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G. C. Turk J. C. Travis J. R. DeVoe\*

T. C. O'Haver

Institute for Materials Research Analytical Chemistry Division National Bureau of Standards Washington, D.C. 20234

Chemistry Department University of Maryland College Park, Maryland 20742

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# $\beta$ -Diketone Reagents for the Determination of Borate in Water

Sir: Boron analysis for water quality and environmental control is becoming more important. Increasing use for boron is being found in a wide spectrum of products and technologies ranging from cosmetics and medicine to nuclear engineering and agriculture (1). The quantity of boron found in water supplies and effluents reflects this rising use of the element and poses problems in agriculture. Concentrations in excess of 2 ppm in irrigation water are deleterious to many plants (2). There is evidence that concentrations as low as 1 ppm adversely affect some plants. Current recommended boron levels for many crops are as low as 0.33 ppm.

One of the widely used analytical procedures for boron in water involves the reaction of curcumin and borate in the presence of oxalic acid (3). The product formed is rubrocurcumin, a 1:1:1 curcumin-borate-oxalate complex (4-6). The procedures developed have been variously reported to be useful from 0.05 to 15  $\mu$ g of boron. These levels are achieved by carefully controlling the reaction temperature, reaction time, rate of evaporation of water from the reaction mixture, prevailing humidity, the water content of the ethanol used to dissolve the colored complex, and the loss of boron as volatile ethvl borate.

The standard method, which is used for water and effluent analyses, uses less rigorous controls. As a result, the method is reportedly useful from 0.1 to 1.0  $\mu$ g of boron (7, 8). Improvements in boron analysis probably will be brought about more readily by improvements in the reagents rather than refinements in the methods. For a reagent to replace curcumin, it would have to have the following: (a) be inherently more stable, (b) have a higher molar absorption coefficient, (c) be applicable over a wider range of boron concentrations, and (d) be applicable for use in established procedures. With the above criteria in mind, a series of four  $\beta$ -diketones were synthesized and investigated as analytical reagents for borate.

#### **EXPERIMENTAL**

**Reagents.** Three compounds, 1,3-bis(4-methoxyphenyl)-1,3-propanedione (I), 1,3-bis(4-dimethylaminophenyl)-1,3propanedione (II), and 1,3-bis(4-acetoamidophenyl)-1,3propanedione (III), were prepared using the procedures of Bloomfield (9). Yields of 92%, 43%, and 43%, respectively, were obtained. The spectral data were:

#### Table I. Colors of Reagents and Their Boron Rubro-Complexes

| Reagent | Reagent solution | Residue after<br>evaporation | Ethanol solution |
|---------|------------------|------------------------------|------------------|
| (I)     | colorless        | dark yellow                  | yellow           |
| (II)    | dark yellow      | red-pink                     | dark yellow      |
| (III)   | light yellow     | dark yellow                  | orange-yellow    |
| (IV)    | colorless        | dark yellow                  | yellow           |

(I) IR (Nujol) 1625, 1310, 1270, 1230, 1175, 1120, 1025, 845, 785, and 725 cm<sup>-1</sup>; NMR (CD<sub>3</sub>COCD<sub>3</sub>),  $\tau = 17.3$  (S, 1H), 7.5 (M, 8H), 7.0 (S, 1H), and 3.8 (S, 6H).

(II) IR (Nujol) 1610, 1240, 1170, 950, 825, and 785  $\rm cm^{-1}; NMR$  $(DCCl_3)$ ,  $\tau = 17.4$  (S, 1H), 7.3 (M, 8H), 6.7 (S, 1H), and 3.1 (S, 12H)

(III) IR (Nujol) 3300, 1670, 1600, 1310, 1270, 1170, 1120, 1040, 1020, 965, 845, 787, 770, and 725 cm<sup>-1</sup>; NMR (CD<sub>3</sub>COCD<sub>3</sub>),  $\tau =$ 17.4 (S, 1H), 10.1 (S, 2H), 8.5 (M, 9H), 7.9 (S, 1H), and 3.6 (S, 6H).

