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# RAPID DETERMINATION OF ALUMINIUM IN BERYLLIUM METAL BY CATHODE RAY POLAROGRAPHY

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## ABSTRACT

A rapid method is presented for the determination of aluminium in beryllium metal by cathode ray polarography using the dye Superchrome Garnet Y. A mercury cathode electrolysis is used to remove heavy metal impurities, but the need for a separation of aluminium from beryllium is avoided. A single determination requiring a 100 mg sample may be completed in little over an hour, with normal polarographic precision.

## CONTENTS

## 1. INTRODUCTION

Despite the rapidly increasing use of beryllium in the atomic energy field, no completely satisfactory procedure has been published for the determination of aluminium, one of the impurities analysed for in beryllium metal most frequently. The principal methods in use appear to be the 8-hydroxyquinoline gravimetric (Melick 1958, U.S.A.E.C. 1958), spectrographic (Smythe and Whittem, 1961), and a polarographic procedure using Solochrome Violet RS (5–sulpho–2–hydroxy–benzene–azo–2–naphthol) (Perkins and Reynolds, 1958). The gravimetric method suffers from the disadvantage of requiring an inconveniently large sample, while the polarographic method as described by Perkins and Reynolds is too lengthy for routine use. Perkins and Reynolds found that beryllium tended to precipitate at the pH normally used for the determination of aluminium with Solochrome Violet RS, but even when precipitation was avoided, a considerable depression of the aluminium–dye reduction step occurred. To overcome this effect they carried out a preliminary separation of aluminium from the bulk of the beryllium by an 8–hydroxyquinoline extraction.

The dye Superchrome Garnet Y (5–sulpho–2',4',2–trihydroxyazobenzene, C.I. 168) is known to react with aluminium at a lower pH than Solochrome Violet RS(Cooney and Saylor, 1959), and when used in conjunction with a highly sensitive cathode ray polarograph, the depressing effect of beryllium is minimized, and the necessity of separating aluminium obviated.

A direct method is described for the determination of aluminium in beryllium metal after a rapid mercury cathode electrolysis to remove iron and other impurities. The sample weight required is only 100 mg, and a single determination may be completed in little over an hour.

## 2. THE REACTION OF ALUMINIUM WITH SUPERCHROME GARNET Y IN THE PRESENCE OF BERYLLIUM

Superchrome Garnet Y, at concentrations below 2 x $10^{-5}$M, exhibits sharp, well–defined "adsorption–reduction" peaks on the cathode ray polarograph (Florence and Smythe, 1960 and Figure 1 in this report).

In the presence of aluminium in acetate buffers, the dye peak is reduced in height, and a new peak appears at a more negative potential, its height being proportional to the aluminium concentration (Figure 2). At pH 3.40 the sensitivity is 6.33 $\mu$A/$\mu$g Al/ml. Although beryllium does not produce a discrete reduction peak, relatively high concentrations cause a depression of the aluminium–dye peak (Figure 3). However, it was found that at a constant beryllium concentration and a favourable pH, a linear relationship was still obtained between peak height and aluminium concentration. A pH range of 3.4 to 3.5 is optimum for the determination, since the sensitivity decreases rapidly at lower pH values, while at higher values the peak height is not proportional to aluminium concentration.

It may be seen from Figure 3 that for an error of less than 2 per cent. in the aluminium determination the sample weight of beryllium metal should be controlled so that the final beryllium concentration is within ± 3 per cent. of that used in the calibration curve. If a sample weight outside this range is inadvertently taken, an approximate result may be obtained by reference to a depression factor curve (ratio of peak height in the presence of beryllium to peak height in the absence of beryllium) such as Figure 3.

## 3. EXPERIMENTAL

### 3.1 Apparatus

Polarograph: The linear–sweep cathode ray polarograph was supplied by Southern Instruments Computer Division, Surrey, England. This instrument has a sweep rate of 0.25V per sec and a delay period of 5 sec. The dropping mercury capillary characteristics were m = 1.14 mg per sec, t = 6.5 sec (–0.5V vs. pool). All measurements were made in a thermostatted bath at 25.0 ± 0.2°C.

