## THE DETERMINATION OF $Cu^{64}$ IN REACTOR EFFLUENT WATER BY ELECTRODEPOSITION

by

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## THE DETERMINATION OF $Cu^{64}$ IN REACTOR EFFLUENT WATER BY ELECTRODEPOSITION

### Introduction

The isotope $Cu^{64}$ is a major short half-life constituent of reactor effluent water. It has a half-life of 12.88 hours and decays by emission of a 0.571 Mev beta and 0.657 Mev positron to stable $Zn^{64}$ and stable $Ni^{64}$ respectively. Stability is achieved also by K capture. An accurate, rapid method for the quantitative determination of $Cu^{64}$ in reactor effluent water was desired for use as a routine control procedure. The procedure would require the separation of $Cu^{64}$ from $Mn^{56}$, $Na^{24}$, $P^{32}$, $As^{76}$, $Si^{31}$, $Ba^{139}$, $Sr^{91-92}$, and rare earths.

The quantitative determination of a radioisotope is facilitated greatly if the isotope is isolated in a thin layer of uniform thickness and defined area. Electrodeposition presents itself as an obvious method for obtaining this type of surface with isotopes which can be electrolytically deposited.

### Summary

It has been found possible by proper control of current, voltage, and solution concentration to electrolytically separate $Cu^{64}$ from the other radioisotopes in reactor effluent water. The procedure adopted consists of the addition of 10 mg of inert copper as a carrier to the reactor effluent water sample. The copper is then electroplated on a small stainless steel disk and the chemical and radiochemical yields determined from the weight of the carrier copper deposited and the counting rate of the sample.

It is apparent from the results obtained that isotopic exchange between the inert copper carrier and the radioactive copper in the sample goes to completion very rapidly in the plating solution.

Decay curves for more than thirty $Cu^{64}$ analyses of reactor effluent water samples have shown that radioactive contamination by other elements is negligible.

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The procedure offers a simple, accurate method for the isolation and measurement of $Cu^{64}$ activity in reactor effluent water.

By use of $Cu^{64}$ obtained from ORNL, self absorption and self scatter curves have been prepared for electrodeposited $Cu^{64}$. These curves were prepared for the correction of both first and second shelf standard mica window counter measurements. These data plus backscatter, counter geometry, source size, and air-mica window factors supply the necessary information for calculation of disintegration rates.

## Analytical Procedure

The method used for the analysis of $Cu^{64}$ in reactor effluent is a modification of a standard electrolytic analysis in which copper is plated from a 1% nitric acid, 2% sulfuric acid solution.[1]

The electroplating unit is a six-position Braun electro-analyzer equipped with stirring motors, rectified voltage supply, and the necessary resistors and meters for voltage and current control. The plating cells consist of 22 ml screw cap vials with the bottoms cut off. A cathode plate with an axial extension is inserted in the bakelite screw cap, the extension passing through a hole drilled through the cap through which electrical connection is made. Upon this cathode plate the actual cathode is placed. The cathode is a stainless steel disk 22 mm in diameter and 0.01" thick. A gasket over the disk seals the cell upon assembly and defines the area of deposition (1.89 $cm^2$). A photograph of a disassembled and assembled cell is shown in Figure 1.

An 18 gage straight platinum wire is used as the stirring anode.

The stainless steel disks are washed with water, acetone, then dried 10 minutes at 110°C, cooled in a desiccator, and accurately weighed. The electroplating vessel is assembled as described above. The vessel is placed in position on the Braun electroplating apparatus and 12.5 ml reactor effluent water, two ml

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Figure 1. Electrodeposition Cell

acid solution (0.8N HNO₃ and 3.6N H₂SO₄) are added. The vessel is then raised until the anode is about 1/2 inch above the cathode. The stirring motor is started and the direct current applied. The voltage is adjusted to 3.5-4.0 volts and the current to 20 milliamperes. After 2-3 hours of plating the electroplating vessel is removed, the solution poured into a beaker and the cathode washed with several portions of distilled water, then with acetone.* The copper plated stainless steel cathode is dried 10 minutes at 110°C, cooled in a desiccator, weighed, and counted. The chemical yield is determined and the counting rate corrected by dividing by the chemical yield.

