ANALYSIS OF RADIOACTIVE METALS BY SPARK SOURCE
MASS SPECTROGRAPHY

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CFSTI PRICES

H.C. $ 2.00 MN .50

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ABSTRACT

A spark source mass spectrograph has been adapted for the
analysis of plutonium and americium metals. Over 70 elements
can be determined in these metals on the same analysis.
Elements such as Cl, F, S, Ta, W, and rare earths, which
require involved procedures to determine by emission spectro-
graphic or chemical methods, can be readily determined by mass
spectrography. A comparison has been made between results
obtained by mass spectroscopy and by conventional methods for
impurity elements. The operations involved in handling radio-
active materials in the mass spectrograph are also discussed.

INTRODUCTION

Improvements in purification techniques and metal production
technology have resulted in plutonium metal of a high degree
of purity. As the degree of purity of the plutonium metal
has increased, there has been a corresponding increase in the
analytical requirements.

(Slide 1) A good determination of the degree of purity requires
that the concentration of elements that are not now routinely
determined be measured. Formerly, a chlorine or sulfur content
of 10 ppm was not very significant when there was a total of
over 400 ppm of routine impurities. Now, the chlorine or
sulfur might be one of the major impurities. It is therefore
necessary to analyze for a greater number of elements in each
sample. This means increased time-of-analysis and cost.

The amount present of the different impurities in the metal
has been constantly lowered, until many are now present at
concentrations below the detection limits of routine emission

spectrographic methods. Analysis of the purer metals will
require separation and concentration techniques for emission
spectrographic measurements. This again means increased time
and costs.

The above considerations indicated that the use of the spark
source mass spectrograph for this type of analysis would be
feasible. A low level of detection limits is attainable, a
large number of elements are detectable, the reported accuracy
seems acceptable, and the probable increased cost of analysis
now appears justifiable. Work was therefore initiated on a
CEC 21-110 mass spectrograph to adapt it for plutonium analyses.

(Slide 2) The instrument is a double-focusing mass spectrometer
equipped with a 15 KVA spark source and photoplate recording.
The double focusing is necessary in spark source work because
of the large energy spread of the ions produced by the disruptive
rf spark. Photoplate recording permits the simultaneous
detection of all ions in the 7-250 mass range. The cabinets
contain the electronics and the vacuum pumps necessary to provide
the 10^{-8} torr vacuum needed for mass spectrographic analyses.

The next slide (Slide 3) shows the ion path through the instru-
ment. The term "double-focusing" refers to the two methods
of focusing the ions. The first focusing is velocity focusing
in the electric sector, and then the mass focusing in the
magnetic sector. For use of this instrument in plutonium
analyses, safe handling practices for plutonium had to be followed.

Safe Handling of Plutonium

The dangers from the radioactivity of plutonium are well known;
in addition it is also a highly toxic material. Plutonium has

been termed one of the most toxic elements on which large scale work is now being performed. All non-solution work with plutonium must be handled in a closed system so that no material is freed into the room atmosphere. This can be done with a completely closed box using rubber gloves, or in an open-front box with controlled draft to keep loose material in the box.

The major plutonium contamination of the mass spectrometer would be in the source section. Provisions had to be made so that the sample holders could be removed for changing samples and all the resultant contamination contained. The electrode positioning controls are on the sample holder, so these had to be manipulated inside the inclosure. Using a completely enclosed box to contain the source section would have necessitated performing these complex operations through heavy rubber gloves. Therefore, an open-front box was designed so as to contain the source and permit working in this box with surgeons gloves. The box, shown in Slide 4, has proven to be satisfactory, with no escaped contamination problems up to this time. Only plutonium metal samples have been handled in this box; no plutonium powders have been analyzed.

Samples are prepared for analysis in a regular closed-system glove box. In addition to the radioactive and toxic character-istics of plutonium metal, it is also pyrophoric. The cutting and filing of the metal into shapes suitable for electrodes is therefore done in an argon atmosphere. Samples are then trans-ferred to the source box shown in the next slide (Slide 5) for loading into the instrument.