Mercury cathode cell: The small "constant–current" mercury cathode cell has been described previously (Florence, 1959).

### 3.2 Reagents

Superchrome Garnet Y: The crude dye was prepared as described by Cooney and Saylor (1959), then purified by a double recrystallization from water. The purity of the final product was not determined.

Acetate buffer: This was prepared by mixing 500 ml of 1M ammonium acetate (from reagent grade ammonia and acetic acid) with 470 ml of 1M HCl, and adjusting to pH 3.40 ± 0.05 on a pH meter. The buffer should be stored in a polythene container.

Beryllium metal standard: "Spec.–pure" beryllium from Johnson, Matthey and Co. Ltd., London, was used for calibration purposes, and was found to contain 120 p.p.m. of aluminium.

The water used throughout was demineralised, then distilled from quartz and collected and stored in a polythene container.

### 3.3 Recommended Procedure

Weigh accurately 100 ± 3 mg of fine beryllium metal filings. Dissolve by warming with 16 ± 1 ml of 1N $H_2SO_4$. Dilute to 25 ml in a volumetric flask. Transfer about 10 ml of the sample solution to the dry mercury cathode cell and electrolyse at 9V (0.5A) for 15 to 20 min. Remove the air condenser and, with current still flowing, withdraw about 5 ml of the solution. Cool to room temperature, take a 2 ml aliquot and neutralize to pH 3 to 4 with 1N $NH_4OH$, using indicator paper. Transfer to a 25 ml volumetric flask, add 5 ml of acetate buffer (pH 3.40), 5 ml of a $5 \times 10^{-5}$ M dye solution, and dilute to volume. Heat at 70°C in a water bath for 10 to 15 min, cool, and transfer a portion to the polarographic cell. After deaeration measure the peak height of the wave at –0.51V vs. Hg pool, using a start potential of –0.32V. A blank must be carefully carried through the procedure and the measured peak height multiplied by the depression factor to obtain a true blank peak height.

### 3.4 Construction of Calibration Curve

A calibration curve was obtained by "spiking" 100 mg portions of "spec–pure" beryllium metal filings with known amounts of aluminium, and carrying through the procedure described above, but omitting the mercury cathode electrolysis step. The relevant depression factor was determined by comparing the slope of this line with that obtained in the absence of beryllium. The minimum concentration of aluminium measurable is governed mainly by the magnitude of the blank, and, using the recommended procedure, is equivalent to about 20 p.p.m. of aluminium in beryllium.

### 3.5 Study of Interferences

The concentration of aluminium in nuclear–grade beryllium metal is usually in the range 100 to 2,000 p.p.m. Other impurities commonly found (Melick 1958) are Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb and Zn. With the exception of iron, these impurities are normally present at a lower concentration than aluminium, but even small amounts of Ni, Pb and Mo interfere with the direct determination of aluminium using Superchrome Garnet Y. A mercury cathode electrolysis employing the cell described rapidly removed all interfering elements from a 0.2N $H_2SO_4$ electrolyte.

### 3.6 Analysis of Synthetic Samples

A series of solutions containing 100 mg of "spec–pure" beryllium metal were "spiked" with known amounts of aluminium, and 500 μg of each of the 14 impurities mentioned above. These solutions were then analysed for aluminium by the recommended procedure. The results are given in Table 1.