## Results

To determine the reproducibility that can be expected in the $Cu^{64}$ analysis, a number of analyses were performed on each of several reactor effluent water samples. The exact conditions of the experiment and results obtained are discussed in the following paragraphs. The concentration of the carrier solution used was 9.8690 mg/ml, except as otherwise noted.

In Table I are presented results from an experiment in which 4.93 mg of copper carrier was used and a two hour plating time employed. Current was 20 ma at 4 volts.

### TABLE I

| Sample Number | mg of Carrier Deposited | c/m | Time Counted | (Corrected for Decay and Chemical Yield) Calculated c/m/sample |
|---|---|---|---|---|
| 1 | 4.1 | 2550 | 1500 | $3.06 \times 10^3$ |
| 2 | 3.1 | 1948 | 1510 | $3.12 \times 10^3$ |
| 3 | 3.4 | 2069 | 1525 | $3.07 \times 10^3$ |
| 4 | 3.6 | 2137 | 1535 | $3.02 \times 10^3$ |

Average = $3.07 \times 10^3$
Standard Deviation = 1.2%

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* In removing the electroplating vessel, the current should not be broken until the vessel has been released and the electrolyte is ready to be poured into a beaker. The vessel is then immediately washed with distilled water from a wash bottle. This prevents the copper from redissolving.

In a second series of five analyses under essentially the same conditions, only fair precision was obtained. Current was 20 ma at 4 volts. Carrier used was 4.93 mg $Cu^{++}$. Results are shown in Table II.

### TABLE II

| Sample Number | mg of Carrier Deposited | c/m | Time Counted | (Corrected for Decay and Chemical Yield) Calculated c/m/sample |
|---|---|---|---|---|
| 1 | 4.3 | 3926 | 1415 | $4.51 \times 10^3$ |
| 2 | 3.3 | 2834 | 1425 | $4.03 \times 10^3$ |
| 3 | 3.8 | 3168 | 1435 | $4.18 \times 10^3$ |
| 4 | 3.6 | 2724 | 1445 | $3.89 \times 10^3$ |
| 5 | 4.0 | 3442 | 1520 | $4.49 \times 10^3$ |

Average $4.21 \times 10^3$

Standard Deviation = 6.1%

In Table III are presented results obtained when a three hour plating time was employed. Current was maintained at 20 ma. Carrier used was 4.93 mg $Cu^{++}$.

### TABLE III

| Sample Number | mg of Carrier Deposited | c/m | Time Counted | (Corrected for Decay and Chemical Yield) Calculated c/m/sample |
|---|---|---|---|---|
| 1 | 4.1 | 1736 | 1515 | $2.09 \times 10^3$ |
| 2 | 4.1 | 1716 | 1525 | $2.08 \times 10^3$ |
| 3 | 4.3 | 1733 | 1535 | $2.02 \times 10^3$ |
| 4 | 4.0 | 1558 | 1545 | $1.97 \times 10^3$ |
| 5 | 4.1 | 1569 | 1600 | $1.96 \times 10^3$ |
| 6 | 4.2 | 1786 | 1620 | $2.19 \times 10^3$ |

Average $2.05 \times 10^3$

Standard Deviation = 3.0%

Only slight improvement in yield was achieved when overnight plating was attempted. In Table IV samples 1-5 were plated for 2.5 hours at 20 ma and 3.5 volts. Samples 6-7 were plated overnight under otherwise the same conditions employed for samples 1-5. Carrier used was 4.93 mg $Cu^{++}$.

