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EMISSION SPECTROSCOPY OF RADIOACTIVE ELEMENTS

John G. Conway

February 1960

Emission Spectroscopy of Radioactive Elements*

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Radioactive materials, which are available in limited quantities because of scarcity or radiation safety hazards, are especially suited to spectro-analytical methods.

The emission spectra of many radioactive elements, especially the actinide group, are very complex. Several ways have been used to overcome this difficulty; among these are higher resolution, physical separation and chemical separation of the impurity and the matrix.

Studies of the distribution and loss of sample during preparation and excitation can be easily made because of the high sensitivity of counting methods.

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

Spectroscopie d'émission des éléments radio-actifs

John G. Conway

Des matériaux radio-actifs disponibles en quantités limitées à cause de leur rareté et de leur danger radio-actif sont spécialement convenables aux méthodes spectro-analytiques. Les spectres d'émission, surtout ceux des Actinides, sont très compliqués. Plusieurs moyens ont été employés pour surmonter cette difficulté; parmi lesquels une résolution plus grande, une séparation physique et une séparation chimique des impuretés et des parents. Des études de distribution et de perte d'échantillon pendant la préparation et l'excitation peuvent être suivies facilement à cause de l'extrême sensibilité des méthodes de comptage.

Emissionsspektroskopie radioaktiver Elemente

John G. Conway

Radioaktive Materiale, welche wegen ihrer Seltenheit und ihrer radioaktiven Gefahr nur in begrenzter Menge zur Verfuegung stehen, eignen sich besonders gut fuer spektralanalytische Methoden. Die Emissionsspektren vieler, radioaktiver Elemente sind sehr kompliziert. Um diese Schwierigkeit zu ueberwinden, wurden verschiedene Schritte unternommen, wie z.B. hoehere Resolution, physische Trennung und chemische Trennung der Unreinheiten und der Matrix. Studien der Probenverteilung und des Probenverlustes waehrend der Zubereitung und der Erregung koennen leicht gemacht werden, dank der grossen Sensitivitaet der Zaehlmethoden.

EMISSION SPECTROSCOPY OF RADIOACTIVE ELEMENTS

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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, mendeleevium, 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 to 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 of 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 (TFA) 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.

Figure captions

- 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.