## 4. REFERENCES

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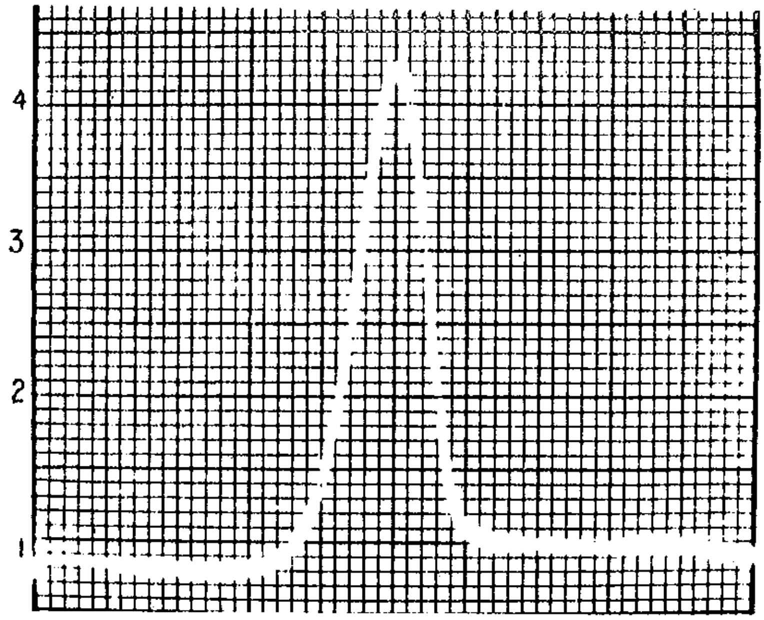
## TABLE 1

Recovery of Aluminium from Beryllium Using Suggested Procedure

Each solution contained 0.100 ± 0.001 g of "spec-pure" beryllium metal, plus 500 $\mu$g of each of the following elements - Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb and Zn.

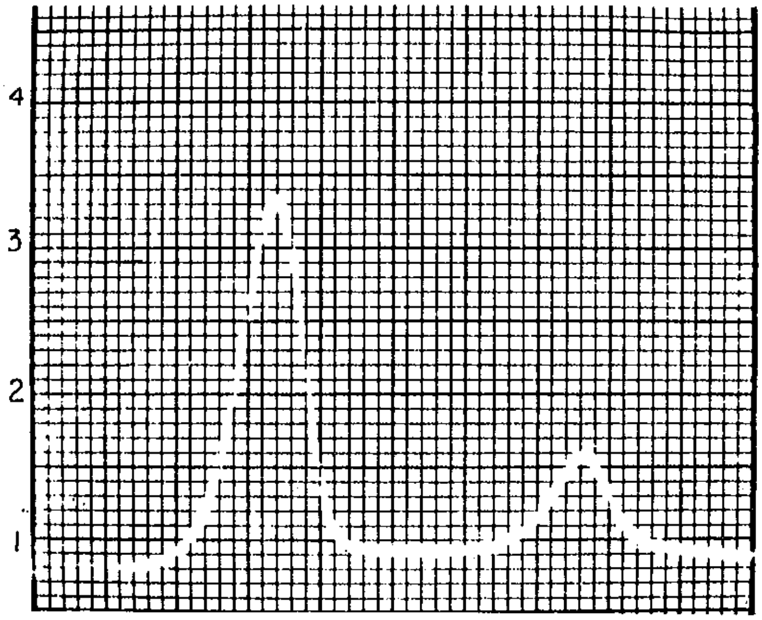
| Al added ($\mu$g) | Al found ($\mu$g) | % recovery |
|---|---|---|
| nil | 12 | - |
| 10 | 20 | 91 |
| 20 | 31 | 97 |
| 50 | 59 | 95 |
| 75 | 85 | 98 |
| 100 | 117 | 105 |
| 150 | 162 | 100 |
| 200 | 208 | 98 |



APPLIED VOLTAGE

FIGURE 1. OSCILLOGRAM OF SUPERCHROME GARNET Y IN AN ACETATE BUFFER OF pH 3.40

DYE CONCENTRATION = 1 x $10^{-5}$M
PEAK HEIGHT = 5.1 μA, PEAK POTENTIAL = −0.30V VS. HG POOL



APPLIED VOLTAGE

FIGURE 2. OSCILLOGRAM OF SUPERCHROME GARNET Y PLUS ALUMINIUM IN AN ACETATE BUFFER OF pH 3.40

DYE CONCENTRATION = 1 x $10^{-5}$M
ALUMINIUM CONCENTRATION = 6 x $10^{-6}$M
1st PEAK HEIGHT = 3.8 μA 1st PEAK POTENTIAL = −0.30V VS. HG POOL
2nd PEAK HEIGHT = 1.0 μA 2nd PEAK POTENTIAL = −0.51V VS. HG POOL

