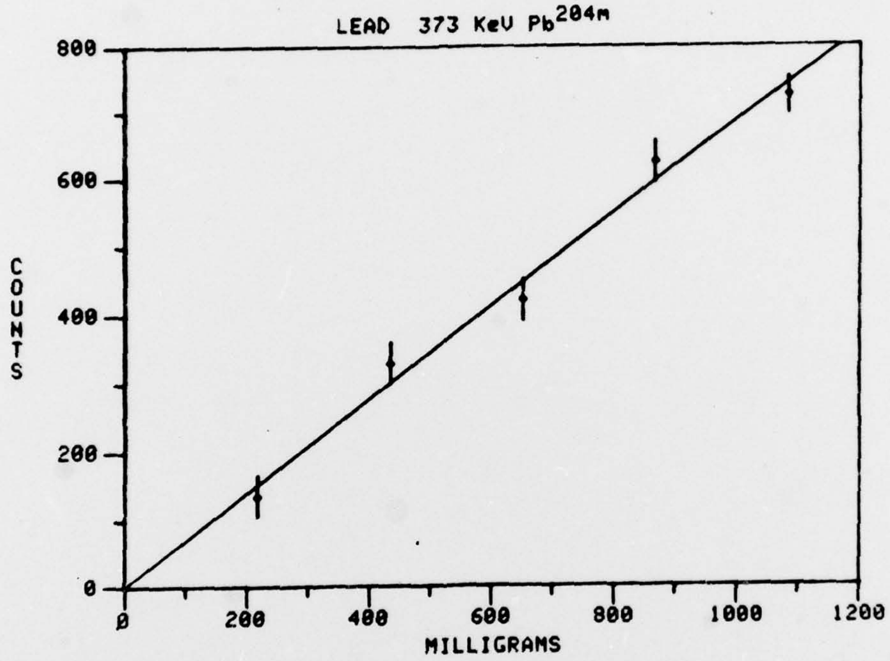

FIGURE A15. 373 KeV CALIBRATION CURVE FOR LEAD.

APPENDIX B

Appendix B is the collection of calibration curves which resulted from the gross gamma analysis of the 13 elements of interest. Each curve is normalized to 40 minutes irradiation/1 minute wait/30 minutes count and 1 mg of ^{252}CF. Data was collected using a 2" x 2" NaI(Tl) well detector and scalar counters.

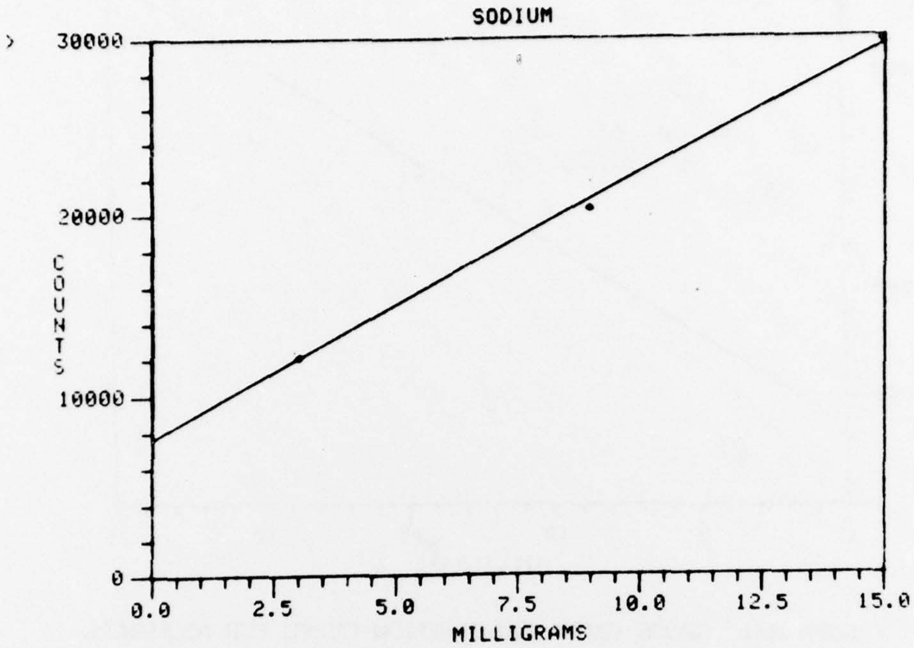

FIGURE B1. GROSS GAMMA CALIBRATION CURVE FOR SODIUM.

