

Lawrence Berkeley National Laboratory

Recent Work

Title

SPECTROSCOPY OF RADIOACTIVE MATERIALS

Permalink

<https://escholarship.org/uc/item/7p00h307>

Author

Conway, John G.

Publication Date

1959-07-08

UNIVERSITY OF
CALIFORNIA
Ernest O. Lawrence
Radiation
Laboratory

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-8674

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
Contract No. W-7405-eng-48

SPECTROSCOPY OF RADIOACTIVE MATERIALS

John G. Conway

July 8, 1959

Printed for the U. S. Atomic Energy Commission

SPECTROSCOPY OF RADIOACTIVE MATERIALS

John G. Conway

Lawrence Radiation Laboratory
University of California
Berkeley, California

July 8, 1959

Every element of the 102 that has been discovered has at least one radioactive isotope. So any discussion of the handling of radioactive materials that attempted to cover all elements would be as varied as the properties of all the elements. There still are seven elements, however, whose emission spectra have not been observed -- francium, berkelium, californium, einsteinium, fermium, mendelevium, and 102. When one speaks of radioactive elements, one usually means the group of elements beyond xenon including the rare earths, thorium, uranium, and the elements beyond uranium. My remarks will be more specifically about the actinide group, the elements beyond thorium.

The solution to the problems of how to handle these various materials depends to a great extent on the nature of the radiation emitted. Elements such as the rare earths, which are primarily β , γ emitters, require lead shielding and remote handling to protect the operator, whereas pure α emitters can be handled safely with rubber gloves. Of course the usual case is that you seldom have a pure α emitter; however there are several elements that may be safely handled with rubber gloves. The α emitter is considered the more dangerous biologically because when deposited in the human body the intense ionization is concentrated in a relatively small volume. The ionization produced from β , γ emitters is distributed over a

greater volume of tissue. About 1 microgram of an α emitter such as plutonium deposited or fixed in the body is considered the level at which a worker should be taken off the job until this amount can be reduced either by medical treatment or natural excretion. A complicating factor in the consideration of all this is that the α emitters tend to lodge in the bone areas and are slowly excreted.

The principle point in the approach to the solution of the handling of radioactive materials at the Lawrence Radiation Laboratory has been to concentrate and confine the material in as small a volume as possible and to then filter the air before discharge into the atmosphere.

Figure 1 is a general view of a gloved box positioned at the end of the optical bench of a spectrograph. Figure 2 is a front view of this box in which sample preparation and excitation is carried out.

Figure 3 is a closer view of the interior of the box. The arc-spark chamber is on the left. To the right of it is the line-up light for positioning the electrodes. Behind the line-up light is a "Millipore" filter. The right hand side of the box is used for sample preparation. In this case the copper-spark method is used extensively. The nichrome wire evaporator is positioned under an exhaust hood.

In the operation of the chamber, the air is drawn through the chamber into the Millipore filter, then outside the box to the two Chemical Warfare Service filters located on the shelf below the box. A vacuum pump is used to move the air. The exhaust is vented on the roof outside the building. The flow rate is about 2.5 cubic feet of air a minute.

Figure 4 is a close-up of a similar chamber. The chamber is made vacuum-tight so that during excitation materials do not escape and contaminate the box more than necessary. The lid is fastened to the base by a quarter-turn breech thread. A rubber "O" ring is used to secure a good vacuum connection.

Vertical motion of the electrode holders is through brass bellows in the base.

Experiments with the filter train have shown that when a sample of 10^{10} counts per minute (cpm) is sparked, some 75% is caught on the first filter. Five to seven percent settles on the wall of the chamber and the tubing to the filter. A monitor filter located after the second filter and before the pump had no detectable activity, which was 0.1 counts per minute.

The great sensitivity of counting methods permits one to study the distribution of materials during the various steps in the operation. Figure 5 is a sketch of such a system. Filter paper is drawn over an air intake then moved under a scintillation counter and the counts recorded. In this case there were two channels. Figure 6 is a plot of the counts per minute versus time. In this experiment the work was extended over a long period of time to allow the box background to return to a low level after an operation. One sampler was a hood that could be placed over an operation; the other sampler was general air in the box. The first peak was due to work in the box and stirring up activity which had settled on gloves and in the work area. When this had subsided, evaporation of 90 micrograms (μg) of plutonium was carried out, followed by the cleaning of pipets and evaporation of another sample. All these operations were under the hood. In these cases the peak count rate was on the order of 10 to 20 cpm. The 90- μg sample represents on the order of 6×10^6 cpm. In fact, it is questionable if any sample is lost, because the evaporation of the 92- μg sample is on the declining part of the peak. The last peak again is the burst of activity due to the manipulation of the spark chamber. Figure 7 is a plot similar to Fig. 6. Again large bursts of activity are released when the equipment or gloves are handled. The evaporation of a 100- μg sample shows no increase in activity. Apparently evaporation of the

sample does not contribute to the contamination of the box. The activity is scattered by handling of the chamber, which is very active from the settling of material on the walls and support pieces of the electrodes.