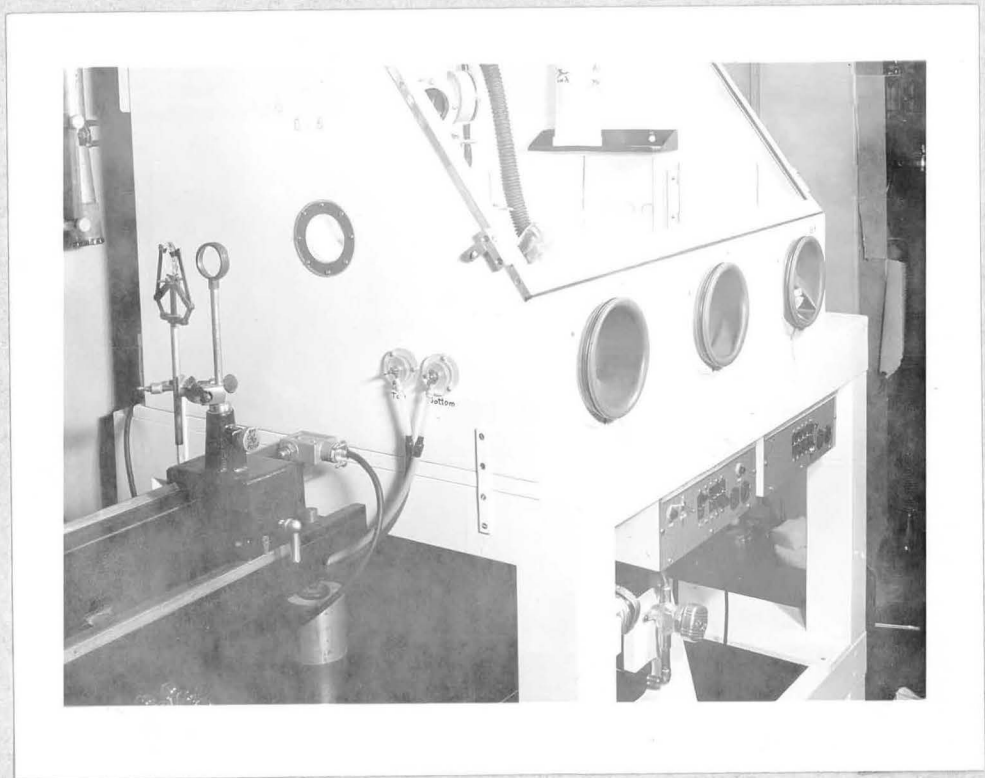


Fig 1

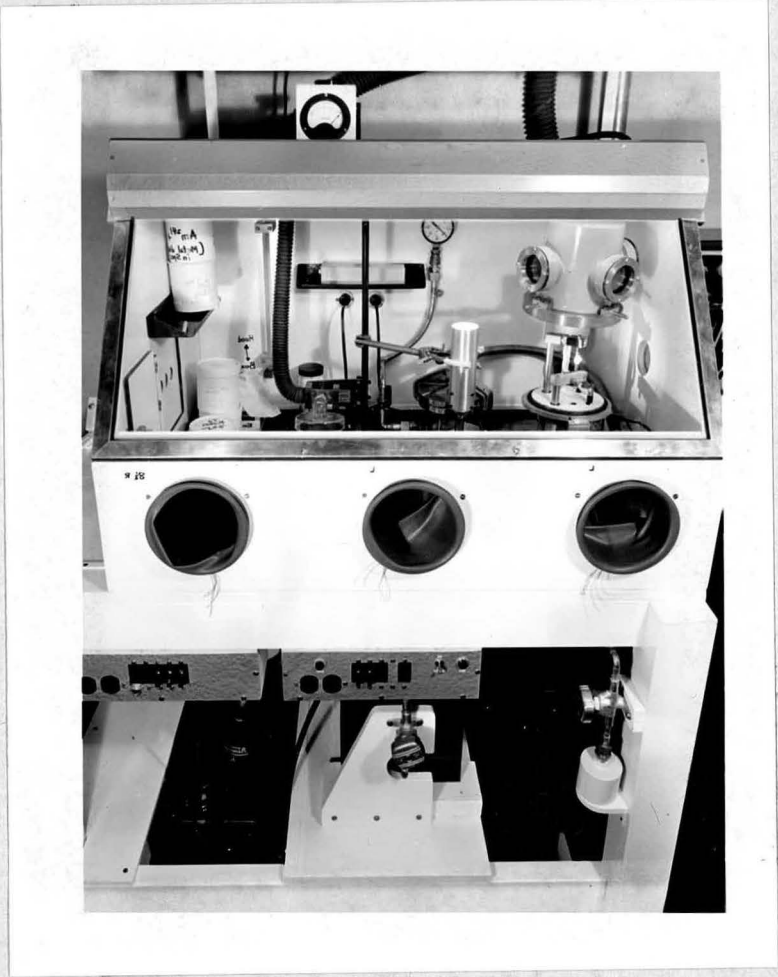


Fig 2



Fig 3

BOAL BOND

Patented