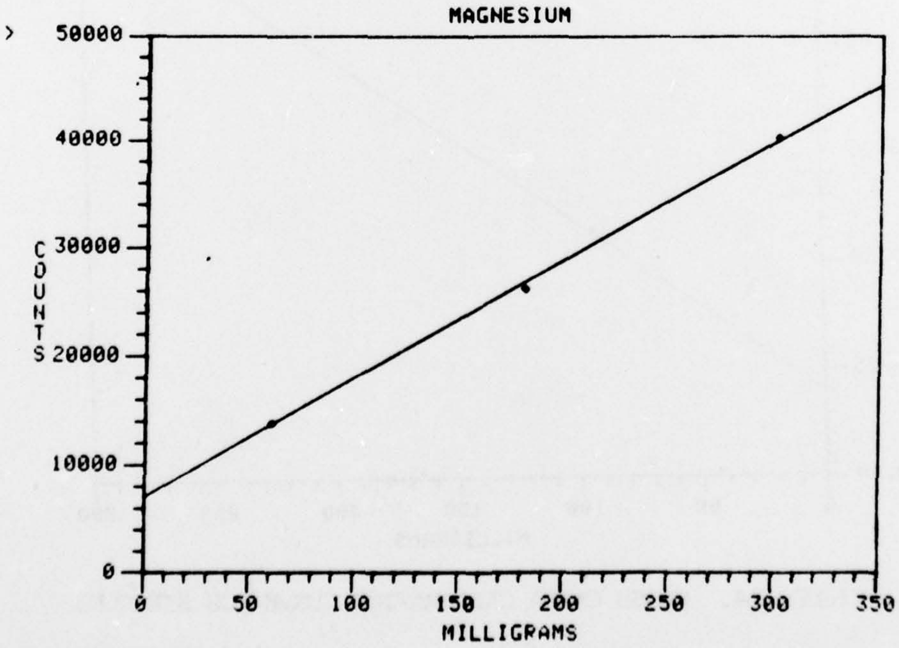

FIGURE B2. GROSS GAMMA CALIBRATION CURVE FOR MAGNESIUM.

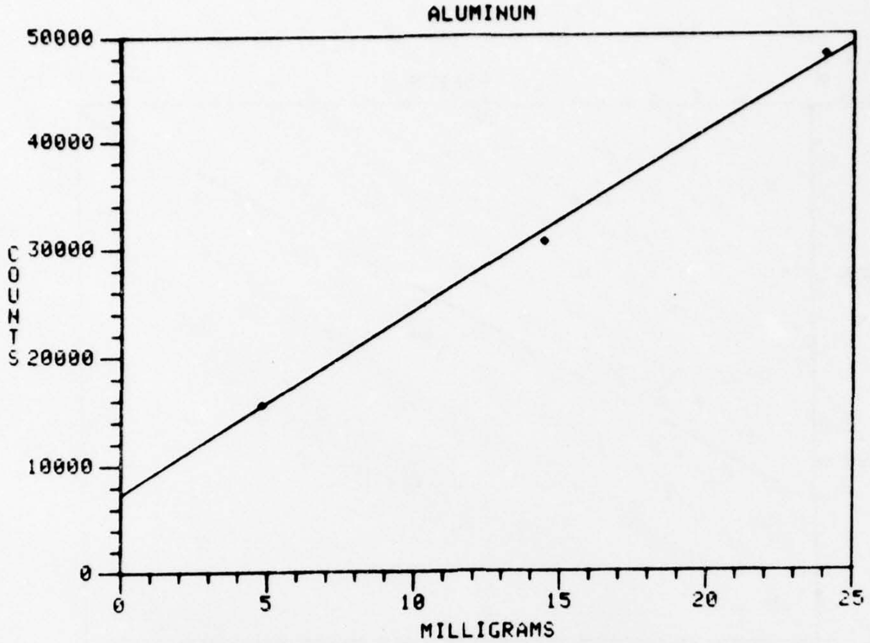

FIGURE B3. GROSS GAMMA CALIBRATION CURVE FOR ALUMINUM.