The source of the instrument became extremely radioactive with the first plutonium sample sparked. An average of 3-4 mg of sample is consumed during each analysis, and most of this material remains in the source. It also was possible that

enough plutonium was going into the instrument to constitute a
hazard when the instrument was opened for necessary maintenance.
After a few months of operation, the instrument was opened and
the inside surfaces monitored with α-counting instruments.
(Slide 3 again, please) The only areas of significant radio-
activity were the slit edges back to and including the beam
monitor. When the instrument is first vented, the slits may be
removed and placed in a plastic bag with little chance of
contamination. However, if the deposited plutonium is allowed
to oxidize, the loose oxide will spread and be a health hazard.

The possible contamination of the photoplate was of prime
interest because of handling difficulties if it were radioactive.
If all of the plutonium passing the beam monitor reached the plate,
the calculated amount deposited there would be about 2.5×10^{-11}
grams. The radioactivity from this amount of material would be
four disintegrations per minute. Actual determinations of con-
tamination have been at the background level of the counting
equipment. No contamination greater than one disintegration
per minute has been detected on a developed plate, an undeveloped
plate, or in the developer and fixing solutions.

Continuous sampling of the laboratory air has shown that the
described method is safe for the handling of plutonium samples
for spark source analysis.

EXPERIMENTAL

Instrumental Parameters

When standardizing and analyzing samples, the instrumental conditions should be constant. The next slide (Slide 6) gives the parameters used. Source conditions which were found to be difficult to reproduce from sample to sample were sample shape, distance of sample electrodes from entrance slit, and spark gap. These varying parameters probably contributed to the experimental error. The spectra of the samples were recorded on Illford Q2 photoplates.

Standardization

There are very few certified standards of any material that contain impurities at the low levels desirable for spark source analysis. A few copper standards and an aluminum standard were obtained and used in the initial development work. There are no plutonium metal standards certified for impurities at this time. Fortunately, two samples of plutonium metal became available that had been analyzed several times by five AEC installations. A comparison could be made between the compiled results and the mass spectrographic results.

Analytical

The visual method of estimating impurity concentration was used for most of the analyses. In this method, as described by Craig and Wolstenholme (1), a graded series of exposures covering the 10^{-12} to 10^{-8} coulomb range is made on each sample. The resultant photoplate is shown in the next slide. (Slide 7)

The impurity concentrations are calculated using the formula shown on the next slide. (Slide 8)

The plutonium samples to be analyzed will present a problem in that the isotopic ratios of the various plutonium isotopes will not be constant. To remove the dependence on an additional isotopic analysis on all samples to determine Cm, an empirical Em was used in the first calculations. The work of Brown, et al (2), has shown the basic ion sensitivity of a "just detectable" line to be about 2×10^{-15} coulombs. This was verified from test plates, and the empirical value used for the matrix exposure in subsequent visual calculations.

RESULTS AND DISCUSSION

The next slide (Slide 9) gives a comparison between mass spectrographic and emission spectrographic results on Sample A. Spark source results for Mg and Zn are considerably higher. Zinc, however, is one of the elements for which very few emission spectrography results were available. These starred elements are not requested in the cooperative analysis and only a few of the laboratories reported these values.

Sample B, on the next slide (Slide 10), is the same type of comparison. A few more impurities are given. About 80% of the values reported by mass spectrography check within a factor of two with the emission spectrography results. This is about the same percentage as in Sample A.

The group of elements shown in the next slide (Slide 11) are some which are not routinely determined in emission spectrographic or chemical analysis. These elements, however, are determined

as readily by the mass spectrographic method as such routinely
determined elements as iron or magnesium. Although no values
are available for comparison, the degree of accuracy on these
elements should be similar to that obtainable on the compared
elements.

For the preceding results, only the empirical formula had been
used and all elemental sensitivities were assumed to be the
same. Other workers (2,3,4), however, have shown that there
are various factors influencing the recording of the ion on the
photographic plate. Among them are emulsion response to mass,
Z focusing, and matrix effect. All of these combined result in
different sensitivity factors for each element.