## TABLE IV

| Sample Number | mg of Carrier Deposited | c/m | Time Counted | (Corrected for Decay and Chemical Yield) Calculated c/m/sample |
|---|---|---|---|---|
| 1 | 3.9 | 1945.6 | 1425 | $2.49 \times 10^3$ |
| 2 | 4.0 | 2118.6 | 1435 | $2.67 \times 10^3$ |
| 3 | 4.0 | 1927.2 | 1445 | $2.46 \times 10^3$ |
| 4 | 3.9 | 1864.2 | 1455 | $2.39 \times 10^3$ |
| 5 | 4.3 | 2088.5 | 1505 | $2.52 \times 10^3$ |
| 6 | 4.6 | 868.6 | 0915 | $2.59 \times 10^3$ |
| 7 | 4.4 | 806.6 | 0925 | $2.53 \times 10^3$ |

Average   $2.52 \times 10^3$
Standard Deviation = 1.1%

A standard deviation of 2.2% for three samples was obtained when 9.87 mg $Cu^{++}$ per sample was used. Current and voltage were 20 ma and 3.5 volts, respectively. Results are shown in Table V.

## TABLE V

| Sample Number | mg of Carrier Deposited | c/m | Time Counted | (Corrected for Decay and Chemical Yield Calculated c/m/sample |
|---|---|---|---|---|
| 1 | 7.7 | 2054.5 | 1455 | $2.74 \times 10^3$ |
| 2 | 7.7 | 2039.1 | 1510 | $2.76 \times 10^3$ |
| 3 | 8.7 | 2162.5 | 1520 | $2.62 \times 10^3$ |

Average   $2.71 \times 10^3$
Standard Deviation = 2.2%

Very good precision was obtained for six samples, each containing 10.27 mg of $Cu^{++}$. Plating was for 2 hours at 20 ma and 3.5 volts. Results are presented in Table VI.

## TABLE VI

| Sample Number | mg of Carrier Deposited | c/m | Time Counted | (Corrected for Decay and Chemical Yield) Calculated c/m/sample |
|---|---|---|---|---|
| 1 | 8.5 | 1575.3 | 1500 | $1.90 \times 10^3$ |
| 2 | 8.0 | 1473.6 | 1510 | $1.91 \times 10^3$ |
| 3 | 8.3 | 1583.8 | 1525 | $2.01 \times 10^3$ |
| 4 | 8.8 | 1597.0 | 1535 | $1.93 \times 10^3$ |
| 5 | 7.4 | 1382.4 | 1545 | $2.01 \times 10^3$ |
| 6 | 7.6 | 1397.6 | 1555 | $1.99 \times 10^3$ |

Average　　$1.95 \times 10^3$
Standard Deviation = 0.24%

Decay measurements were made on at least one sample from each of the above tables. All decay measurements show a high radiochemical purity. A typical decay curve for $Cu^{64}$ electroplated from reactor effluent water is shown in Figure 2.

### Self-Absorption and Self-Scatter Determination

Approximately 50 mg of a $Cu^{64}$ sample obtained from ORNL was dissolved in 0.1 ml of conc. $HNO_3$. This solution was diluted to 10 ml with distilled water and used as a source of $Cu^{64}$ for making subsequent dilutions.