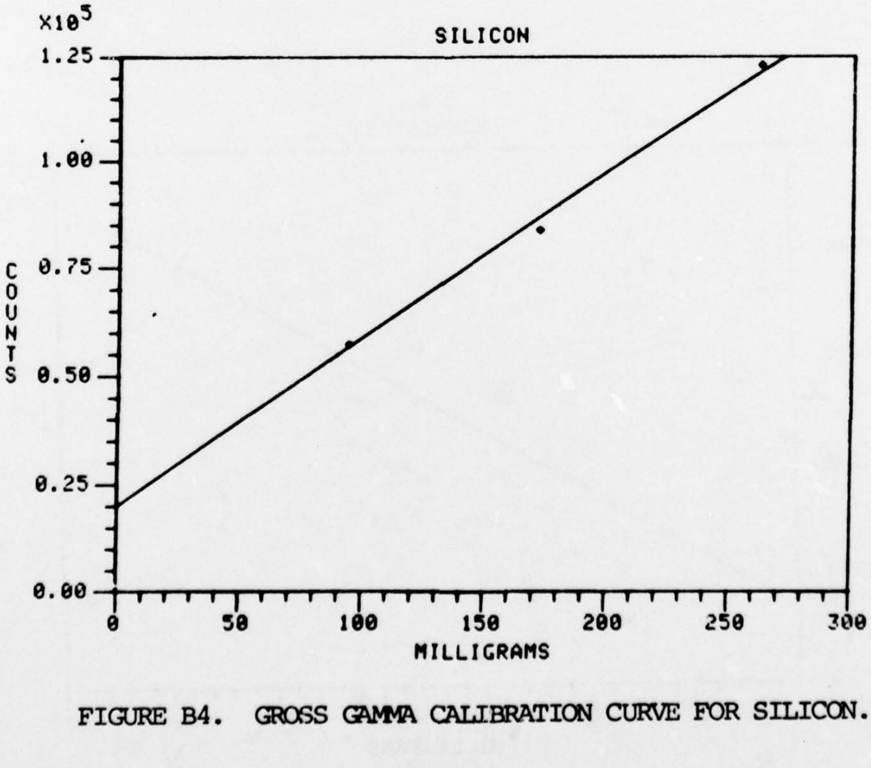

FIGURE B4. GROSS GAMMA CALIBRATION CURVE FOR SILICON.

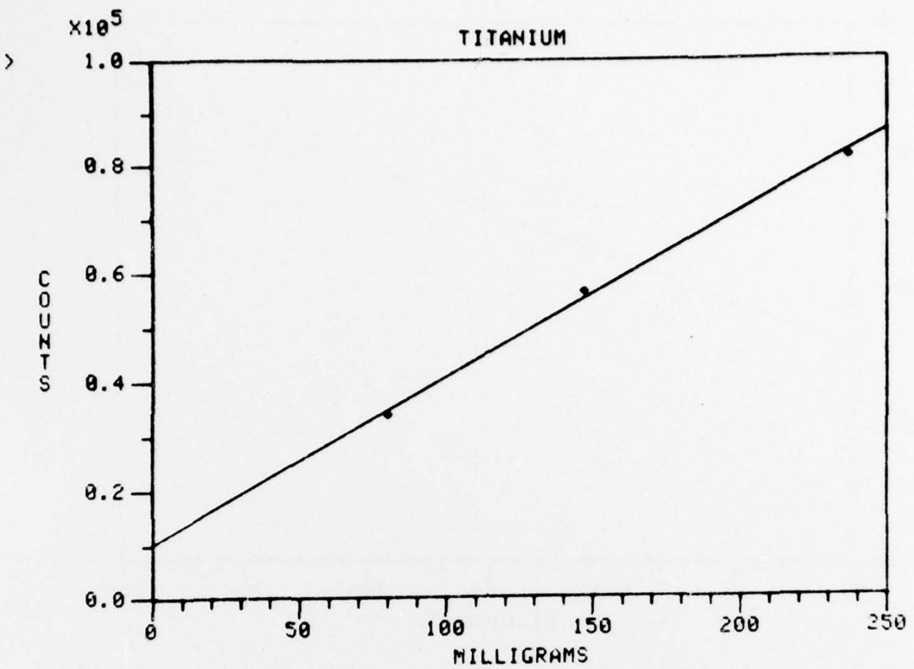

FIGURE B5. GROSS GAMMA CALIBRATION CURVE FOR TITANIUM.