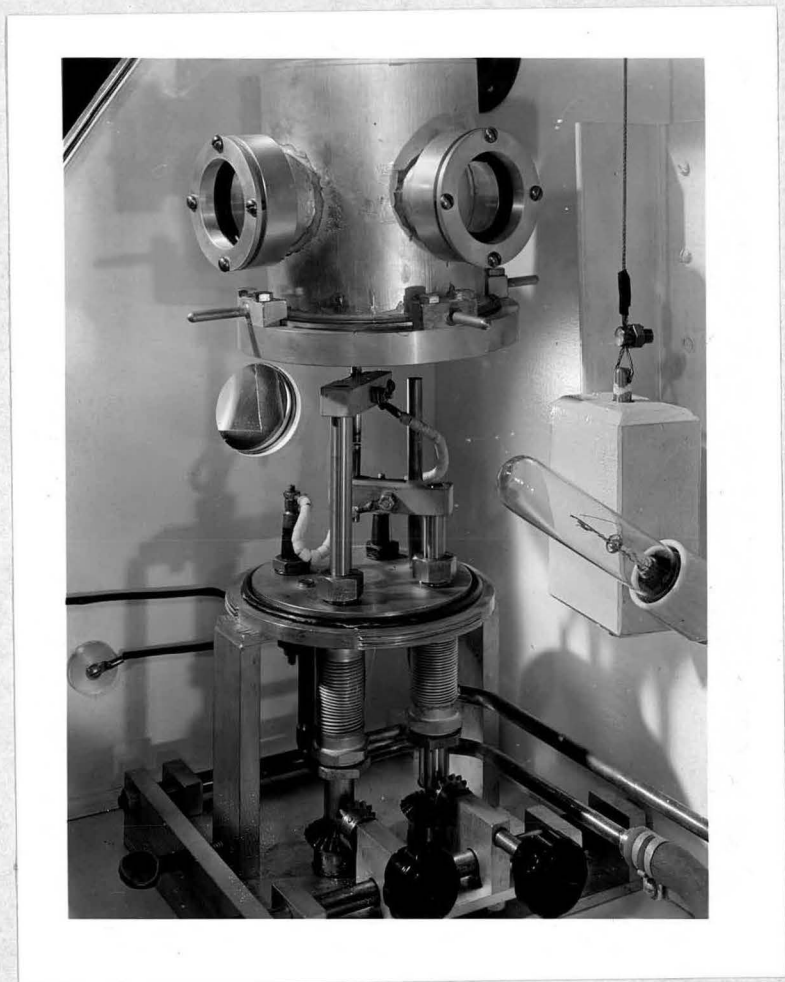


Fig 4

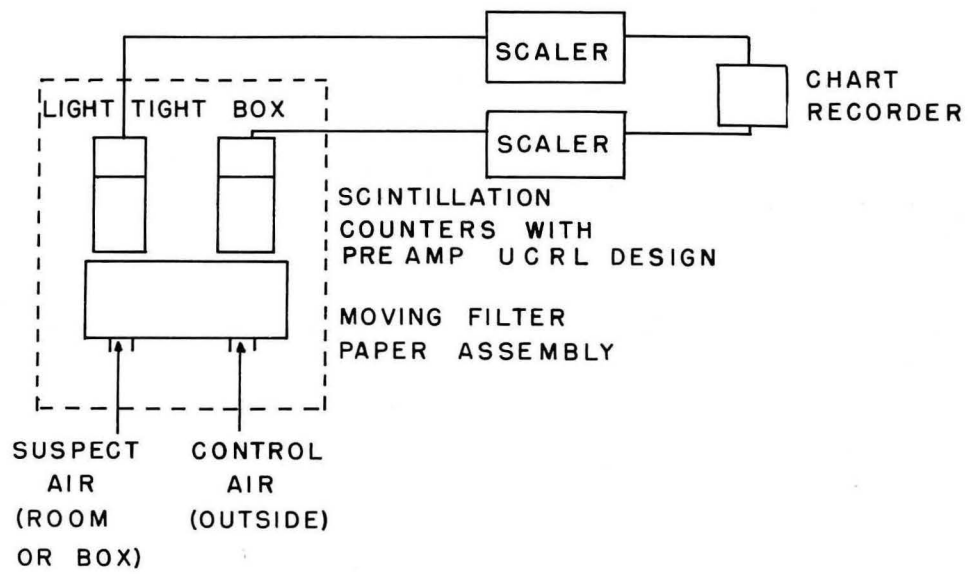


FIG. 1 AIR CONTAMINATION DETECTOR