1,3-Bis(4-hydroxyphenyl)-1,3-propanedione (IV) was prepared by demethylating (I) with boron tribromide using the procedures of McOmie, Watts, and West (10). A yield of 54% was obtained. The spectral data were:

(IV) IR (Nujol) 3500, 3250, 1610, 1270, 1225, 1170, 1120, 840, 785, and 720 cm<sup>-1</sup>; NMR (CD<sub>3</sub>COCD<sub>3</sub>),  $\tau = 17.5$  (S, 1H), 9.7 (S, 2H), 7.5 (M, 8H), and 7.0 (S, 1H).

The band at or near 1600 cm<sup>-1</sup> is indicative of  $\beta$ -diketones (11). Procedures. The borate complexes of (I), (II), (III) and (IV) were formed using the procedures outlined in "Standard Methods for the Examination of Water and Wastewater" (8). Each run consisted of a blank and six samples of varying borate concentration. Spectrophotometric measurements were made in 1-cm cuvettes within a 1- to 2-h period following evaporation of the samples, as recommended for the curcumin-oxalic acid method (12).

The reaction of borate, oxalic acid, and  $\beta$ -diketone was brought about by complete evaporation of the solvent system. The resultant colored residue indicated the formation of the "rubrocomplex" (Table I). In all cases, a visual ordering of boron levels from highest to lowest was possible after dissolution of the residue in ethanol. The rubro-complex of (I) exhibited a marked visual fluorescence at concentrations as low as 0.1 ppm boron. This corresponded to a relative intensity of 34 at a sensitivity setting of 10 on the fluorometer. The emission spectra of samples



Figure 1. Fluorescence characteristics of 1,3-bis(4-methoxyphenyl)-1,3-propanedione

Table II.Net Absorbancies of Reagents (I) and (II)Compared to Curcumin

| Boron<br>added,<br>µg | Net absorb-<br>ancy of<br>curcumin <sup>a</sup> | Net absorb-<br>ancy of<br>reagent (I) <sup>a</sup> | Net absorb-<br>ancy of<br>reagent (II) <sup>a</sup> |
|-----------------------|---|--|---|
| 0.2                   | 0,030   | 0.040  | 0.018   |
| 0.4                   | 0.047   | 0.075  | 0.038   |
| 0.6                   | 0.085   | • • •  | • • •   |
| 0.8                   | 0.110   | 0.120  | 0.073   |
| 1.0                   | 0.140   | • • •  |   |
| 1.2                   |   | 0.175  | 0.110   |
| 1.6                   | • • •   | 0.215  | 0.143   |
| 2.0                   | • • •   | 0.270  | 0.165   |

<sup>a</sup> Measurements made in 1-cm cells. Correlation coefficients: curcumin, 0.995; (I), 0.999; (II), 0.997.

| Table III.          | Net Absorbancies of Reagents (III) and (IV) |  |   |  |
|---------------------|---|--|---|--|
| ]                   | Boron<br>added<br>µg                        | Net absorb-<br>ancy of<br>reagent (III) <sup>a</sup> | Net absorb-<br>ancy of<br>reagent (IV) <sup>a</sup> |  |
|                     | 0.5   |  | 0.115   |  |
|                     | 1.0   |  | 0.225   |  |
|                     | 1.5   |  | 0.335   |  |
|                     | 2.0   | 0.155  |   |  |
|                     | 2.5   | • • •  | 0.570   |  |
|                     | 3.5   | • • •  | 0.770   |  |
|                     | 4.0   | 0.295  |   |  |
|                     | 4.5   |  | 1.010   |  |
|                     | 6.0   | 0.482  |   |  |
|                     | 8.0   | 0.655  |   |  |
|                     | 10.0  | 0.835  |   |  |
| <sup>a</sup> Measur | ements i                                    | made in 1-cm cells                                   | . Correlation coef-                                 |  |

ficients: (III), 0.999; (IV), 0.999.

containing 10 to 100 ppb boron indicated high degrees of internal contamination; hence, results were nonlinear and not reproducible. Excitation and emission occurred at 420 and 450 nm, respectively (Figure 1).