The calculation of mass spectrographic sensitivity factors for
the elements determined using the emission spectrographic
results did not appear promising. Although this worked quite
well for steel analysis (5) where the calculations were made
based on an NBS certified standard, the plutonium metal
analyzed could certainly not be considered as meeting the
requirements of a basic standard. - It would also be advantageous
to have the mass spectrographic method independent of present
methods.

A method of standardization that would combine most of the
previously mentioned factors into a single factor was desirable.
A program was therefore started of sparking plutonium and other
pure elements and recording their spectra under the same conditions
used for the sample analyses. The only difference was that the
spectra were recorded at small incremental increases in the beam
monitor readings. By this method the exposure of a "just
detectable" line could be more accurately estimated. The sensi-
tivities of the various elements were then calculated relative
to plutonium.

The next slide (Slide 12) contains the results on some of the
elemental sensitivities that have been calculated. These
factors should include most of the recording variables except
for matrix effect. This method can thus also be used to deter-
mine which elements exhibit significant matrix effects. A
good example of a large matrix effect is shown in the case of
lead. The factor calculated from the pure lead photoplate was
2.6, a value which gave extremely high comparative answers when
used in the analytical calculations. The sensitivity factors
calculated for lead in both a copper matrix standard and in
two steel standards agreed very closely; this factor was used
in calculating the lead values in the plutonium samples. The
galium factor was calculated in the same manner as that of lead.

The next slide (Slide 13) shows the use of these factors in the
analysis of the plutonium. Improved agreement in all of the
elements except Cr can be seen. In the next slide (Slide 14),
again there is generally improved agreement. The poor agreement
between Mg results has not yet been explained.

AMERICIUM ANALYSIS

Results obtained on the plutonium metal samples previously
described, and on subsequent samples, indicated that comparative
good results could be obtained without the use of standards.
The next metal analyzed was again one for which no standards
were available. This was americium.

The americium was to be used for a half-life determination by
calorimetric methods. This necessitated a knowledge of the
purity of the sample, as this would enter into the half-life
calculation. Spark source mass spectrographic and emission
spectrographic methods were both used to analyze the metal.

The results show some of the advantages of the spark source method.

The next slide (Slide 15) contains results on the more common impurities. Two different laboratories using different methods, analyzed the metal by emission spectrographic techniques. Results compare quite well. The major advantage of the spark source is in the lower limits of detection.

In the next slide (Slide 16), the results on rare earths are compared. Rare earths are often found in americium, as they are concentrated along with americium in the plutonium-americium separation process. The last group of rare earths are those which were not present in detectable amounts.

The third group of impurity elements, given in the next slide (Slide 17), are those that are not routinely determined by emission spectrographic methods. These impurities were quite important in the americium sample, as their added concentrations represented a high percentage of the total impurities. Chlorine was the second highest impurity in both samples.

The impurity listed as mass 242 brings out an interesting feature of spark source analysis. In the method used for these analyses, it was not possible to determine the element represented by this isotope of 242 atomic mass units. However, the amount present could be calculated. Radiochemical work indicated later that this was Pu-242, and also confirmed the presence of neptunium.

In conclusion, let us look at the first slide again:

Item 1 - Over 70 elements are determined in the same sample.

Item 2 - Levels of detection down to 0.2 ppm can be reached.

Item 3 - An accuracy of a factor of three is considered adequate below 10 ppm.

Item 4 - A cost comparison of the mass spectrographic method and the other analytical methods is difficult to make, as many of the elements determined by the spark source method are not now being routinely determined. The total time of analysis, however, has been estimated to be about 2-1/2 faster by use of the spark source for total trace impurity determination. The elements F, Na, S, and Cl are included in the spark source time, but not in the "other methods" time.

Results of this time, therefore, indicate that most of the requirements for pure metal analysis have been met by the spark source mass spectrographic method.

REFERENCES

1. R. D. Craig, W. A. Wolstenholme, Ind. Chim. Belge, <u>29</u> (1964).

2. R. Brown, R. D. Craig, and J. D. Waldron, "Analysis of Impurities by Spark Source Mass Spectroscopy," Preparation of III-V Compounds, R. K. Willardson and H. J. Goering, Eds., To be published.

