

Wide Range Analysis for Zinc Using Spectrographic Line Widths

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A spectrographic method has been developed for determination of zinc in biological ashes by use of line width as a concentration index. Synthetic standards and analytical samples, in the form of sulfates, are mixed with a potassium sulfate-graphite buffer containing barium and cadmium as internal controls. Samples are excited in a direct-current arc and spectra recorded with a Littrow quartz spectrograph. The contour of Zn 2138A is recorded with a recording microphotometer and the width determined at the maximum density of the control lines Ba 2255A or Cd 2288A. A plot of the logarithm of this width *versus* logarithm of zinc concentration prepared from standard samples containing 0.004 to 10 percent zinc serves as an analytical curve. Results determined by ordinary density measurements have been compared with those from width measurements. Although the two methods show comparable reproducibility of repeated exposures at the lower limit of the analysis range, the width method is more precise at higher ranges and has proven applicable even at concentrations where the line density method is limited by self-reversal and low photographic plate contrast. Concentrations as high as 10 percent have been determined, indicating possible application of such a method to the estimation of major constituents in such biological ashes or inorganic powders.

INTRODUCTION

CONSIDERABLE attention at this laboratory has been directed toward developing a spectrographic procedure for estimating, over wide ranges, the concentration of metals in the variety of different materials encountered. One of the chief difficulties was found in the estimation of zinc. In order to extend the lower limit of the analysis range to cover the small concentrations often occurring in the samples submitted, it was necessary to use the most sensitive zinc line at 2138.56A. However, the usable range of analysis with the usual line density methods was found to be quite limited. This is due to the tendency of the line to be easily self-reversed. Furthermore, the precision attainable was poor, probably partially due to the lack of control over self-reversal and partially to the low contrast of the photographic emulsion in this wavelength region resulting in only small changes in line density with changes in zinc concentration.

At the same time, as zinc concentration increased the increased *width* of the line was easily noticeable even after self-reversal had reduced the density at the center of the line. It appeared that a method such as suggested by Coheur¹

using line widths as a concentration index might be applicable to advantage in this instance. It should be noted, however, that his first method of measuring a broad line of the fundamental or control element at the varying maximum densities of the additional element is, in the present instance, subject to the same difficulties as the line density method. The procedure then has been to measure the varying width of the additional element, zinc, at the maximum density of a weak internal control line.

A comparison of results from intensity ratio measurements and line-width measurements has been carried out and the width results show better precision and an extended analytical range.

ANALYTICAL TECHNIQUE

Preparation of Materials

In order to make the method as generally applicable as possible, work was carried out with inorganic powders since most of our samples are either inorganic powders as received or reducible to this form. It has been found advantageous to convert the samples to sulfates whenever possible. Dry plant materials were sulfated by adding a solution of sulfuric acid in ethyl alcohol (1:9 by volume) and charred by burning off the alcohol. Solutions were dried and partially charred under

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¹ P. Coheur, J. Opt. Soc. Am. 36, 498 (1946).

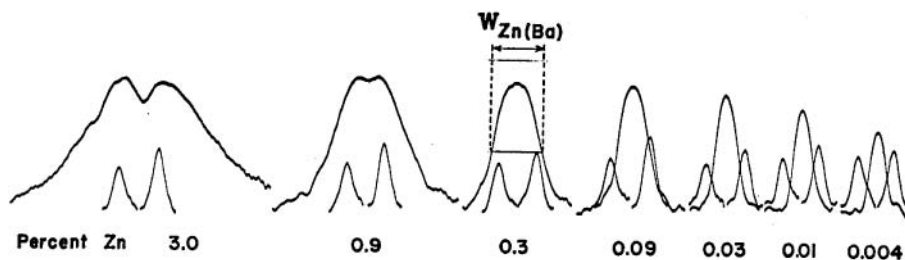


FIG. 1. Line contour recordings of typical exposures of synthetic zinc standards. The lines in each group of three are Cd, Zn, and Ba in that order from left to right. The measurement of zinc width at barium maximum, $W_{Zn(Ba)}$, is illustrated for the 0.3 percent standard.

an infra-red lamp before sulfating. The char was further ashed in a muffle furnace at 450–500°C.

Standards were prepared from the following base approximating the qualitative composition of a typical sample: 2 percent sodium chloride; 4 percent calcium sulfate; 6 percent basic magnesium carbonate; 0.4 percent silicic acid; 10 percent potassium phosphate (Di-H); 77.6 percent potassium sulfate. Suitable aliquots of a standard zinc solution were added to portions of this base and the mixture dried and ground in a mortar.