Fig 5

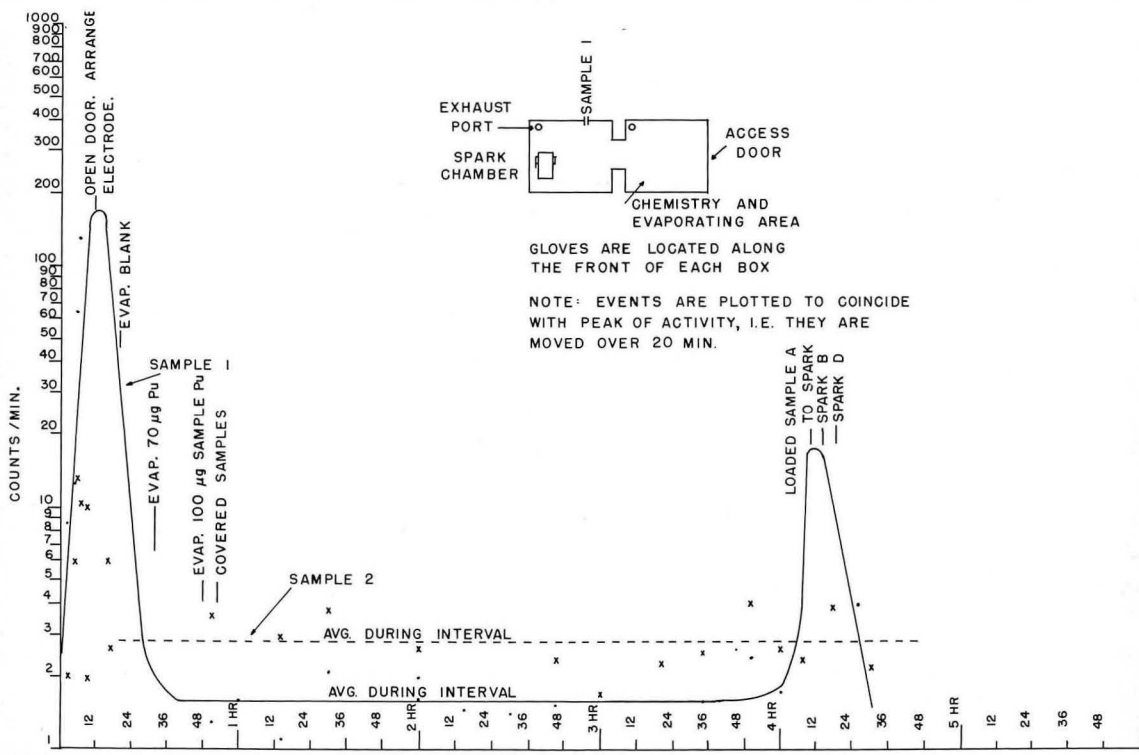


FIG. 4 (EX P. 1)

Fig 6

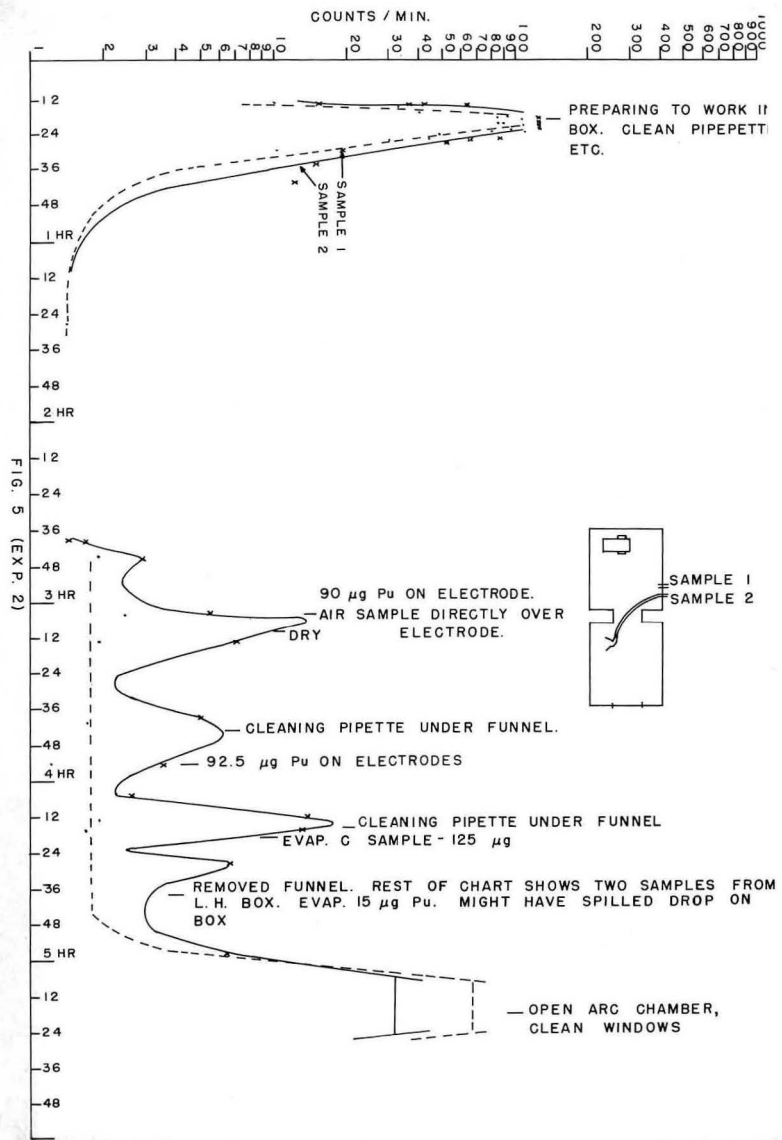


Fig 9