Emission spectroscopy can be used to determine many interesting properties of atoms and nuclei, but the largest use is in analytical spectroscopy.

The very complex spectra of the actinides and rare earths make the determination of trace impurities difficult. As an example, both thorium and uranium spectra have been measured, and each element has on the order of 20,000 lines. The need for exceedingly pure materials is of great importance to the nuclear applications of these elements, and this has placed a burden on the spectroscopists to search out new methods.

By increasing the resolution and dispersion of the spectrograph, certain gains may be realized, but these are definitely limited. While these gains obtained by using specially built large spectrographs may be several times what is normally achieved, this approach alone does not satisfy the needs.

One of the first successful attempts to increase the sensitivity of detection of impurities was perfected by Scribner and Mullin. In their method, called the carrier-distillation method, a few percent of gallium oxide is added to a 100-mg charge of uranium oxide. The effect as the arc is struck is to warm up the electrode system to the sublimation temperature of the gallium oxide. This temperature remains the same until all the gallium is gone, and then the temperature rises to the normal arc temperature. During the time of the distillation of the gallium, some thirty elements which have similar volatilization temperatures are also brought into the discharge. There is very little uranium in the arc at this lower temperature, whereas at the normal arc temperature the system is rich in uranium lines. Not all of the impurities are distilled, but a reproducible amount does come out, so that the method is

very satisfactory. This method has been extended to other matrix elements, and a variety of carriers have been used. This physical means of separating the impurities and matrix allows one to analyze for parts per million of impurities in a sample with very little handling of the sample.

Chemical methods are now becoming of interest. Extraction of impurities and matrix and the subsequent analysis of the impurity fraction allows for concentration gains which are only limited by distribution coefficients, and these may be very large. Cupferron and thenoyl trifluoroacetone (TTA) have been used for years in the analysis of actinides. Recently attention has been directed to the use of ion-exchange columns to analyze rare earths and actinides. This additional handling of samples requires rigid control over the impurities in the reagents and takes a longer time to analyze the sample; however, the gain in sensitivity is very striking. Detection of impurities in the range of parts per million is readily achieved.

The field of absorption spectroscopy has been very productive of information both in liquid and solid phases. The liquid includes the recent studies of molten salts of radioactive ions as well as the more conventional spectra of ions of various oxidation states in a variety of solvents.

Figure 8 shows a Beckman DU spectrophotometer attached to a gloved box. Figure 9 is a closer view of the enclosed portion. This is not the most desirable application, because the phototube compartment can become contaminated. Other forms consist of a well which replaces the sample compartment leaving both the spectrophotometer and phototube outside the box.

Recently I have been working with the absorption spectra of solids. In this work, one must prepare single crystals of good optical quality. The ions of interest are diluted into these matrix crystals. The most satisfactory matrix to date has been lanthanum trichloride -- this has a hexagonal

