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The Atomic Absorption Spectrophotometric Determination of Zinc in Premixed Inert Gas(Entrained Air)-Hydrogen Flames and the Measurement of the Flame Temperature

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Previous studies have indicated that the premixed inert gas(entrained air)-hydrogen flame produced with a "multi-flame" burner[1] can be used as a suitable atom reservoir for the determination of bismuth[2] and tin[3] by atomic absorption spectrophotometry. This paper will describe the application of this flame to the atomic absorption spectrophotometric determination of zinc and, in addition, the measurement of its temperatures using a thermocouple probe.

Whereas the temperatures of most flames can only be measured satisfactorily by such spectroscopic techniques as the Ornstein iron two-line method[4–6] and the sodium line-reversal method,[5,7] the cool inert gas-(entrained air)-hydrogen flame gives a temperature of only a few hundred degrees centigrade,[8] and it can be measured fairly reliably by inserting a thermocouple probe into the flame.[9]

1) T. Nakahara, H. Date, M. Munemori, and S. Musha, This Bulletin, **46**, 637 (1973).

2) T. Nakahara, M. Munemori, and S. Musha, *ibid.*, in press.

3) T. Nakahara, M. Munemori, and S. Musha, *Anal. Chim. Acta*, **62**, 267 (1972).

4) J. D. Winefordner, J. M. Mansfield, and T. J. Vickers, *Anal. Chem.*, **35**, 1611 (1963).

5) L. de Galan and J. D. Winefordner, *J. Quant. Spectrosc. Radiat. Transfer.*, **7**, 703 (1967).

6) G. F. Kirkbright, M. K. Peters, M. Sargent, and T. S. West, *Talanta*, **15**, 663 (1968).

7) J. H. Gibson, W. E. L. Grossman, and W. D. Cooke, *Anal. Chem.*, **35**, 266 (1963).

8) R. M. Dagnall, K. C. Thompson, and T. S. West, *Analyst* (London), **92**, 506 (1967).

9) R. Smith, C. M. Stafford, and J. D. Winefordner, *Anal. Chem.*, **41**, 946 (1969).

Experimental

Apparatus. All the atomic absorption measurements were made using a Nippon Jarrell-Ash Model AA-1 atomic absorption/flame emission spectrophotometer. A long-path "multi-flame" burner[1)] constructed in the authors' laboratory was mounted on a Techtron nebulizer chamber, and a single pass system was used. The height in the flame was taken as zero when the light beam from the hollow-cathode lamp just touched the top of the burner head. The analytical wavelength was 213.9 nm, and the light source was a multi-element (Cu–Fe–Mn–Zn) hollow-cathode lamp (Westinghouse, Type No. 45492), operated at 10 mA. The gas-flow rates were carefull regulated by means of needle valves and were monitored on calibrated flow meters.

Reagents. A standard zinc solution containing 1000 ppm of zinc was prepared by dissolving 1.000 g of high-purity zinc metal in 10 ml of hydrochloric acid and by then diluting this mixture to 1000 ml with distilled water. Various concentrations were made by diluting the stock solution.

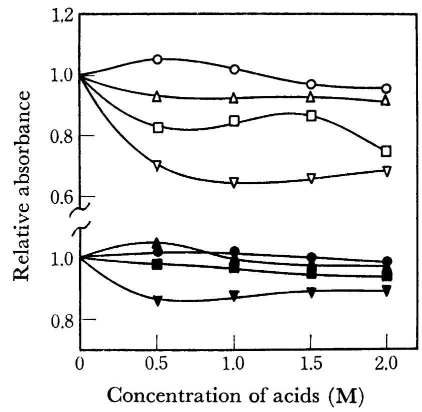

Fig. 1. Effect of acids on zinc atomic absorption. Concentration of zinc: 0.5 ppm. In an argon(entrained air)-hydrogen flame: (●) hydrochloric acid; (▲) nitric acid; (■) sulfuric acid; (▼) perchloric acid. In a nitrogen(entrained air)-hydrogen flame: (○) hydrochloric acid; (△) nitric acid; (□) sulfuric acid; (▽) perchloric acid.

Results and Discussion

Flame Parameters. The flames employed in this study produced 5 and 8% absorptions respectively when nitrogen and argon were used as the nebulizing gases. The absorbance values cited in this study were corrected for this background absorption.

The optimum flame parameters for zinc atomic absorption are summarized below. Argon(entrained air)-hydrogen flame: hydrogen flow rate, 3.6 l/min; argon flow rate, 4.5 l/min; argon pressure, 1.5 kg/cm^2; height of the flame, 4 mm above the top of the burner head. Nitrogen(entrained air)-hydrogen flame: hydrogen flow rate, 5.4 l/min; nitrogen flow rate, 5.0 l/min; nitrogen pressure, 1.5 kg/cm^2; height of the flame, 6 mm above the top of the burner head. Under these flame conditions, the hydrogen flames are almost invisible and are very quiet. The sample aspiration rates were 8.90 and 8.95 ml/min with argon and nitrogen respectively.

Calibration Graph for Zinc. Under the optimum conditions outlined above, the straight calibration graphs were obtained over the range of 0—0.5 ppm of zinc in argon(entrained air)-hydrogen and nitrogen-(entrained air)-hydrogen flames. The sensitivities for 1% absorption for zinc were 0.005 and 0.007 ppm in argon(entrained air)-hydrogen and nitrogen(entrained air)-hydrogen flames respectively.