The absorption spectra of the rubro-complexes of (I), (II), (III), and (IV) were linear and reproducible over a wide range of boron concentrations. Typical results are listed in Tables II and III. Absorption maxima for the rubro-complexes of (I), (II), (III) and (IV) occur at 420, 525, 480, and 420 nm, respectively (Figure 2). The molar absorptivities,  $\epsilon$ , of the rubro-complexes are as follows: curcumin,  $3.79 \times 10^4$ ; (I),  $3.64 \times 10^4$ ; (II),  $2.29 \times 10^4$ ; (III),  $1.98 \times 10^4$ ; and (IV),  $5.70 \times 10^4$ . Reagents made from these compounds have useful shelf lives, without refrigeration, of at least one month.

## **RESULTS AND DISCUSSION**

The adaptation of the reagents evaluated into the standard method for boron analysis requires no modifications of existing procedures. Reagent (III) extended the upper limits of the



Figure 2. Absorption spectra of the rubro-complexes of reagents (I), (II), (III), and (IV)

#### Scheme I



method from 1 to 10 ppm boron. Results were very linear and reproducible. The use of (IV) gave excellent results in the range from 0.1 to 4.5 ppm boron. The increased sensitivity of (IV) offers the possibility of its use in the 10- to 100-ppb range. At these concentrations, boron contamination from glassware and reagents is a serious problem. The use of a one-tenth slide was the only modification necessary to the procedure. The increased sensitivity offered by the fluorescence of the rubro-complex of (I) makes possible the quantitative measurement of concentrations as low as 1 ppb. Again, boron contamination poses more of a problem than detection. Improved shelf life was an inherent characteristic of all the reagents evaluated. Reagent stability was improved by a factor of six over curcumin. Although (I), (III), and (IV) offer greater sensitivity and range than curcumin, the precision and accuracy of the method is ultimately dependent upon controlling contamination and the parameters that affect the rate and uniformity of sample evaporation.

The nature of the reactions between borate and reagents (I), (II), (III), and (IV), as well as curcumin is probably one of induced resonance to produce a cyanine-type dye. If curcumin is represented as R-CH==CH-CO-CH<sub>2</sub>-CO-CH= CH-R, the reagents discussed herein are R-CO-CH<sub>2</sub>-CO-R. The reactions of the latter can be generalized. See Scheme I. The electron transitions indicated in these reactions give rise to greater absorption (a more highly-colored dye) than would a compound exhibiting complete conjugation throughout.

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<sup>1</sup>Present address, the Dow Chemical Co., Freeport, Texas,

Jack L. Lambert\* Joseph V. Paukstelis Roderick A. Bruckdorfer<sup>1</sup>

Department of Chemistry Kansas State University Manhattan, Kansas 66506

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# AIDS FOR ANALYTICAL CHEMISTS

# Problems in Obtaining Adequate Seals with Screw Cap Containers and Their Daily Variation in Weights

#### Larry E. DeVries,\* Elmer Gubner, and Linda D. Jackson

Naval Surface Weapons Center, Electrochemistry Branch, Materials Division, White Oak Laboratory, Silver Spring, Maryland 20910

When experimenting with lithium-boron alloys (1, 2), it was necessary to transfer the alloys to experiments outside of glove boxes and to weigh samples outside of glove boxes. The alloys react more rapidly with air than pure lithium does. Screw cap tubes or bottles which had low helium leakage rates seemed the best solution to the problem of handling the alloys in air. Helium was used for the atmosphere in the glove boxes. Experiments revealed three problems: many screw cap containers leak excessively, many cap liners contain reactive materials, and nonleaking containers change weight from day to day.