A spectroscopic buffer-control mixture was prepared as follows: 10.000 g. high purity graphite powder, 3.000 g. potassium sulfate, 0.233 g. barium sulfate, 1 ml 0.01 percent cadmium solution. This mixture was also dried and ground in a mortar. The barium and cadmium are present in quantities sufficient to give lines suitable for use as internal controls for both density and line width measurements. The standards (or analytical samples) were mixed with this buffer-control in a ratio of 2:1 by weight.

Excitation and Photography

The 2:1 sample:control mixtures were tamped into the sample electrodes with a flat-ended nickel rod. The lower (+) electrode was cut with a $\frac{1}{8}$ -inch center post with central sample cavity 2 mm in diameter and 4 mm deep. The upper (–) electrode was cut with a solid $\frac{1}{8}$ -inch center post. Regular grade $\frac{1}{4}$ -inch diameter spectroscopic graphite rods were used. The samples were excited with a 250-volt 15-ampere direct current arc.

The image of the arc was focused on a 13 mm diaphragm at the collimating lens of a large quartz prism Littrow spectrograph. The slit

width used was 0.02 mm. Exposures were continued until the entire sample of approximately 15 mg was burned. Exposure times averaged about 50 seconds.

Type I-O ultra-violet-sensitized photographic plates were used and developed under standard temperature-controlled conditions. The emulsion was calibrated for intensity measurements by means of selected iron lines of known relative intensity. These relative intensities had been determined from a calibration curve established by use of a split-field filter² and preliminary curve procedure.³

Measurement of Densities and Line Widths from Spectrograms

A combined comparator, densitometer, and recording microphotometer⁴ was used to measure both line transmissions and line widths. Transmissions were measured on the direct reading densitometer. Intensity ratios of zinc 2138.56Å to barium 2254.73Å or cadmium 2288.02Å were calculated using the emulsion calibration curve and a standard calculating board. For width measurements, line contours were recorded on photographic plates with the 16 mm microscope objectives, a 0.5 mm slit and a 64X magnification on the recorder. The widths of the zinc line at maximum density of the same barium and cadmium lines were measured from this photographic recording by means of a small scale-magnifier (see Fig. 1).

² R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.* **33**, 247 (1943).

³ J. R. Churchill, *Ind. Eng. Chem. (Anal. Ed.)* **16**, 653 (1944).

⁴ P. A. Leighton, S. Smith, and F. C. Henson, *Rev. Sci. Inst.* **5**, 431 (1934).

Analytical Curves

Analytical curves were obtained from measurements of spectrograms of standard samples ranging from 0.004 percent to 10 percent zinc in the powder base. The density results are plotted in the usual way as logarithm intensity ratio *versus* logarithm zinc concentration. The width results are plotted in a similar fashion as logarithm of zinc width at the maximum intensity of the control line (width as measured on the recorded contour) *versus* logarithm of zinc concentration (see Fig. 2).

RESULTS AND DISCUSSION

Limitation of the Density Method

As has already been stated the density measurements are limited by self-reversal and lack of contrast effects. This is apparent in Fig. 1 where the height of the maximum (which is related to density) shows very little increase with zinc concentrations above about 0.03 percent. This is further emphasized by the steepness of the analytical curve seen in Fig. 2 above this point. The self-reversal at still higher concentrations is also apparent in both figures. The curve from intensity ratios has been dotted in above this

point since it is obviously invalid over the higher range.

Comparison of Precisions of the Two Methods

Reproducibility tests in the lower part of the range, where the density method could be used, show precision of the same order only at the lowest point, i.e., around 0.004 percent zinc. (It is at this point that the density results should show their best precision since the density of the test and control lines are approximately equal. At the same point the width of the zinc line is determined near the tip and therefore will probably show lowest reproducibility). The precision of the width results gets progressively better than the density results as zinc concentration increases. Repeated exposures of the same sample at 0.03 percent indicate this. Density measurements showed standard deviations from the mean of 10 percent with barium as a control and 14 percent with cadmium. Width measurements on the same exposures show standard deviations of only 4 percent with barium and 5 percent with cadmium.