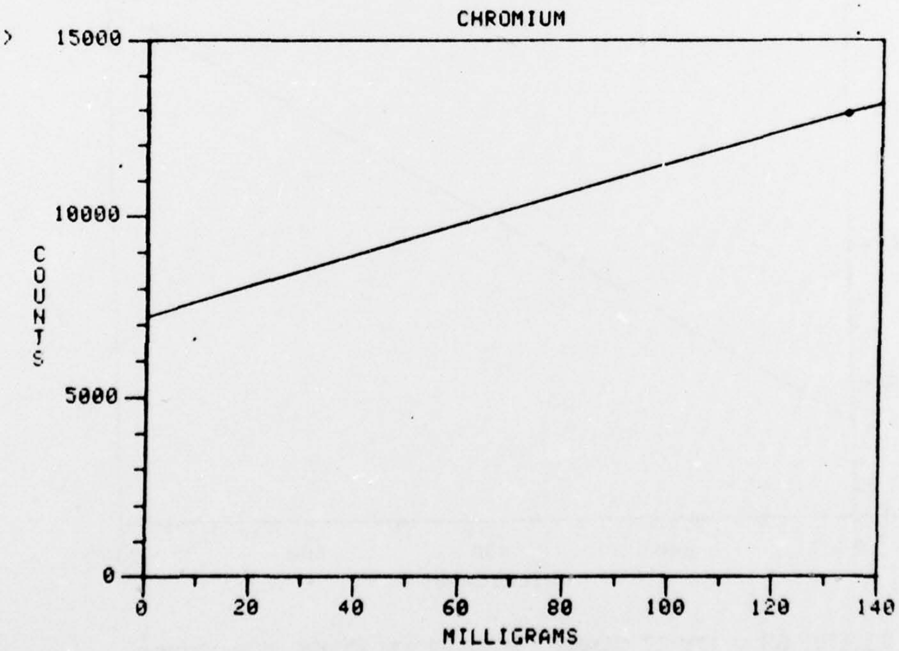

FIGURE B6. GROSS GAMMA CALIBRATION CURVE FOR CHROMIUM.

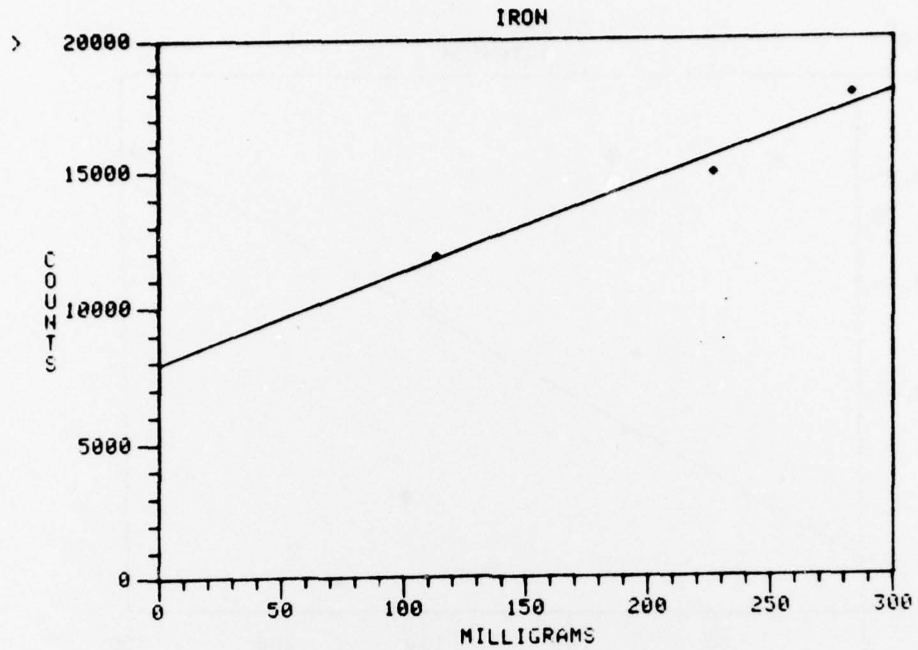

FIGURE B7. GROSS GAMMA CALIBRATION CURVE FOR IRON.