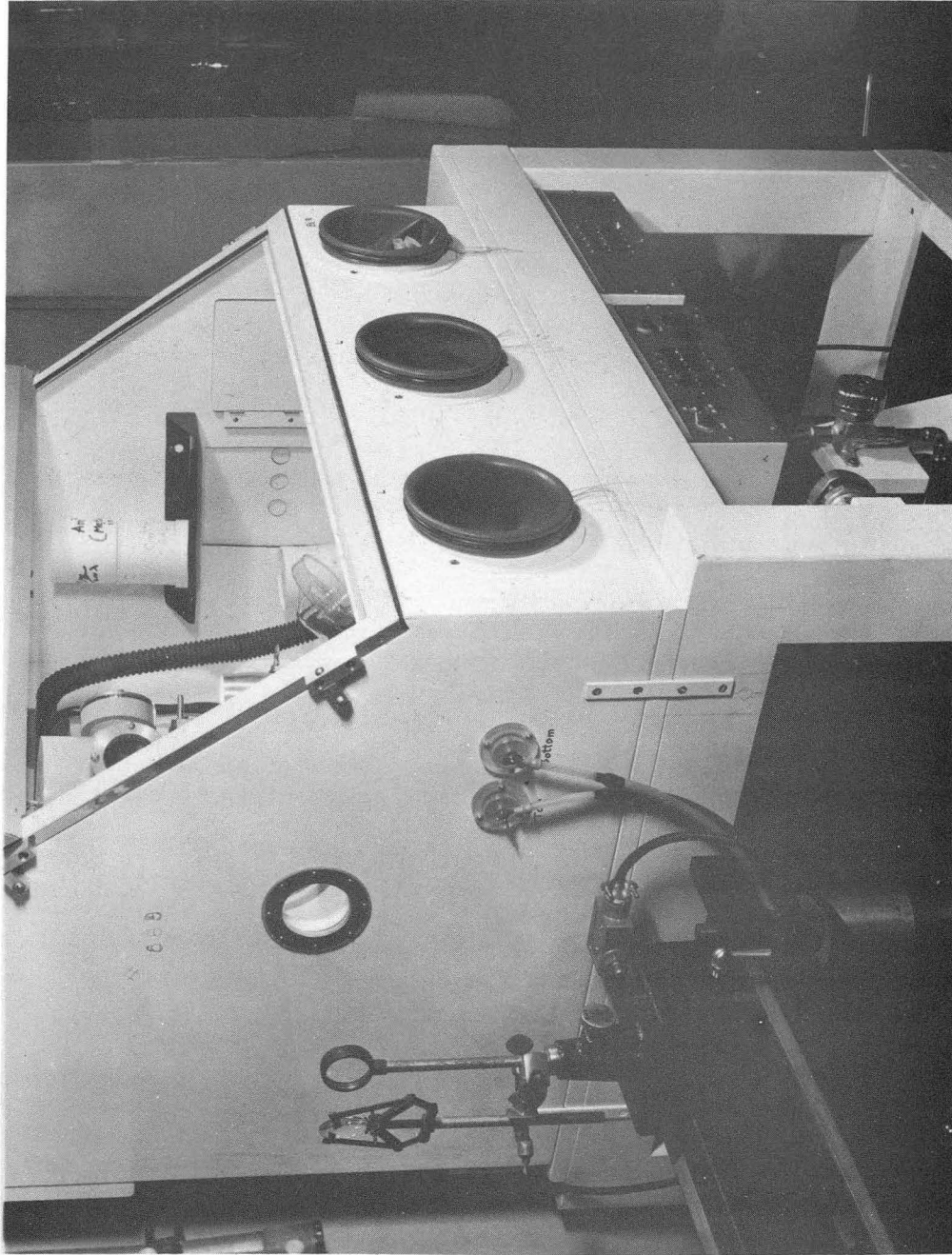
crystal structure. Single crystals of lanthanum trichloride have been prepared containing varying concentrations of uranium, neptunium, plutonium, americium, or curium. The concentration range is between 0.1 and 10%. The actinide chloride and lanthanum chloride are dried in a stream of hydrogen chloride at 250°C. The mixture is then placed in a quartz tube, evacuated, and sublimed at 1000°C. The sublimate is flowed into a side arm which is then sealed off and detached. The sidearm or crystal-growing tube is then lowered at 1/16 inch per hour through a furnace operating at 880°C. The tube after passing through the furnace contains a single crystal which is removed and cleaved and polished in the conventional manner. The crystal is oriented in a quartz absorption cell and spectra are taken. In this case a variety of experimental arrangements are used.

Polarization spectra and Zeeman spectra are usually taken at temperatures of liquid nitrogen, hydrogen, and helium. An analysis of this data allows one to determine the energy levels of the ions in the solid state.

These are but a few examples of how experiments may be performed with radioactive substances. With proper care in handling, and with time and a lot of patience, experiments of the most difficult nature can be carried out with safety to the experimenter.