#### **RESULTS AND DISCUSSION**

Tests revealed that some types of glass containers were unacceptable because their screw caps leaked helium at a high rate (>1.5 ×  $10^{-4}$  cm<sup>3</sup>/s). In some cases, the cap liners themselves appeared to react with the alloys. In other cases, the liners were porous and contained air, moisture, or organic solvents. Before bottles and caps were put into a glove box, they were treated in the entry port of the box. The entry port was evacuated three times and filled with helium each time after evacuation. This did not remove air or volatile materials sufficiently from the caps. In a few days the alloys reacted with these materials. Bottled samples would not necessarily be used for a few days so those caps could not be used. For caps that leaked helium at a high rate, various films (Teflon, polyethylene, and Parafilm) were used to see if the leakage rate could be reduced. One to five layers were put over the top of the bottle and the cap screwed tightly against the bottle top. Films generally did not reduce the leakage rate much below  $1.5 \times 10^{-4}$  cm<sup>3</sup>/s for bottles leaking at or above that rate initially.

Glass tubes which did give adequate protection if treated properly were culture tubes manufactured by Corning Glass Works (Corning, N.Y. 14830). The screw caps had a Teflon liner with a rubber backing. Large tubes  $25 \text{ mm} \times 150 \text{ mm}$ with a helium leakage rate at/or below  $1 \times 10^{-6}$  cm<sup>3</sup>/s were used. They had an average cap weight of about 6.4 g and an

| Table I.         Variation in Weight of Selected Culture Tubes <sup>a</sup> |                                  |              |                                  |              |  |  |
|---|----------------------------------|--------------|----------------------------------|--------------|--|--|
| Days after<br>initial weight  | Av wt<br>change, mg <sup>b</sup> | Stand<br>dev | Av wt<br>change, mg <sup>b</sup> | Stand<br>dev |  |  |
|   | A <sup>c</sup>                   |              | B <sup>c</sup>                   |              |  |  |
| 3   | -1.0                             | 0.2          | +0.2                             | 0.2          |  |  |
| 5   | -1.2                             | 0.2          | +0.1                             | $0.4^{d}$    |  |  |
| 7   | -1.2                             | 0.2          | +0.6                             | 0.2          |  |  |
| 9   | -1.1                             | 0.2          | +1.5                             | 0.3          |  |  |
| 11  | -0.5                             | 0.2          | +2.7                             | $0.4^{d}$    |  |  |

<sup>a</sup> The 11 glass tubes were 13 mm  $\times$  100 mm, <sup>b</sup> The values are the average difference between the initial weight and the weight on the day given. <sup>c</sup> Group A contained six tubes and group B five. <sup>d</sup> Tube 19 showed a -0.5-mg variation from the average weight change on the fifth day and tube 23 showed a 0.5-mg variation on the eleventh dav.

average total tube weight of 38.7 g. Small tubes were also used. They were  $13 \text{ mm} \times 100 \text{ mm}$  with an average total tube weight of 14.6 g and an average cap weight of 2.4 g. The tubes had a helium leakage rate of 1  $\times$  10<sup>-9</sup> cm<sup>3</sup>/s. In the initial experiments, it was found that the tubes continuously lost weight. A check revealed that the porous rubber was filled with an organic solvent. Some solvent distilled away each time the tubes and caps were under vacuum prior to being filled with helium. The caps were baked at 393 K for 109 h and then under vacuum at 393 K for an additional 1428 h. The large caps lost an average of 0.23 g/cap for 12 caps. About 80% of the loss occurred during the first 109 h. Twelve small caps lost an average of 0.09 g/cap with most of the loss coming during the first 109 h. After this treatment, the caps leaked very badly. The rubber backing had shrunk causing the leaks.

In a new experiment, new small caps were heated at 308 K to 311 K for 384 h under vacuum. They reached a "constant" weight. The loss in cap weight for small caps averaged 0.05 g/cap. The helium leakage rate was  $1 \times 10^{-9}$