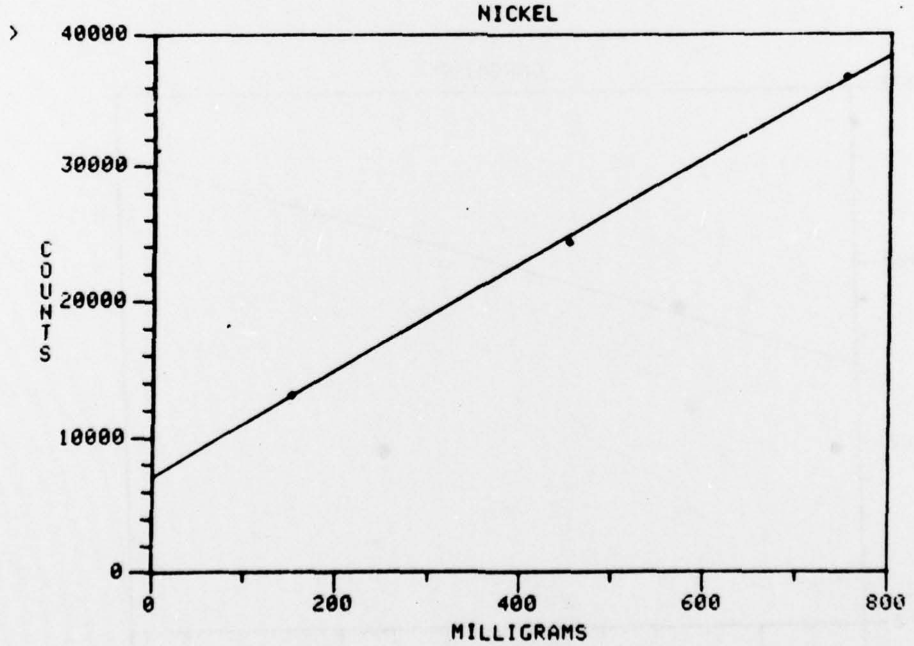

FIGURE B8. GROSS GAMMA CALIBRATION CURVE FOR NICKEL.

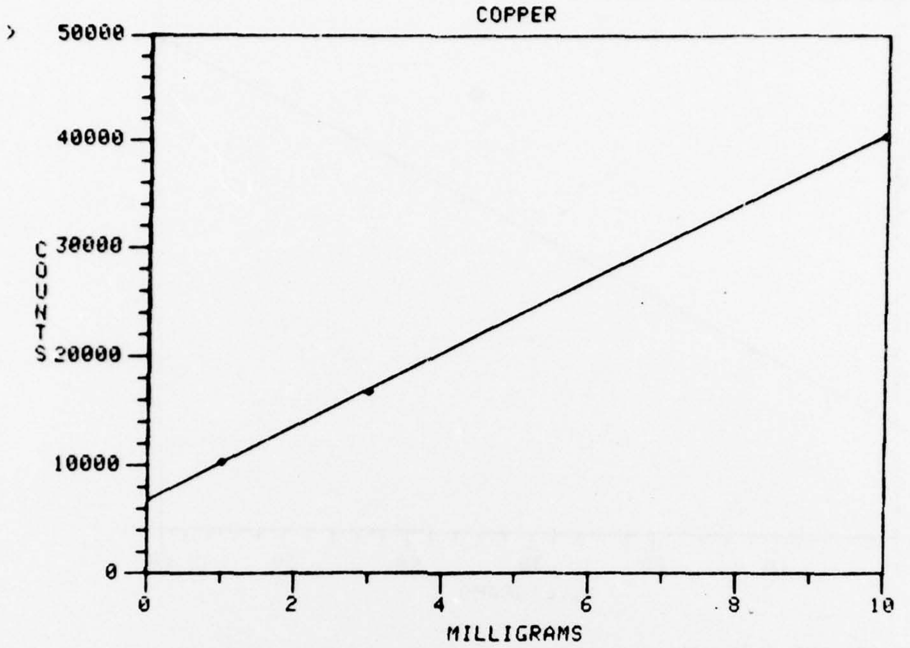

FIGURE B9. GROSS GAMMA CALIBRATION CURVE FOR COPPER.