A 0.250 ml portion of the $Cu^{64}$ solution was placed in a 50 ml volumetric flask and diluted to 50 ml with an inert copper solution (9.8690 mg copper per ml in $N$ $HNO_3$). This solution was used as a source of spiked copper in preparing a series of copper plated stainless steel disks for self-absorption and self-scatter measurements.
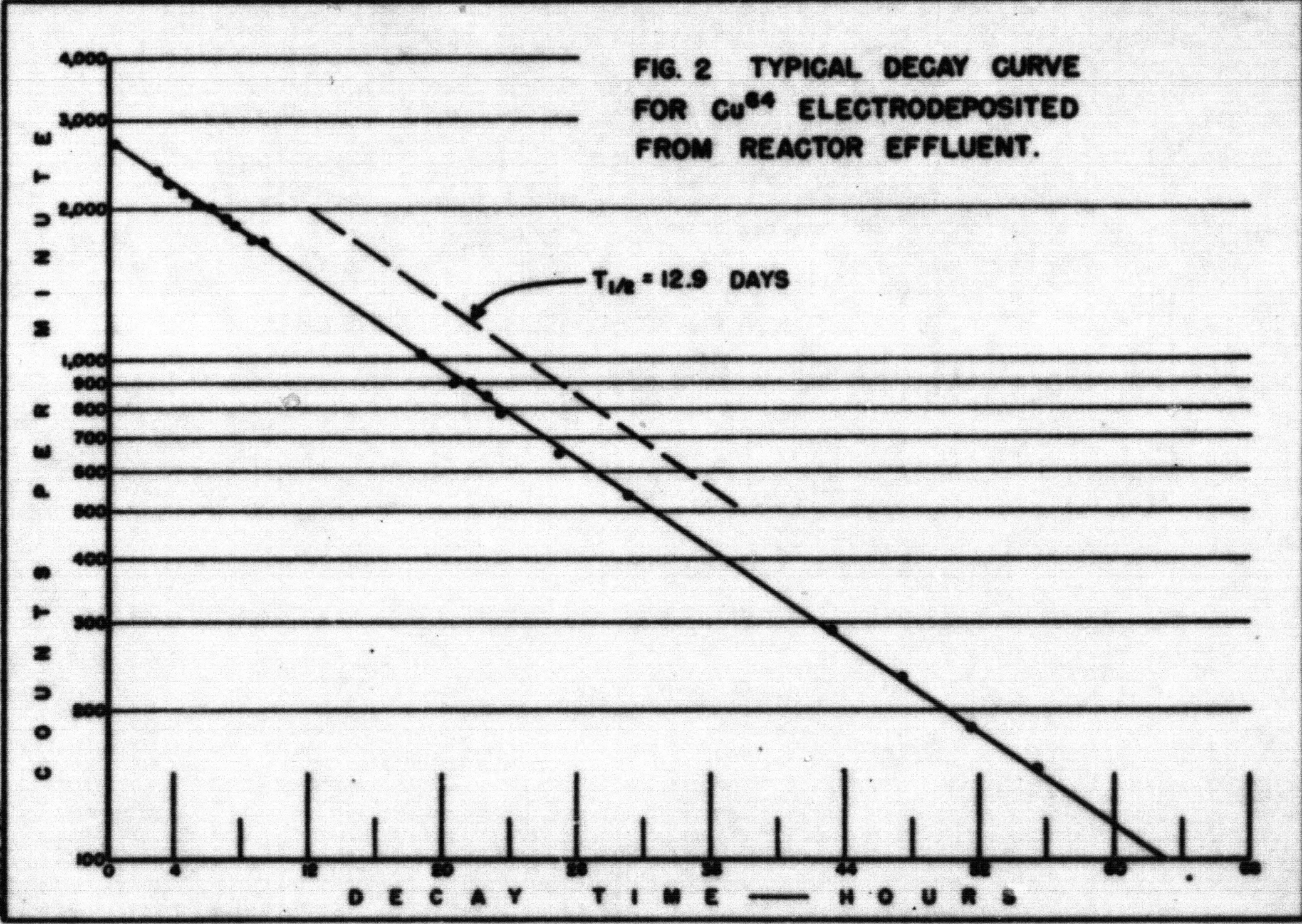
A 0.250 ml portion of the original $Cu^{64}$ solution was diluted to 50 ml with distilled water. This solution was used to prepare carrier-free spread sources of the same shape and area as the electroplated sources. These carrier-free spread sources provided a method of determining the counting rate that the electroplated sources would exhibit if no carrier were present, and thus give a measure of the true activity density of the electroplated copper samples.

FIG. 2 TYPICAL DECAY CURVE FOR $Cu^{64}$ ELECTRODEPOSITED FROM REACTOR EFFLUENT.

$T_{1/2} = 12.9$ DAYS

Using the spiked copper solution, a series of copper plated stainless steel disks was prepared. The diameter of the plated surface was 1.55 cm giving a circular area of 1.89 $cm^2$. The weight of spiked copper electrodeposited varied from 1 to 23 mg per disk.