Effects of Acids. The interference effect of acids on the determination of zinc was studied. The concentration of zinc was 0.5 ppm, and the concentration range of acids was from 0.5 to 2.0M. The acids examined were hydrochloric, nitric, perchloric, and sulfuric acids. The results obtained in both inert gas(entrained air)-hydrogen flames are shown in Fig. 1. It can be seen from Fig. 1 that the interference from the acids is greater in the nitrogen(entrained air)-hydrogen flame than in the argon(entrained air)-hydrogen flame. Hydrochloric and nitric acids caused little or no interference with the determination of zinc, but perchloric and sulfuric acids, particularly in the nitrogen(entrained air)-hydrogen flame, had a depressing effect on the zinc atomic absorption. Furthermore, the depressing interference from perchloric and sulfuric acids was considerably dependent upon the flame composition, becoming greater as the flames became reducible.

Effects of Various Other Elements. The effects of the presence of 10- and 100-fold weight excesses of various diverse elements on the determination of zinc were studied at the 0.5 ppm level. Some severe chemical interferences were observed to depress the zinc atomic absorption. The refractory compound-formers, such as aluminum, beryllium, boron, silicon, and vanadium, exhibited a greater depressing interference with the zinc atomic absorption.

Because flame composition and flame height have been found to be important parameters in the study of interference,[10)] the hydrogen-flow rate and the flame height in the inert gas(entrained air)-hydrogen flames were varied to see what effect, if any, would be produced on the depressing interference; it was found that the depressing interference was dependent on these parameters.

Effect of Lanthanum on the Depressing Interference. In an attempt to eliminate the depressing interference due to aluminum, beryllium, boron, *etc.*, the effects of third elements on the depressing interference were studied. The elements examined were barium, iron, mercury, lanthanum, lithium, magnesium, sodium, lead, antimony, tin, and yttrium. Some elements were found to eliminate the depressing interferences. Lanthanum was the most effective of the elements examined. When solutions were prepared so as to contain 2000 ppm of lanthanum(as chloride) as an interference-releasing agent, all the chemical interferences were completely removed. This phenomenon would be applicable to the determination of zinc in various practical samples.

Measurement of the Flame Temperatures. Dagnall

10) J. A. Dean and T. C. Rains, "Flame Emission and Atomic Absorption Spectrometry," Vol. 1, Marcel Dekker, New York, N. Y. (1969).

et al.[8] have reported that the hydrogen-nitrogen diffusion flame and the shielded air-hydrogen flame give temperatures of only a few hundred degrees centigrade, and that they can be measured fairly reliably by inserting a calibrated thermocouple probe into the flame. Furthermore, Smith *et al.*[9] have described the temperature profiles of turbulent hydrogen diffusion flames, the temperatures of which were measured with the aid of an iridium/60% iridium-40% rhodium thermocouple.

The temperatures of the inert gas(entrained air)-hydrogen flames were measured in this study by inserting a platinum/90% platinum-10% rhodium thermocouple probe into the flames. The thermocouple was made of 0.2 mm diameter platinum and platinum-rhodium (90—10%) wires which were welded to give a bead junction *ca.* 0.4 mm in diameter. The joined wires were mounted in two-bore, ceramic insulators of high-purity alumina. The thermocouple was mounted on a manually-operated horizontal/vertical traverse mechanism. The thermoelectric emf was measured on a millivoltmeter calibrated in units of 0.05 mV, and the temperature was determined by referring to a calibration table.[11]

The variation in the flame temperature with the flame height and the hydrogen-flow rate, at the flame center only, was measured for the argon(entrained air)-hydrogen flame and for the nitrogen(entrained air)-hydrogen flame with the aspiration of distilled water. The results obtained are shown in Fig. 2. For both the flames, the temperatures could be reproduced to ±10 K at any point on the central axis of the flame. As the hydrogen flow rate was increased, the flame became larger and the flame temperature increased, as is shown in Fig. 2. Furthermore, the maximum

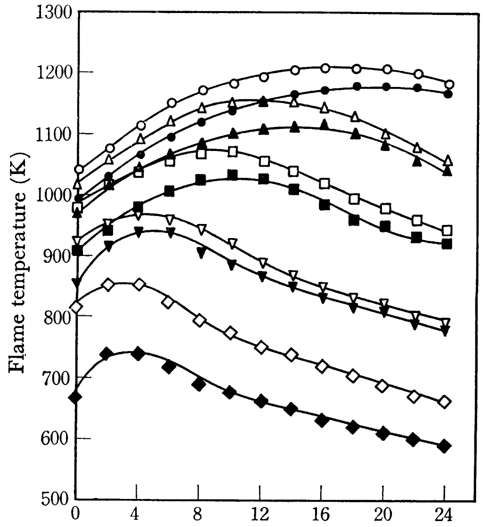

Fig. 2. Flame-temperature variation along central, vertical axis of the inert gas(entrained air)-hydrogen flames. Hydrogen flow rate in an argon(entrained air)-hydrogen flame: (◇) 3.6 l/min; (▽) 5.4 l/min; (□) 7.2 l/min; (△) 9.0 l/min; (○) 10.8 l/min. Hydrogen flow rate in a nitrogen (entrained air)-hydrogen flame: (◆) 3.6 l/min; (▼) 5.4 l/min; (■) 7.2 l/min; (▲) 9.0 l/min; (●) 10.8 l/min.

temperature shifted toward the higher part in the flame with the increase in the hydrogen flow rate. When distilled water is not sprayed into the flame, the flame temperatures about 4 mm above the top of the burner head increase by only 20 K. It may be noticed in Fig. 2 that the temperature in the argon-(entrained air)-hydrogen flame was higher at any point than that in the nitrogen(entrained air)-hydrogen flame. This is presumably due partially to the differences in interference effects on the zinc atomic absorption described above.

11) The Chemical Society of Japan Ed., "Kagaku Binran," (Kisohen), Maruzen, Tokyo (1966), p. 1096.