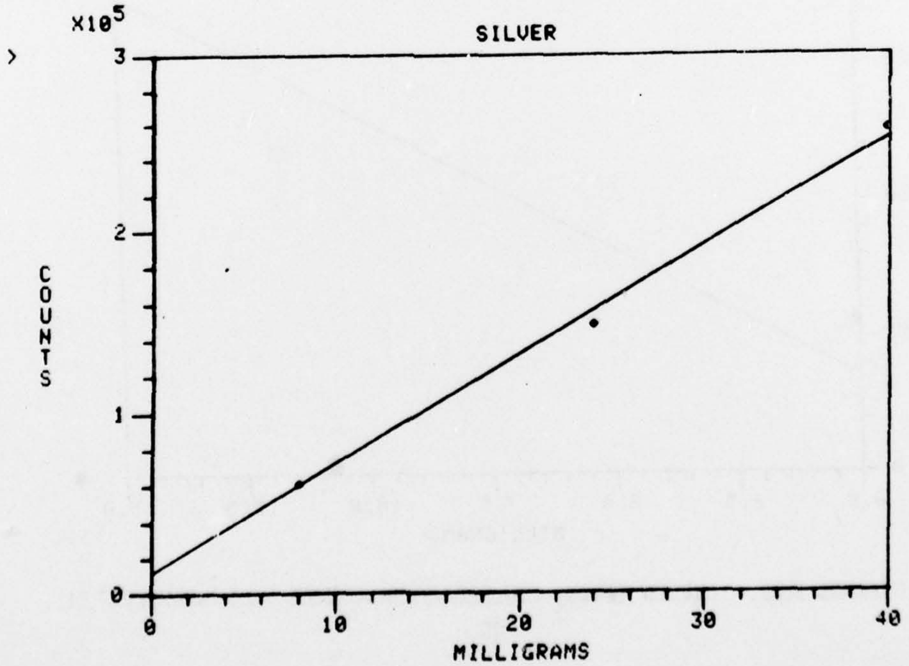

FIGURE B10. GROSS GAMMA CALIBRATION CURVE FOR SILVER.