The electroplated copper sources along with the carrier-free spread sources were counted on the first and second shelves of a standard mica window counter.

The ratio of the observed specific activity $C_{obs}$, to the true activity density $C_1$ (determined from the carrier-free sources) gives the combined self-absorption and self-scatter correction factor for the sample:

$$F_{ssa} = \frac{C_{obs}}{C_1} \quad F_{ssa} = \text{self-absorption and self-scatter correction factor.}$$

Figures 3 and 4 give the value of the self-absorption, self-scatter correction factor as a function of sample thickness for copper.

## Discussion

In beginning the work on $Cu^{64}$ determination, it was considered advantageous to use a very small amount of carrier, about 3-4 mg. This, it was thought, would minimize self-absorption, giving a higher counting rate and thus increase the accuracy of the determination. It can readily be seen from the self-absorption and self-scatter curves, however, that the counting rate is actually increased by increasing the amount of carrier up to about 3.5 $mg/cm^2$ (six to seven mg of carrier per plate). This phenomenon is due to self-scatter and has been shown to exist for several other radioisotopes by Nervik and Stevenson[2].

In the case of $Cu^{64}$ it is now apparent that there are two disadvantages in depositing only 3-4 mg of carrier. First, the self-absorption, self-scatter correction curve is so steep in this region that it is difficult to be certain of the correction factor. Second, the accuracy in weighing with the ordinary analytical balance used in this work is at best ± 0.05 mg. For a 3 mg sample this would allow a ± 1.5 - 2% weighing error on each of the two weighings
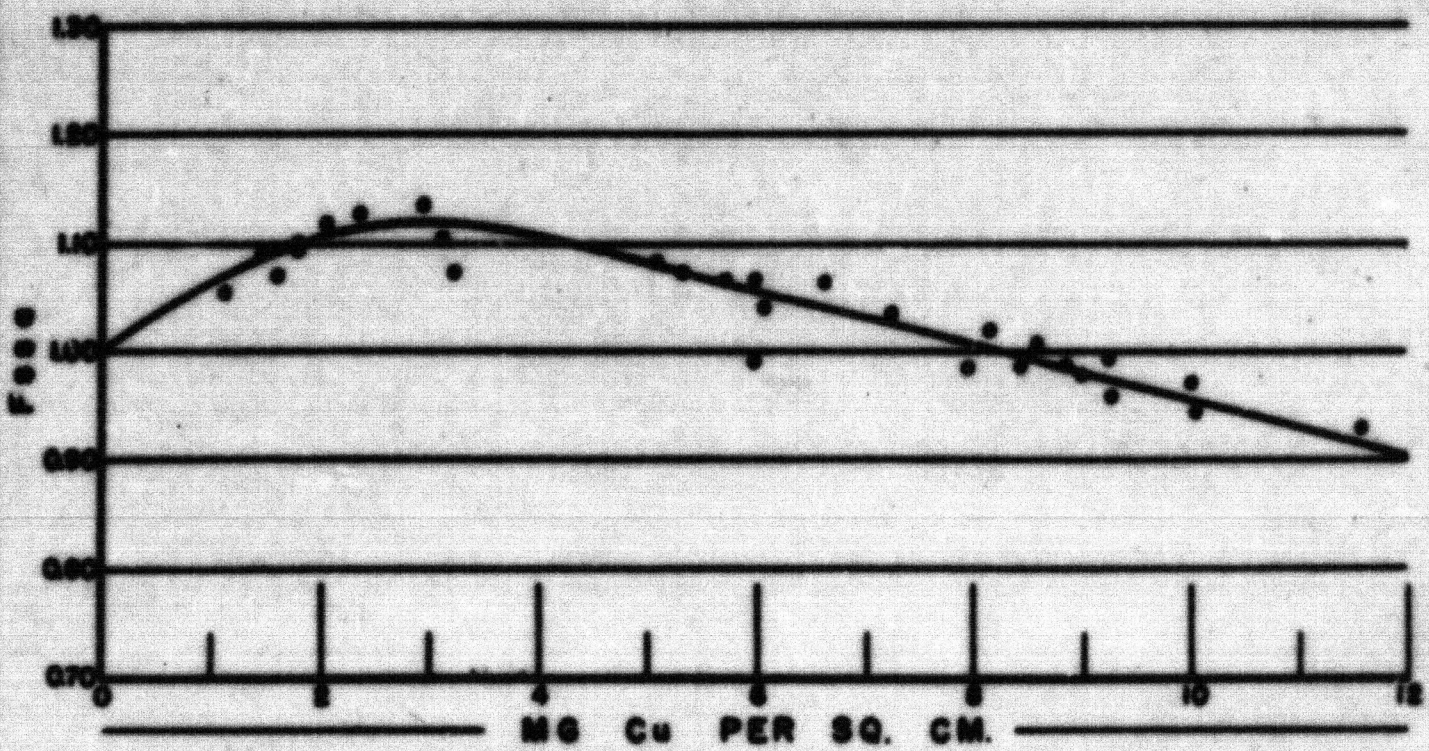
FIG. 3  CORRECTION FACTOR, $F_{sse}$, AS A FUNCTION
OF SAMPLE THICKNESS. ELECTROPLATED $Cu^{64}$
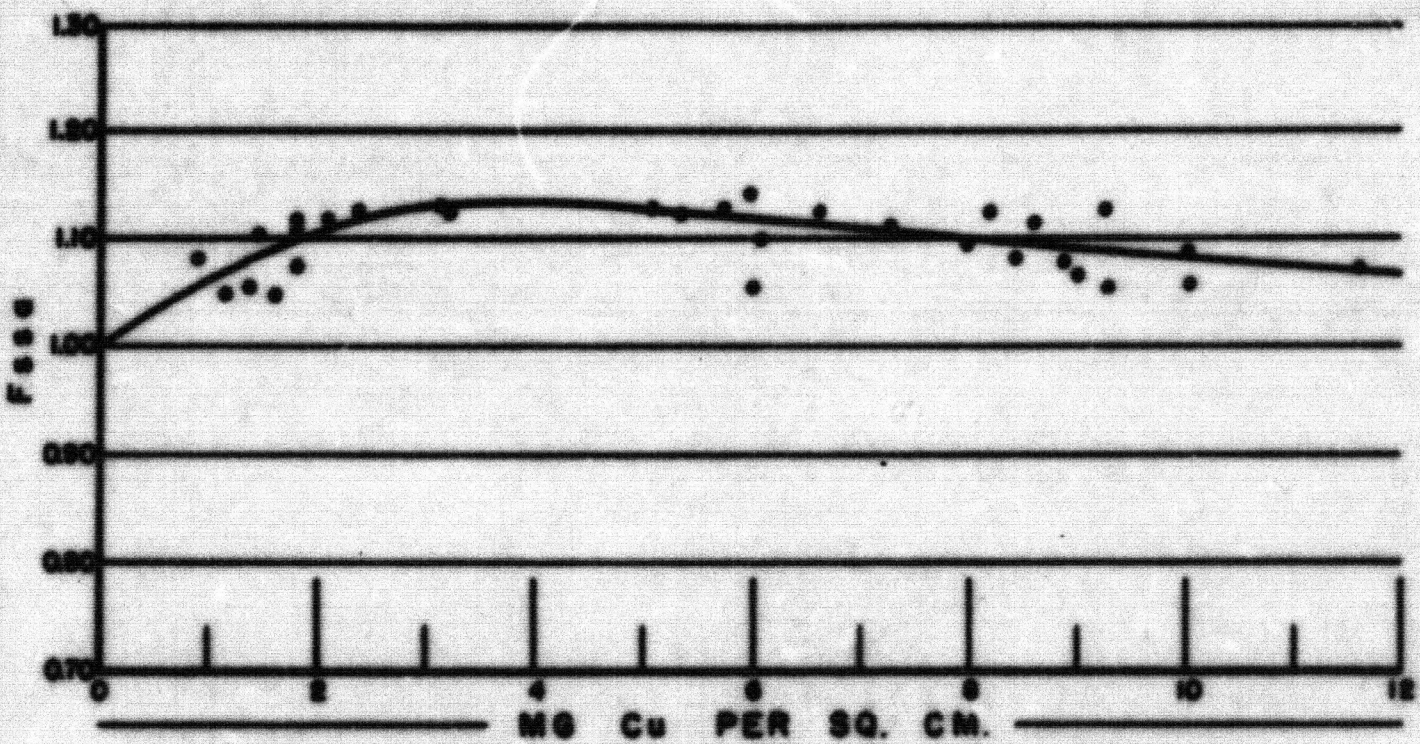WITH CARRIER COPPER. FIRST SHELF OF MICA
WINDOW COUNTER.