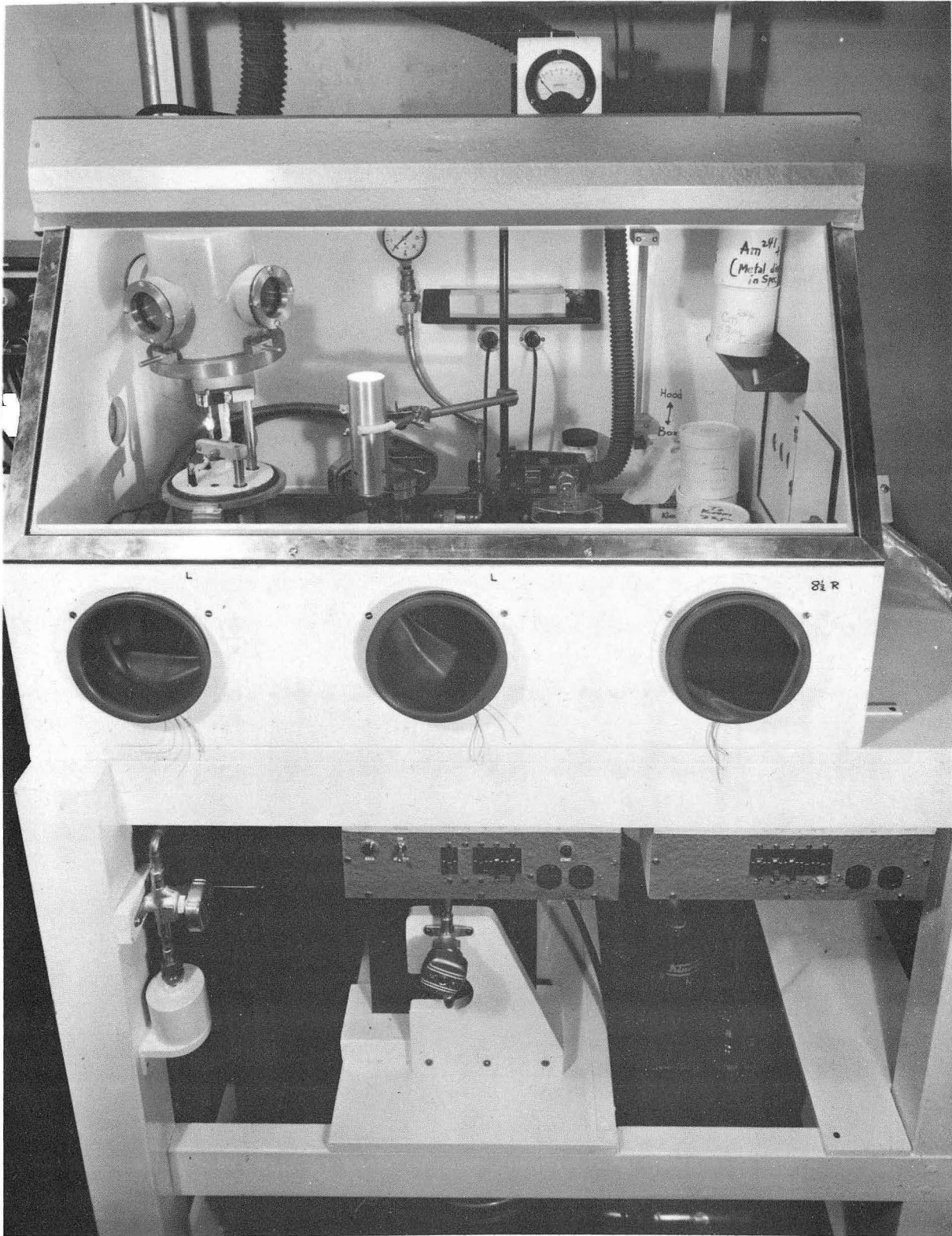
Figures

- Fig. 1. Gloved box positioned at the end of the optical bench of a spectrograph.
- Fig. 2. Front view of gloved box.
- Fig. 3. Interior view of box.
- Fig. 4. Close-up view of arc-spark chamber.
- Fig. 5. Diagram of continuous air monitor system.
- Fig. 6. Plot of counts per minute versus time for a series of experiments involving operations in a gloved box.
- Fig. 7. Additional operations showing contamination of air in a gloved box.
- Fig. 8. A view of a spectrophotometer attached to a gloved box.
- Fig. 9. Close-up view of sample compartment of the spectrophotometer.