3. R. M. Elliott, R. D. Craig, and G. A. Errock, Instruments and Measurements, Vol. 1, Academic Press (1961).

4. E. B. Owens, N. A. Giardino, Anal. Chem. <u>35</u>, 1173 (1963).

5. W. L. Harrington, R. K. Skogerboe, and G. H. Morrison, Anal. Chem. <u>37</u>, 1480 (1965).

LANTERN SLIDES

Slide Number	Description
1	Pure Plutonium Metal Analysis
2	Photograph of CEC 21-110
3	Ion Path through Instrument
4	Photograph of B-Box for Source
5	Photograph of Electrode Clamps in Source
6	Source Parameters
7	Sample Photoplate
8	Equations Used for Impurity Concentrations
9	Results on Pu Sample A
10	Results on Pu Sample B
11	Results on Non-routine Elements in A and B
12	Sensitivity Factors
13	Use of Factors - Sample B
14	Use of Factors - Sample A
15	Results on Americium Samples
16	Results on Americium Samples
17	Results on Americium Samples

SLIDE 1

PURE PLUTONIUM METAL ANALYSIS

1. As many elements determined as feasible.
2. Low levels of detectability.
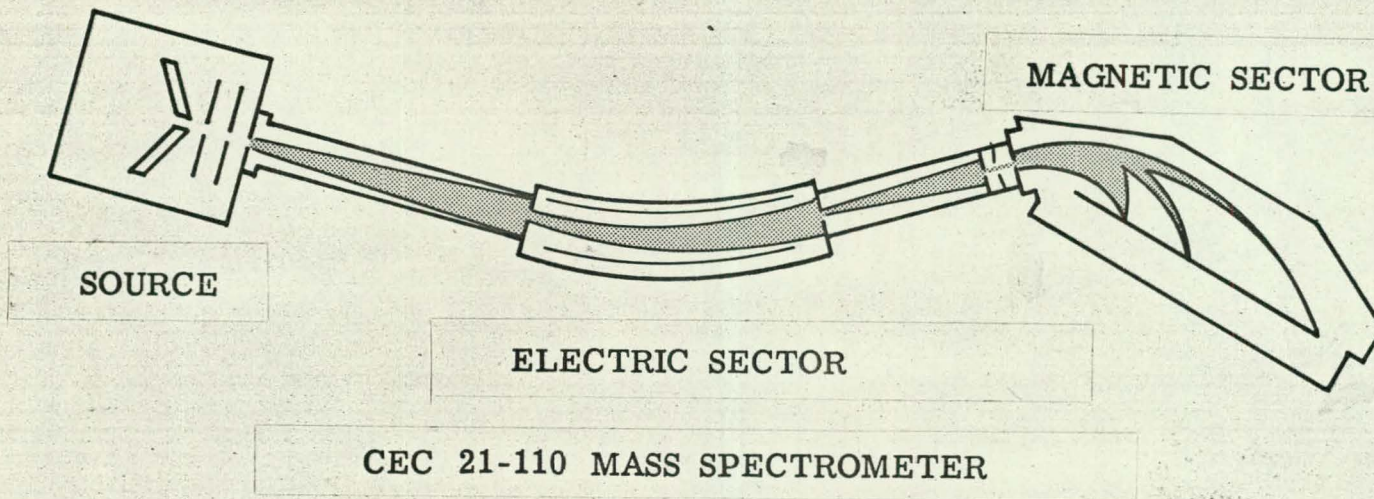3. Adequate accuracy.
4. Justifiable cost of analysis.