FIG. 4  CORRECTION FACTOR, $F_{sse}$, AS A FUNCTION
OF SAMPLE THICKNESS. ELECTROPLATED $Cu^{64}$
WITH CARRIER COPPER. SECOND SHELF OF MICA
WINDOW COUNTER.

necessary. By using enough carrier to electrolytically deposit 7.5 mg or more, the accuracy of the self-absorption and self-scatter correction factor can be increased and the percent weighing error decreased. Since the rate of electro-deposition decreases with decrease in concentration of the copper, it is apparent that the time required for the determination could also be reduced by using a larger amount of carrier.

A thorough study has not been made as to the effect of voltage and amperage increase on the radiochemical purity of copper plated from reactor effluent samples. It was noted however, that at potentials above 4 volts and current flow greater than 20 ma the radiochemical purity of the electrodeposited $Cu^{64}$ was decreased.
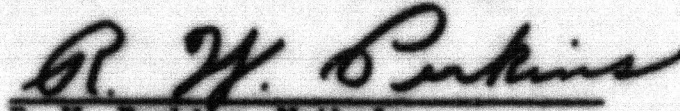
It is evident from the results obtained in $Cu^{64}$ analyses that essentially complete isotopic exchange does take place. This is borne out by the fact that the calculated counting rate per sample was not dependent on the amounts of carrier deposited, except as reflected by the self-absorption, self-scatter correction.

Efforts to electrodeposit all of the carrier added in $Cu^{64}$ analysis have proved unsuccessful. It may be noted that in samples 6 and 7 of Table IV, only about 95% of the carrier was electrodeposited during plating overnight.

## Conclusion

A suitable electrodeposition method has been developed for the isolation and determination of $Cu^{64}$ in reactor effluent water. Activity measurements on repli-cate samples have been shown to have a maximum standard deviation of 2.4% when 7 to 8.5 mg of copper are plated from an electrolyte containing 10 mg of carrier.

Self-absorption and self-scatter correction curves have been prepared for first and second shelf mica window counter measurements of $Cu^{64}$ activity.

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## ABSTRACT

An analytical method for $Cu^{64}$ in reactor effluent has been studied based upon electrodeposition of the active copper with inert copper carrier. A two hour plating time was employed at a current density of 10 ma/sq cm and four volts across the cell. A stainless steel cathode plate was used. Carrier yields of greater than 80% were obtained with a standard deviation of the yield-corrected counting rate as low as 0.24%. Very little, if any, contamination by other radioactive elements present was shown by decay curve studies. Self-absorption and self-scatter factors to correct the counting rate were obtained.

References

(1) Kolthoff, I. M., and Sandell, E. B., *Textbook of Quantitative Inorganic Analysis*, New York: The Macmillian Company, 1947; pp. 420-425.

(2) Nervik, W. E., and Stevenson, P. C., Self-Scattering and Self-Absorption of Betas by Moderately Thick Samples, *Nucleonics* Vol. 10, No. 3 (March 1952); pp. 18-22.

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