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ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH *p*-CHLORO- OR *p*-BROMOMANDELIC ACID.<sup>1, 2</sup>—Hahn and Weber (1956) have reported a spectrophotometric method for determining zirconium by measuring the absorbance at 258  $m\mu$  of the soluble compound obtained when the precipitate formed by the reaction of zirconium and mandelic acid is dissolved in aqueous ammonia.

Spectrophotometric studies of the solutions obtained by dissolving the zirconium mandelates of *p*-chloro- and *p*-bromomandelic acids in ammonia, using a Beckman Model DB spectrophotometer, also show absorption in the ultraviolet region (figure 1). The absorption curves obtained were very similar to those obtained by Collopy and Klingenberg (1961) for *p*-chloro- and *p*-bromomandelic acids respectively, indicating that the absorption is due to the phenyl groups present in the absorbing species. The absorbance of the ammonia solution of the zirconium *p*-chloromandelate at 266  $m\mu$  (258  $m\mu$  for zirconium *p*-bromomandelate) was found to follow Beer's Law in the range of 0.2 to 10 mg of zirconium per 100 ml of solution. The use of this absorbance as the basis for an analytical method for the determination of zirconium was then investigated.

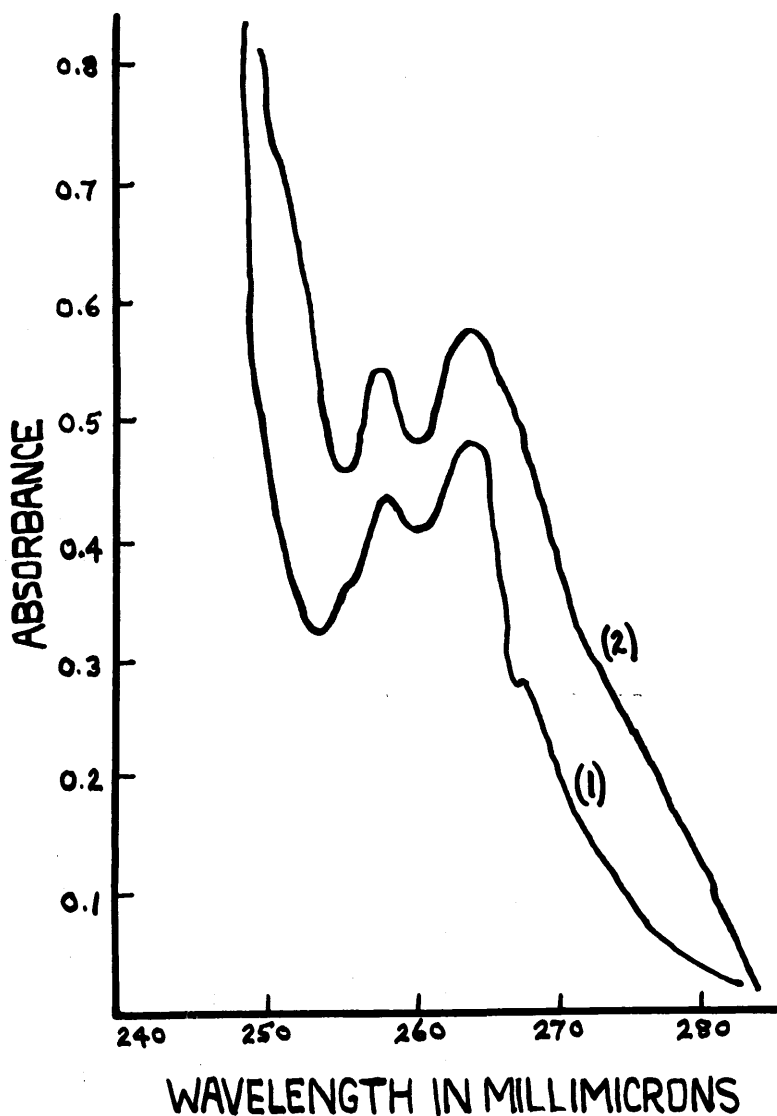
The procedure employed was essentially the same as that employed by Hahn and Weber. Twenty milliliters of a solution containing 0.2 to 8.0 mg of zirconium were treated with 15 ml of concentrated (12 M) hydrochloric acid and the zirconium chloro(bromo)mandelate precipitated by the dropwise addition of 25 ml of a 0.10 M solution of *p*-chloro(bromo) mandelic acid at 85°C. The precipitate was filtered by suction, using a sintered glass crucible, and washed with distilled

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water. The precipitate in the filter crucible was then dissolved by treatment with three to four 5-ml portions of 6 M ammonia. The crucible was washed with three 5-ml portions of distilled water and the combined solutions transferred to a 50-ml volumetric flask and diluted to volume. The absorbance of the solution was then measured at the selected wave length, using the same quantity of 6 M ammonia



diluted to 50 ml as a blank. The ammonia solutions were stable for at least 24 hours.

The procedure was tested in the presence of diverse ions and showed no significant deviation when Al, Cd, Cr, Mg, Sn, Sr, Th, Zn, nitrate, or sulfate ions were present in 100-mg amounts and Fe and Ti in 20-mg amounts. The presence of V and Mo caused the results to be high. When tested with an alloy containing known amounts of zirconium, the results given in Table 1 were obtained.

TABLE 1.  
*Determination of zirconium in an iron, aluminum zirconium alloy*

| Sample | Ions present, mg |      |       |      | Zr found, mg |           | Error % |
|--------|------------------|------|-------|------|--------------|-----------|---------|
|        | Al               | Fe   | Ti    | Zr   | (p-ClMaA)    | (p-BrMaA) |         |
| 1      | 0.96             | 0.56 | 0.011 | 1.44 | 1.40         | —         | -2.9    |
| 2      | 1.2              | 0.68 | 0.013 | 1.76 | —            | 1.84      | 4.7     |
| 3      | 1.8              | 1.1  | 0.020 | 2.74 | —            | 2.68      | -2.2    |
| 4      | 1.9              | 1.1  | 0.020 | 2.83 | 2.74         | —         | -3.2    |
| 5      | 2.3              | 1.3  | 0.026 | 3.39 | —            | 3.44      | 1.2     |
| 6      | 2.4              | 1.4  | 0.027 | 3.66 | —            | 3.88      | 6.1     |
| 7      | 2.8              | 1.6  | 0.032 | 4.18 | 4.00         | —         | -4.5    |
| 8      | 3.2              | 1.8  | 0.036 | 4.73 | 4.36         | —         | -7.9    |
| 9      | 3.3              | 1.9  | 0.037 | 4.92 | —            | 5.10      | 3.7     |
| 10     | 4.0              | 2.3  | 0.044 | 5.99 | —            | 5.80      | -3.1    |
| 11     | 4.1              | 2.4  | 0.046 | 6.12 | 5.72         | —         | -6.5    |
| 12     | 4.5              | 2.6  | 0.051 | 6.73 | —            | 6.32      | -6.1    |
| 13     | 6.0              | 3.5  | 0.067 | 8.91 | 8.74         | —         | -1.9    |

The halomandelate reagents possess a slight advantage over mandelic acid in the form of increased sensitivity, no observed interference from nitrate ion, and simpler washing techniques for the mandelate precipitate, because distilled water may be used and the ethanol-ether washes are unnecessary. The halomandelates were prepared by the method described in Organic Syntheses (Klingenberg, 1955). —JOSEPH J. KLINGENBERG and J. MICHAEL ERNST, *Xavier University, Cincinnati, Ohio*.

#### LITERATURE CITED

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