SLIDE 2

SOURCE

ELECTRIC SECTOR

MAGNETIC SECTOR

CEC 21-110 MASS SPECTROMETER
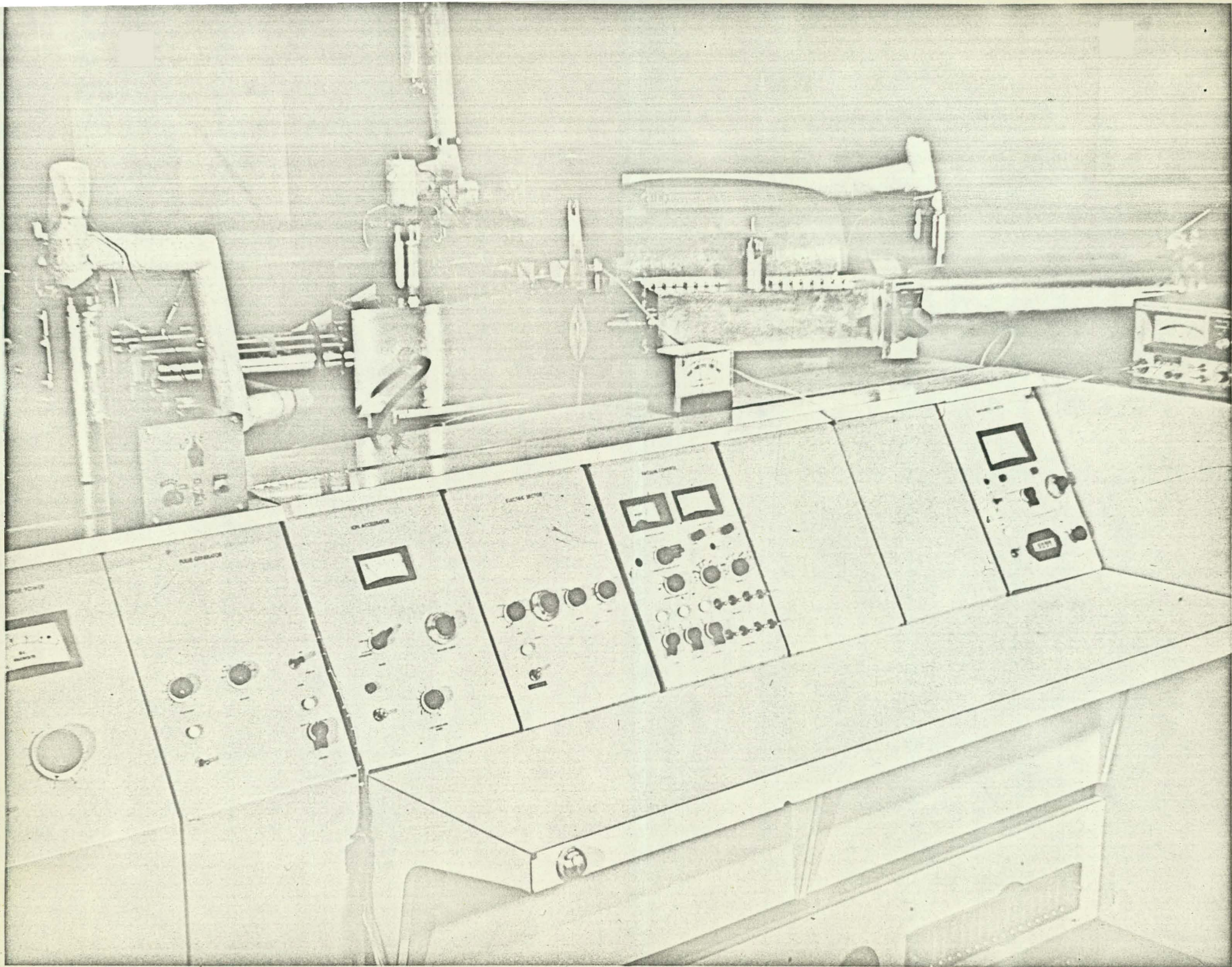