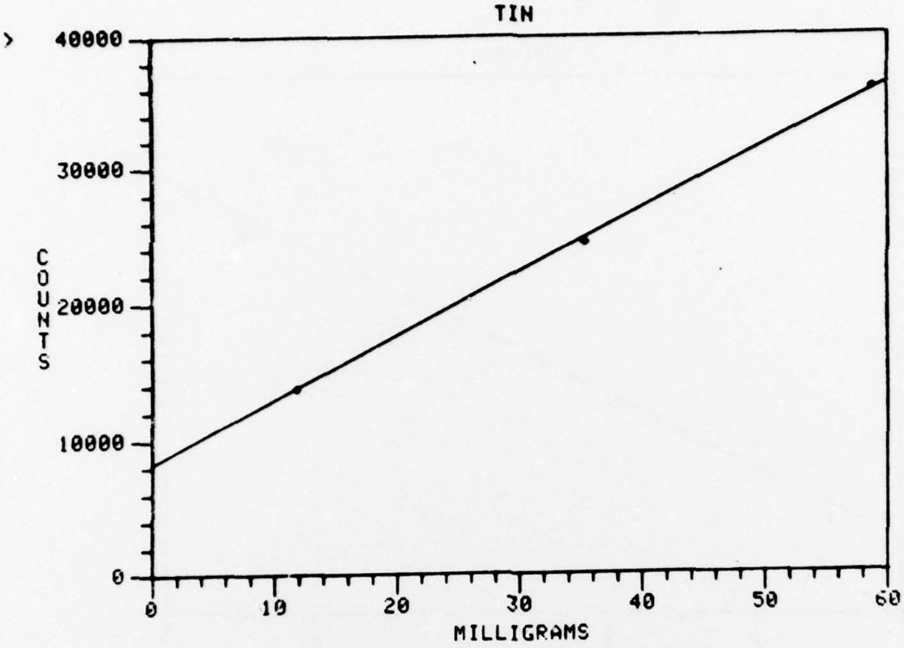

FIGURE B11. GROSS GAMMA CALIBRATION CURVE FOR TIN

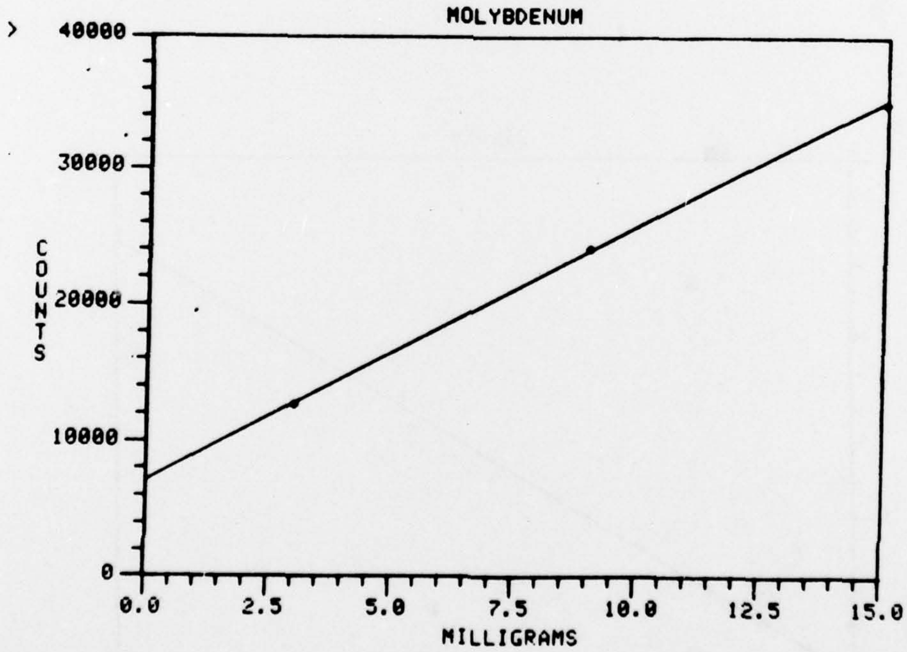

FIGURE B12. GROSS GAMMA CALIBRATION CURVE FOR MOLYBDENUM

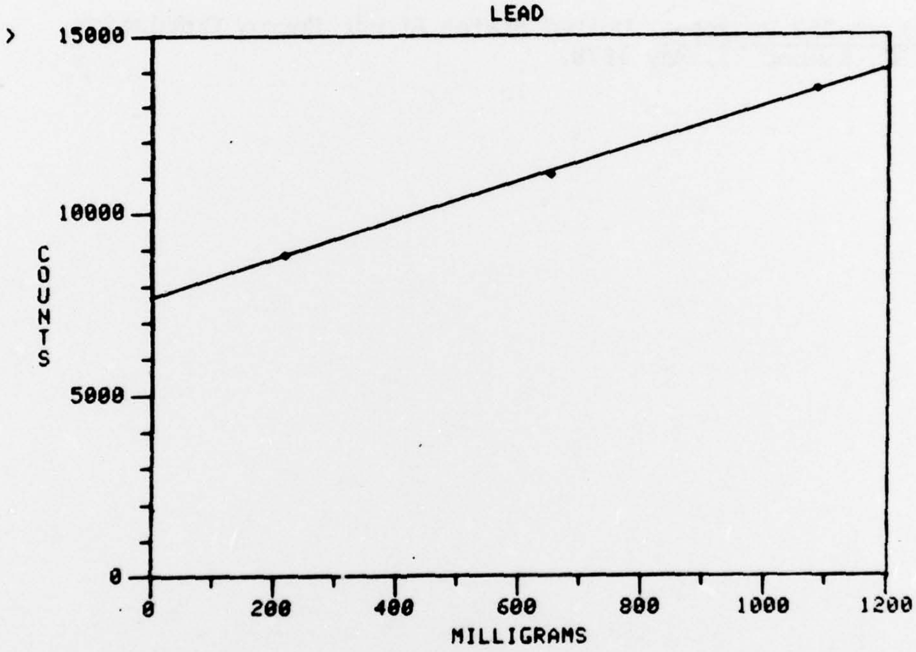

FIGURE B13. GROSS GAMMA CALIBRATION CURVE FOR LEAD.

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3. Mr. Julius Stagner, Director Ft. Carson SOAP Laboratory, telephone conversation on 24 November 1978.

4. Californium-252 Progress, United States Atomic Energy Commission, Aiken, SC, Number 12, July 1972.

5. Californium-252 Progress, United States Atomic Energy Commission, Aiken, SC, Number 14, January 1973.

6. Californium-252 Progress, United States Atomic Energy Commission, Aiken, SC, Number 22, May 1978.