Additional tests have also been carried out in which known amounts of zinc were added to samples of inorganic powder of unknown zinc

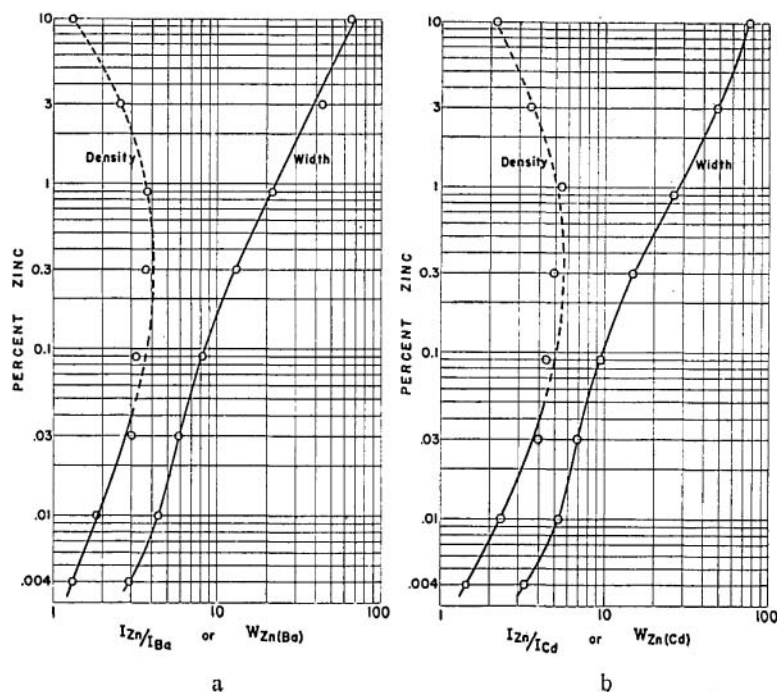


FIG. 2. Working curves as determined by intensity ratio and line width measurements with (a) barium as a control and (b) cadmium as a control. The zinc concentration is expressed as percent of the ash or inorganic sample before addition of buffer.

content and also to samples of agricultural plant material before ashing. We have been unable to observe increments with reasonable accuracy by line-density measurements even well within the apparently usable range of the working curve. On the other hand, the line width measurements on the same spectrograms give very satisfactory values for these increments even in the range beyond where the influence of self-reversal is apparent. Results from different tests of this sort are listed in Table I.

Range of Analysis by Line-Width Method

The above results show that by use of the line-width method an analytical range of at least 1000-fold is possible with a single analytical procedure. The two methods generally used to extend the single procedure range of the density method to higher concentrations, namely (1) by use of a stepped sector to reduce density, and (2) by use of less sensitive lines, are not feasible in the present instance. The use of the sector is not applicable when the line is subject to self-reversal. The next most sensitive lines of zinc, 3345.02 and 3302.59A, are not only subject to

TABLE I. Results of tests with known amounts of Zn added to samples.

Material	Zn added	Zn observed Density	Zn observed Width
Potato ash (Zn added after ashing)	0.03% 0.08%	0.024% 0.039%	0.029% 0.081%
Dried potato (Zn added before ashing)	0.0015% 0.004%	0.0014% 0.0011%	0.0016% 0.0038%
Mixed agri- cultural ash (Zn added to ash)	0.08% 0.24%	—* —*	0.09 0.26

* Zinc concentrations not in workable density range.

interference from calcium and sodium commonly found in the samples under examination, but they lack sensitivity and do not appear in measurable density until a concentration of about 0.3 percent is reached.

The fact that concentrations as high as 10 percent have been determined is of interest since it indicates the possible application of a line width method to the estimation of major constituents in agricultural ashes or inorganic powders.

Report on Colorimetry and Artificial Daylight

Copies of the report of the U. S. Secretariat on Colorimetry and Artificial Daylight, prepared in connection with the I.C.I. meeting in Paris this summer, are now available. The following subjects are considered: (1) Proposed standard illuminant *E*, (2) definitions of colorimetric purity, (3) adequacy of standard observer for technical colorimetry, (4) definition of standard illuminants in the ultraviolet for the colorimetry of fluorescent materials, (5) illuminants for color matching, (6) specification of color-rendering properties, (7) color discrimination, (8) color terminology. The progress in colorimetry since the 1939 session is indicated by a bibliography of several hundred references. Copies of this report may be obtained by writing Dr. K. S. Gibson, Chairman, Tech. Com. 7, U. S. National Committee, I.C.I., National Bureau of Standards, Washington, D. C.