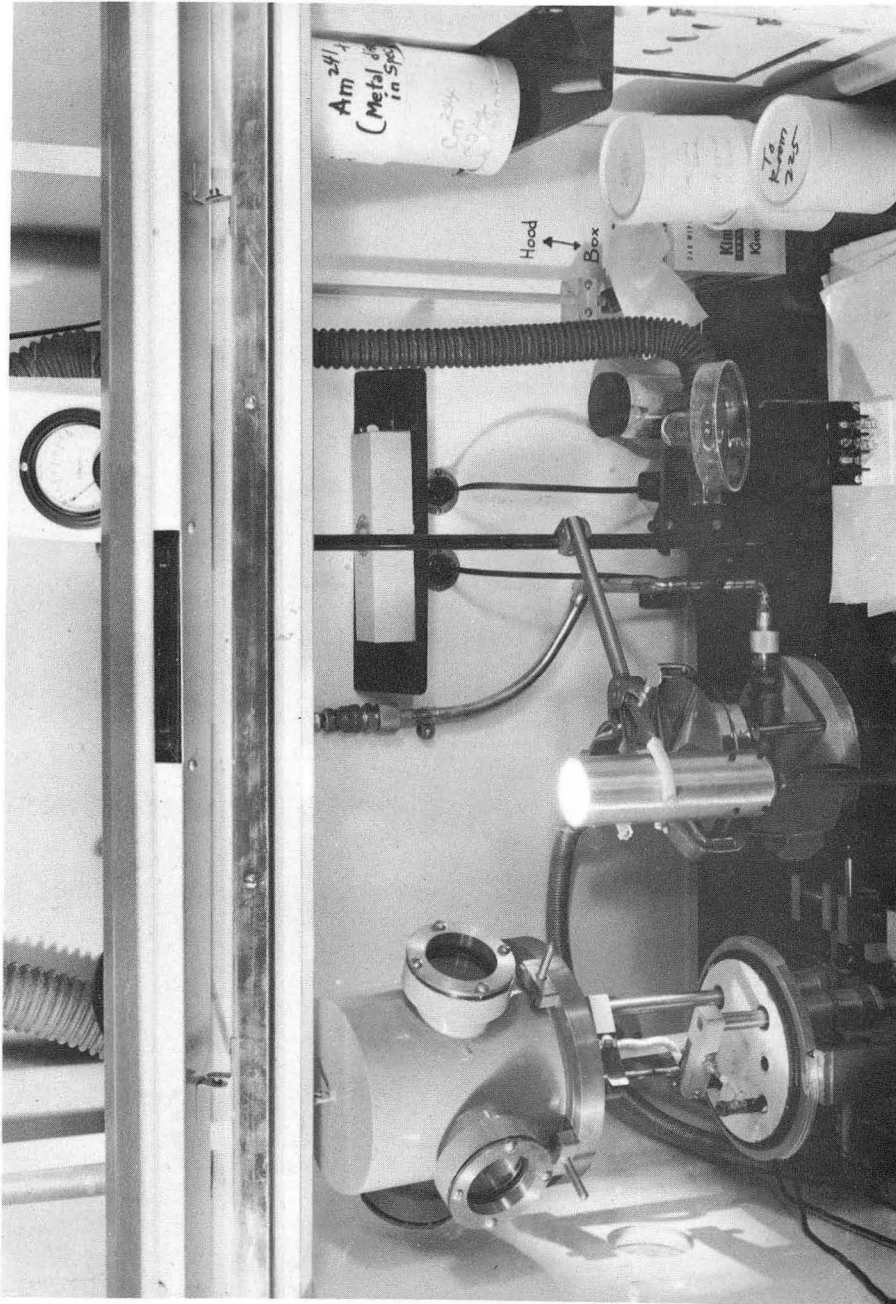
ZN-2190

Fig. 1



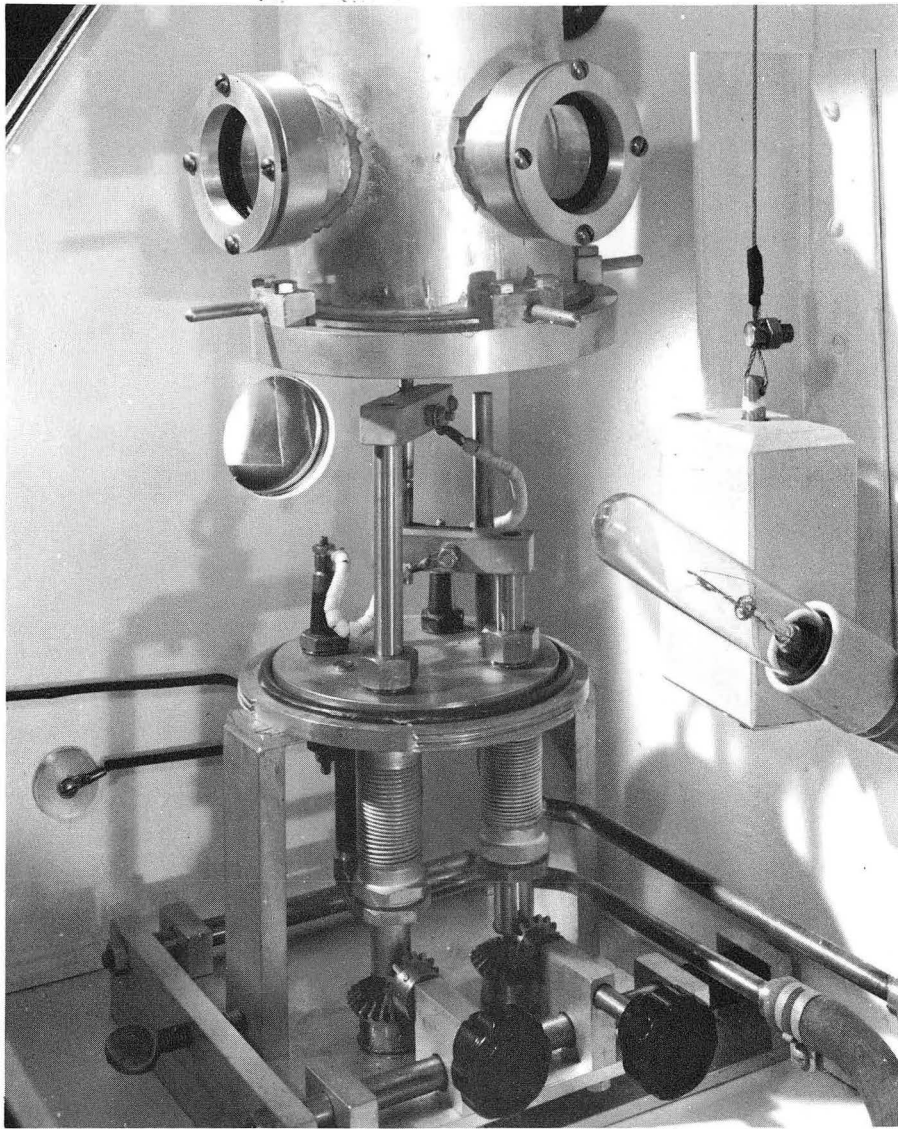
ZN-2191

Fig. 2



7.N-2188