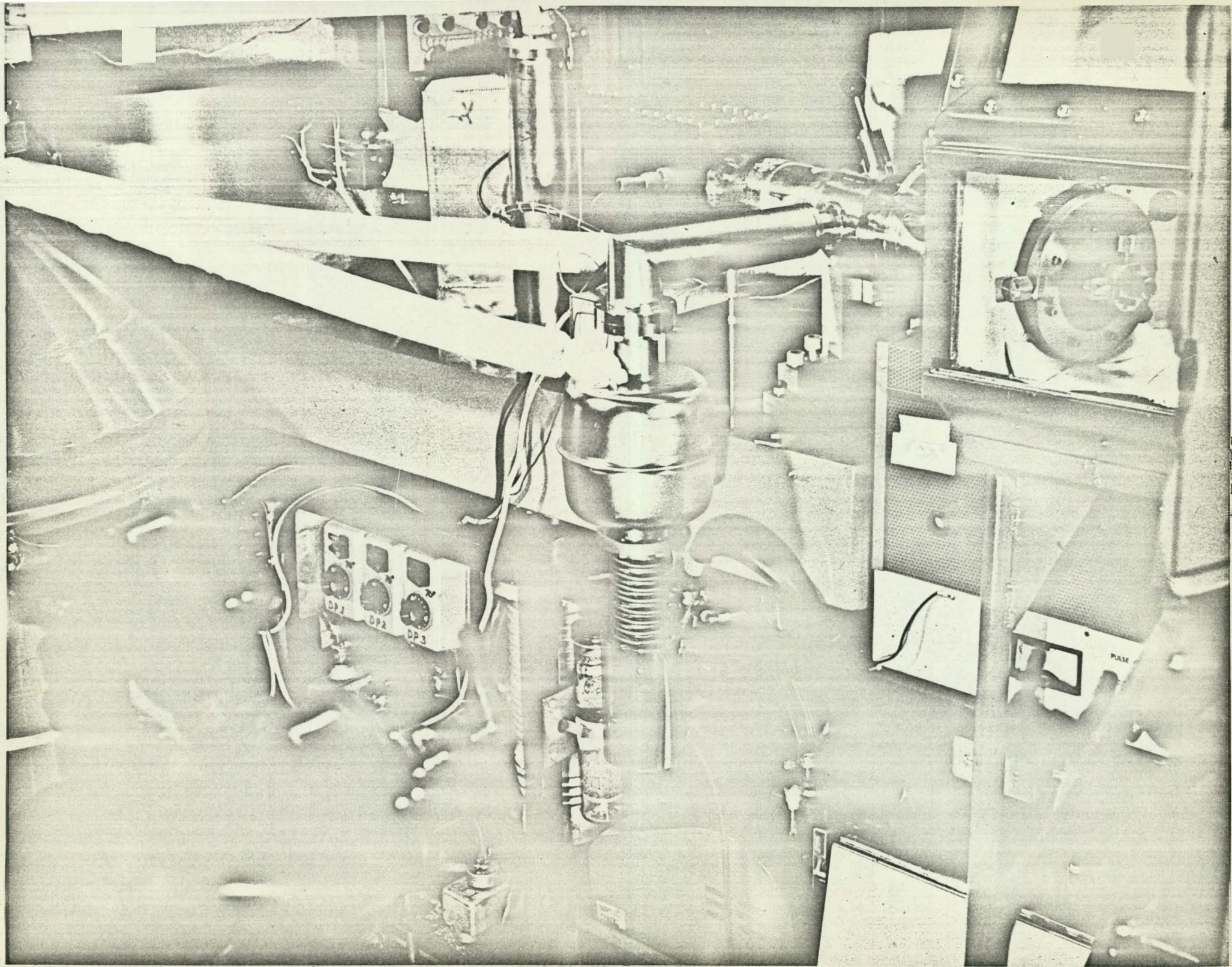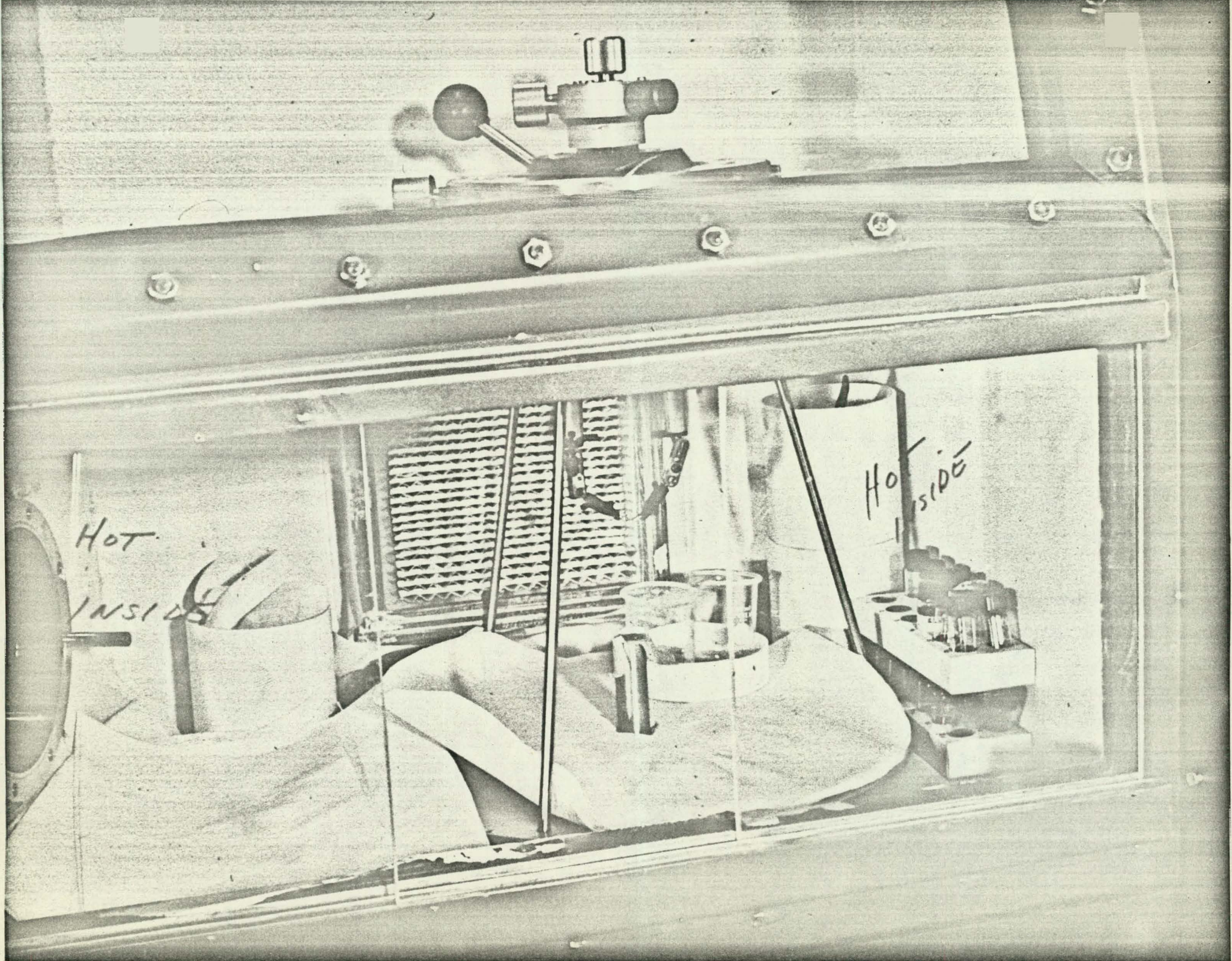
SLIDE 4