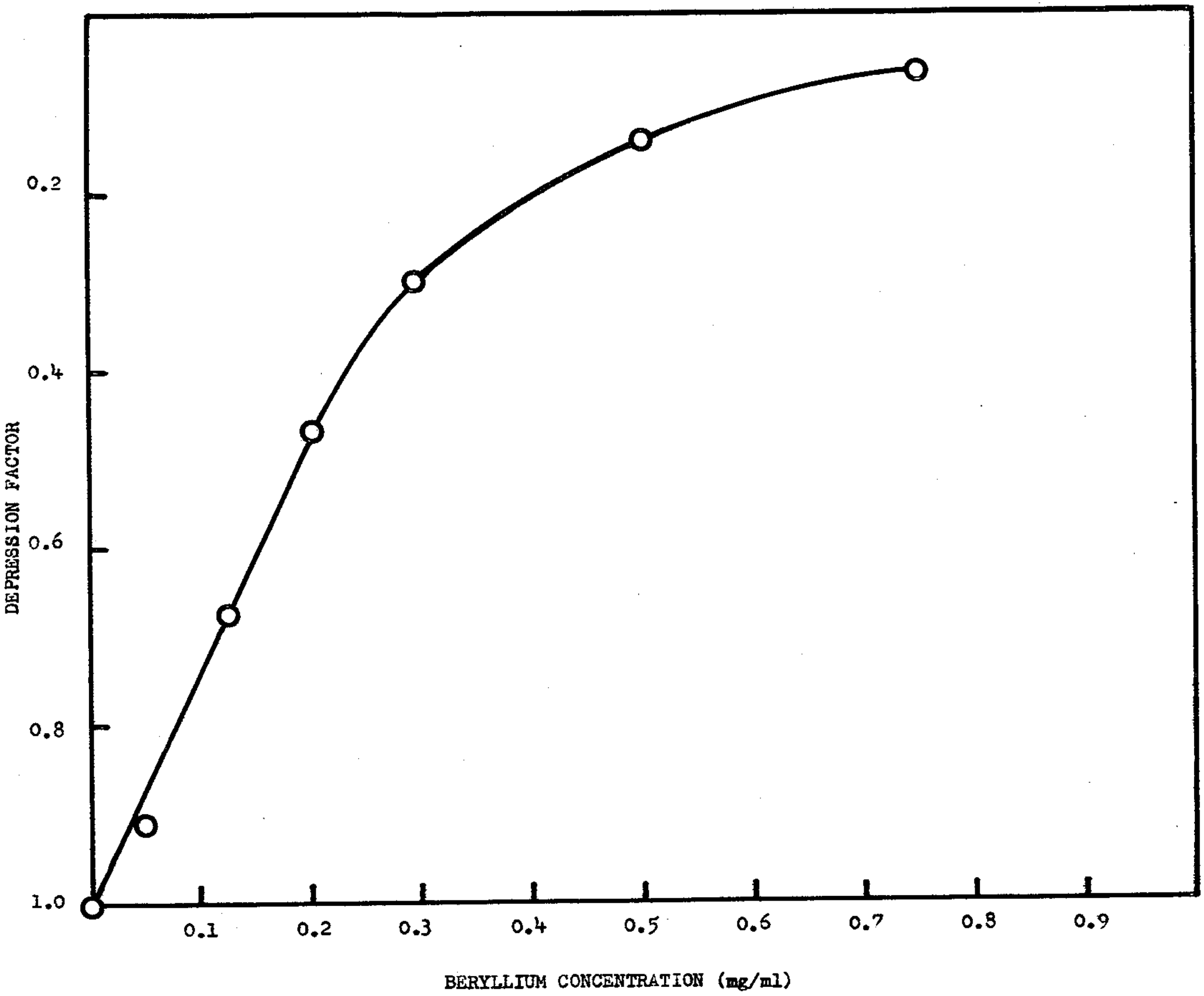


FIGURE 3. DEPRESSION BY BERYLLIUM OF THE ALUMINIUM-DYE REDUCTION PEAK