Fig. 3



ZN-2192

Fig. 4

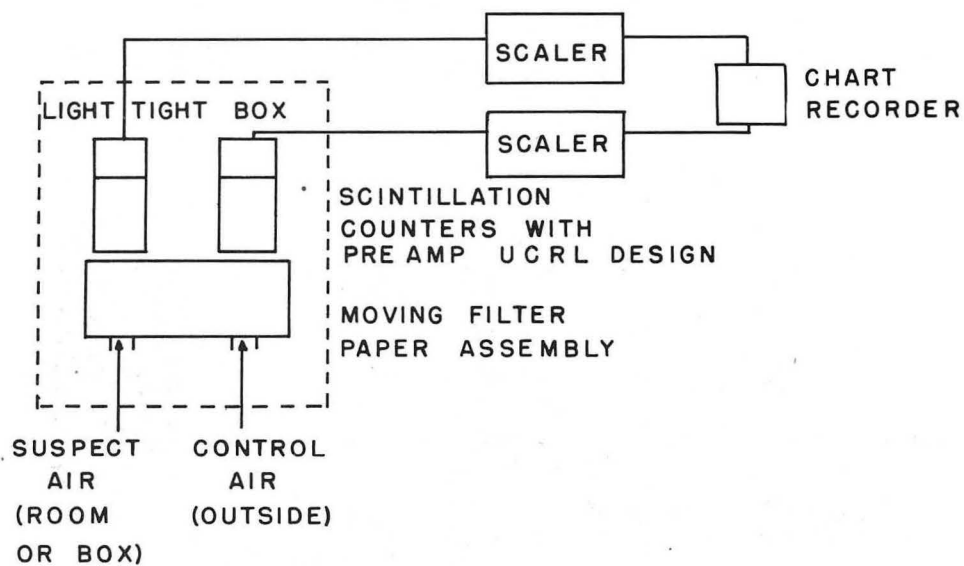


FIG. 1 AIR CONTAMINATION DETECTOR

MU 2168

Fig. 5