SLIDE 6

INSTRUMENT PARAMETERS

1. Accelerating Voltage   15 KV.
2. Repetition Rate   300 cps.
3. Pulse Length   17 μ Sec.

SLIDE 8

ESTIMATION OF CONCENTRATION OF IMPURITIES

$$C_i = \frac{2 \times 10^{-15}}{E_i} \times \frac{C_m}{I_i} \times \frac{A.W._i}{A.W._m} \times 10^6 \text{ ppm (by weight)}$$

C_i Impurity concentration (by weight).

E_i Exposure at which an isotope line of the impurity element becomes "just detectable."

C_m The % concentration of the matrix.

I_i The % abundance of the impurity isotope.

$A.W._i/A.W._m$ Ratio of atomic weights of impurity element and matrix element.

SLIDE 9

PLUTONIUM SAMPLE A
(Results in ppm by weight)

Element	Emission Spectrographic	Mass Spectrographic@
Mg	8	36
Al	13	28
Si	31	31
Cr	3	3
Mn	5	7
Fe (Chem)	40	29
Fe (Spec)	24	29
Ni	7	7
Cu	2 ≠	1
Zn	4 ≠	18
Ga	3 ≠	1
Pb	3	5

≠ Insufficient data

@ Equal sensitivity to 2×10^{-15} coulombs

SLIDE 10

PLUTONIUM SAMPLE B

(Results in ppm by weight)

Element		Emission Spectrographic	Mass Spectrographic⊖
B		1 ≠	0.4
Na		5 ≠	5
Mg		7	11
Al		29	65
Si	(Chem)	90	105
Si	(Spec)	84	105
K		20 ≠	1
Ca		4 ≠	2
Cr		43	54
Mn		10	14
Fe	(Chem)	223	308
Fe	(Spec)	163	308
Ni	(Chem)	54	68
Ni	(Spec)	43	68
Cu		15	22
Zn		15 ≠	19
Ga		25	50
Pb		5	14

≠ Insufficient data

⊖ Equal sensitivity to 2×10^{-15} coulombs

SLIDE 11

ELEMENTS REPORTED ONLY BY
MASS SPECTROGRAPHIC ANALYSIS

(Results in ppm by weight)

Element	Sample A	Sample B
As	<0.07	0.2
Cl	2	4
P	1	8
Ta	1	5
V	<0.03	0.1
Co	0.05	2
F	0.2	0.2
S	9	4

SLIDE 12

RELATIVE SENSITIVITIES - VISUAL METHOD

$$\frac{\text{Pu Plate Sensitivity}}{\text{Element Plate Sensitivity}} = \text{Relative Sensitivity}$$

Element	Relative Sensitivity to Pu	Cu/Fe Matrix
Pu	1.0	
U	1.6	
Pt	1.9	
In	5.8	
Zn	6.1	
Fe	7.2	
Cr	5.4	
Mg	11.1	
C	18.5	
Pb	2.6	18.1
Ga	-	11.1

SLIDE 13

PLUTONIUM SAMPLE B
(Results in ppm by weight)

Element	Emission Spectrographic	(1) Mass Spectrographic	(2) Mass Spectrographic
Fe (Chem)	223	308	262
Fe (Spec)	163	308	262
Mg	7	11	6
Cr	43	54	61
≠ Ga	25	50	27
Zn	15	19	19
≠ Pb	5	14	5

(1) Equal sensitivity to 2×10^{-15} coulombs
(2) Elemental sensitivity to Pu
≠   Determined by Cu and Fe standards

SLIDE 14

PLUTONIUM SAMPLE A
(Results in ppm by weight)

Element	Emission Spectrographic	(1) Mass Spectrographic	(2) Mass Spectrographic
Fe (Chem)	40	29	25
Fe (Spec)	24	29	25
Mg	8	36	20
Cr	3	3	3
Ga	3	1	0.4
Zn	4	18	18
Pb	3	5	2

(1) Equal sensitivity to 2×10^{-15} coulombs
(2) Elemental sensitivity to Pu

SLIDE 15

ANALYSIS OF AMERICIUM METAL
COMMON IMPURITIES

(All values are in ppm by weight)

Element	Mass Spec	Sample 1 E. Spec A	Sample 1 E. Spec B	Mass Spec	Sample 2 E. Spec A	Sample 2 E. Spec B
Cr	60	50	< 50	60	50	< 50
Fe	105	150	50	100	< 50	50
Ni	8	< 50	< 50	5	< 50	< 50
Y	200	50	200	120	20	100
Zn	4	<100	<100	2	<100	<100

ANALYSIS OF AMERICIUM METAL
RARE EARTHS
(All values are in ppm by weight)

| Element | Mass Spec | Sample 1 | | Mass Spec | Sample 2 | |
		E. Spec A	E. Spec B		E. Spec A	E. Spec B
Eu	12	< 12	< 50	20	12	< 50
Sm	35	< 25	<100	55	.60	<100
Tm	0.2	6	< 50	0.2	< 6	< 50
Yb	20	< .1	< 5	45	6	< 5
Dy, Er, Gd, Ho, Nd, Pr	< 0.2	< 18	<75	< 0.2	<18	< 75

SLIDE 17

ANALYSIS OF AMERICIUM METAL
OTHER IMPURITIES

(All values are in ppm by weight)

Element	Sample 1	Sample 2
Cl	1000	390
F	15	40
Np	185	120
S	8	2
M^{242}	600	40