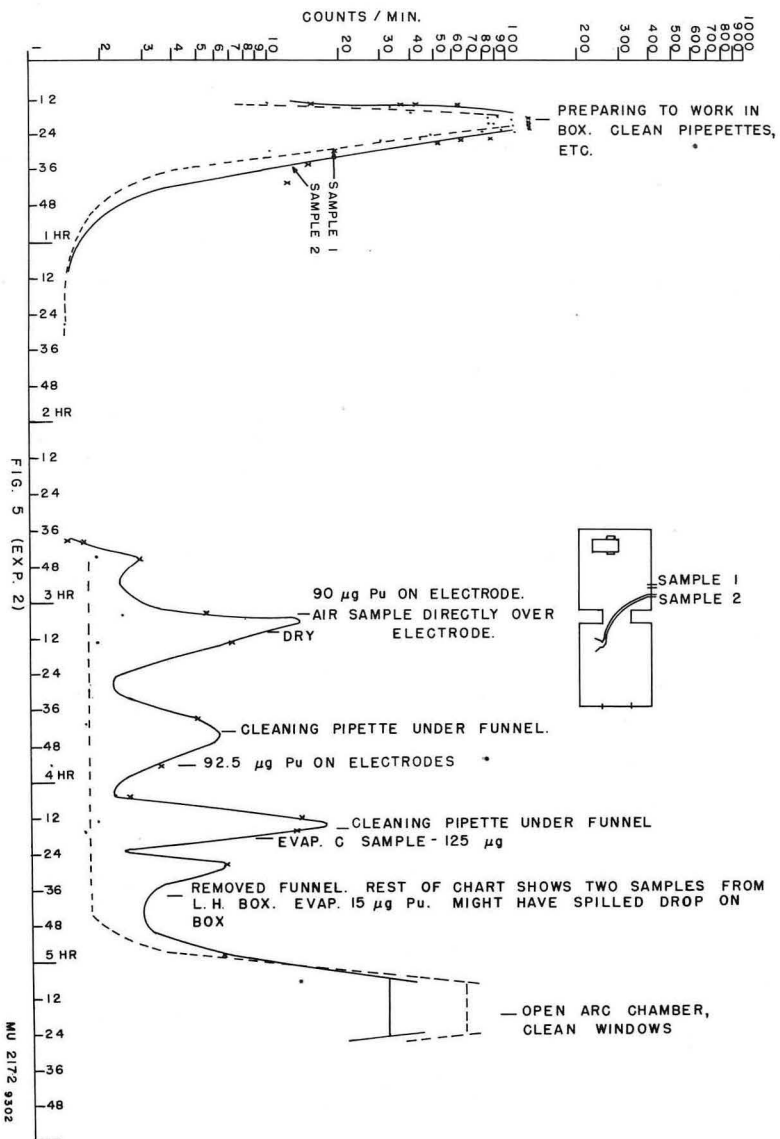


Fig. 6

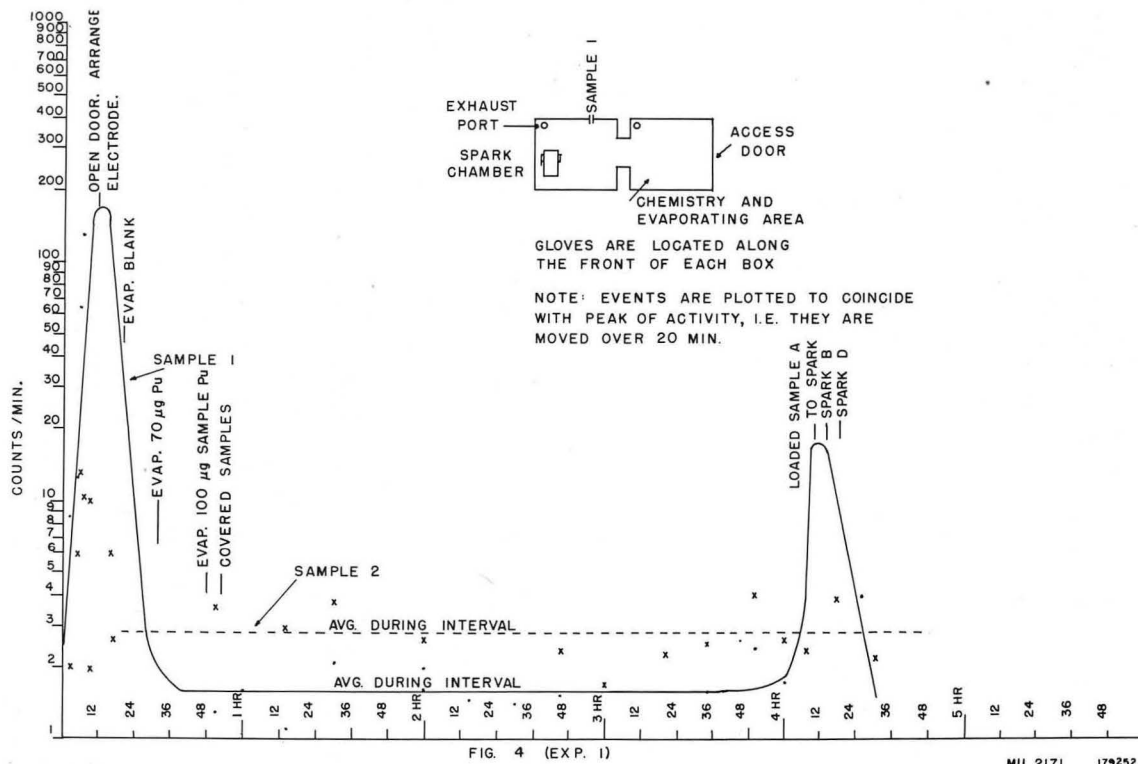
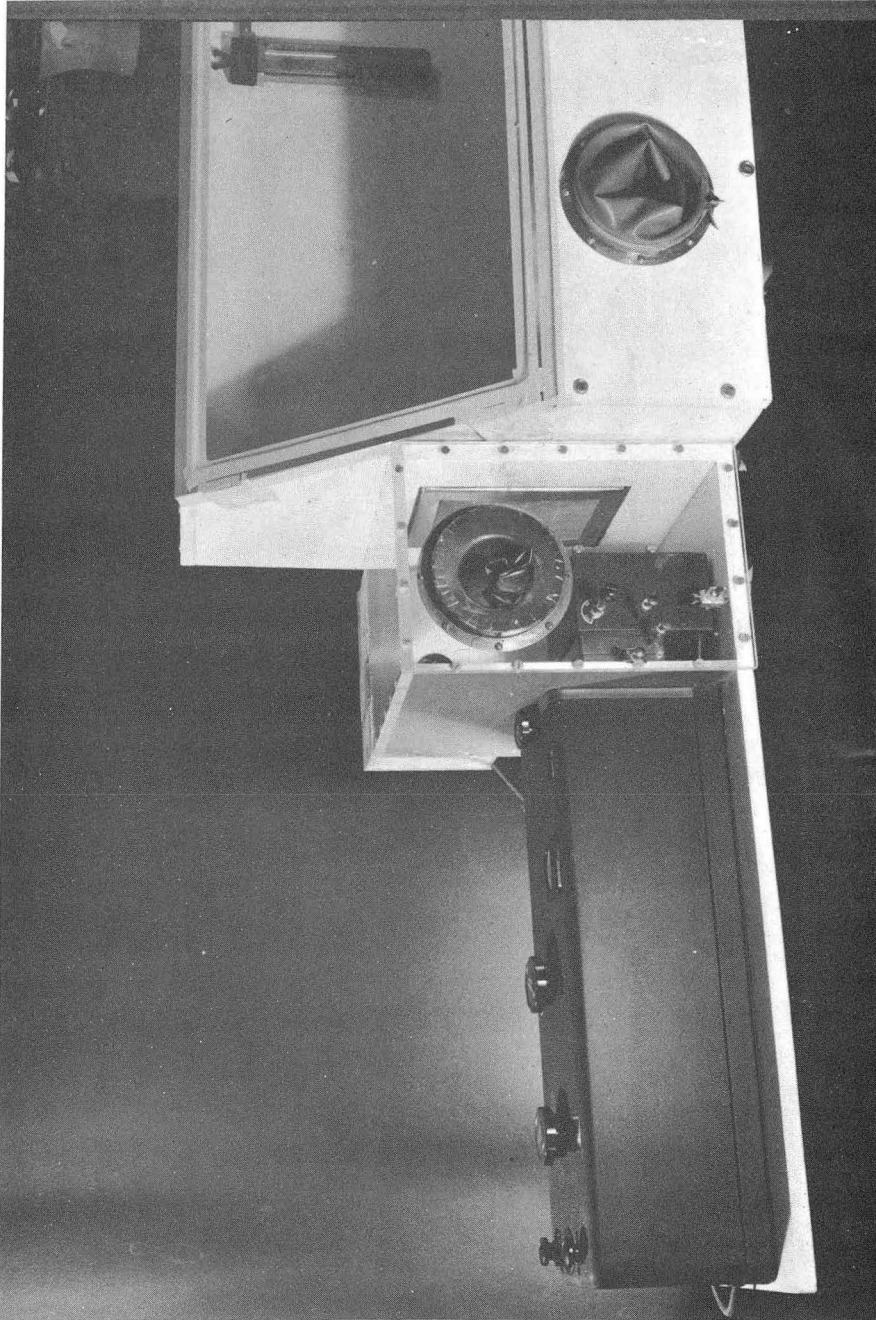
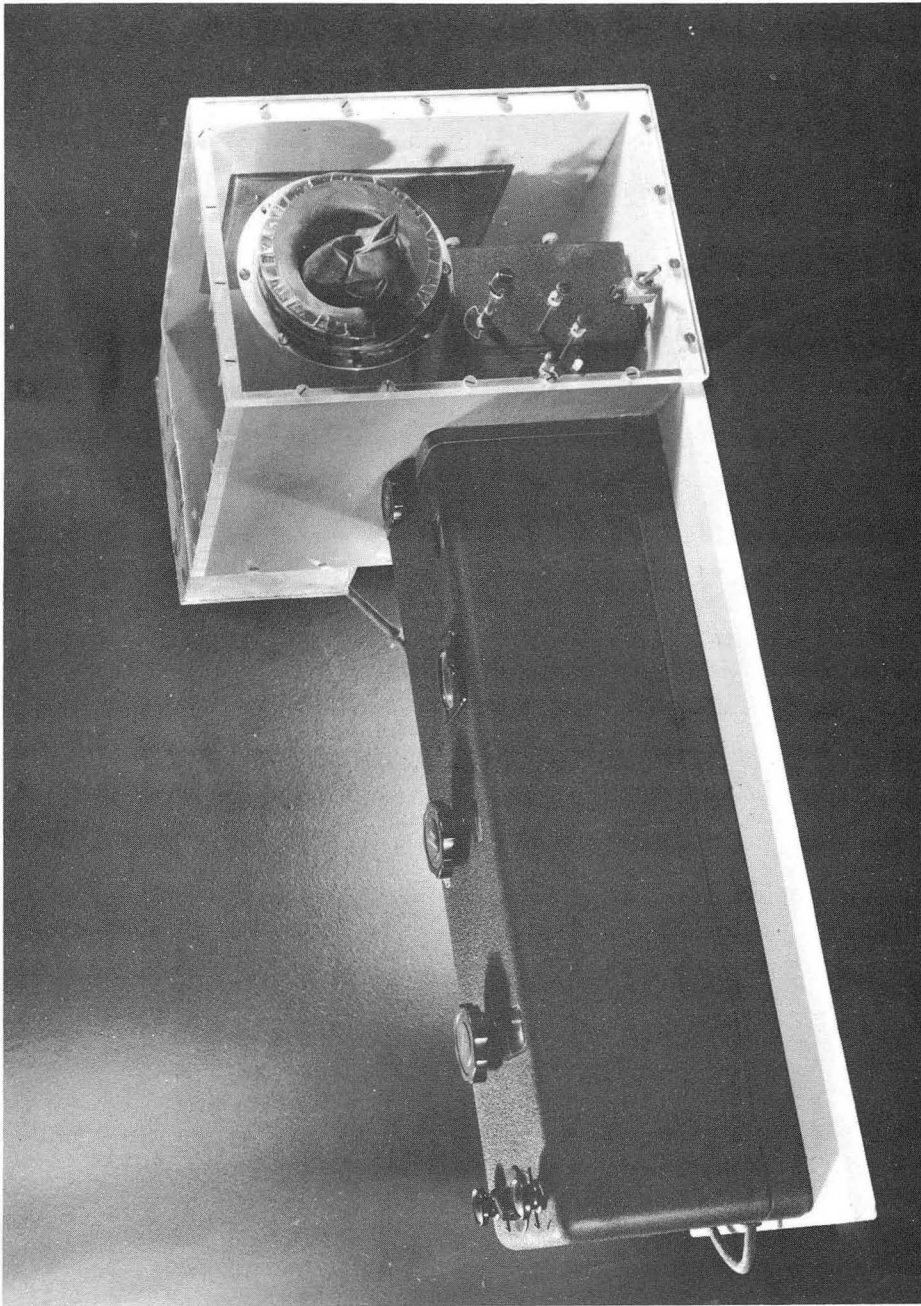


Fig. 7



ZN-2187

Fig. 8



ZN-2189

Fig. 9

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.