The Determination of Zinc in Agricultural Materials by Atomic-absorption Spectrophotometry

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An investigation of various aspects of the determination of zinc in agricultural materials by atomic-absorption spectrophotometry is described. Satisfactory recoveries for zinc were obtained from fertilisers, soils, soil extracts and plants. The method is rapid and accurate, and with the apparatus used the limit of sensitivity is 0·025 p.p.m. of zinc. Coefficients of variation of 2 to 3 per cent. are obtained over the range 0·3 to 8·0 p.p.m. of zinc.

THE use of atomic-absorption spectrophotometry for determining zinc in plant material was described by David,[1] who found that no interference was caused by the other elements present in plants and considered that the technique was superior to chemical and polarographic

methods for determining this element.   Gidley and Jones[2] have reported the successful application of atomic-absorption spectrophotometry to the determination of zinc in a variety of metallurgical materials.   They investigated many elements for interference effects and found that only silicon caused depression of absorption.   In this laboratory, atomic absorption has been successfully used for the past 3 years for the routine determination of zinc in a variety of agricultural materials, and the results are presented in this paper.

MEASUREMENT OF ZINC ABSORPTION

APPARATUS AND METHODS—

The general arrangement of the apparatus and the method of measurement were described previously for the determination of magnesium.[3]   Two types of hollow-cathode lamp have been used.   One (kindly supplied by Mr. A. Walsh, C.S.I.R.O., Melbourne, Australia) had a zinc cathode and was operated at a current of about 10 to 12 mA; the other (obtained from Hilger & Watts Ltd., London) had a brass cathode and was operated at about 40 to 45 mA.
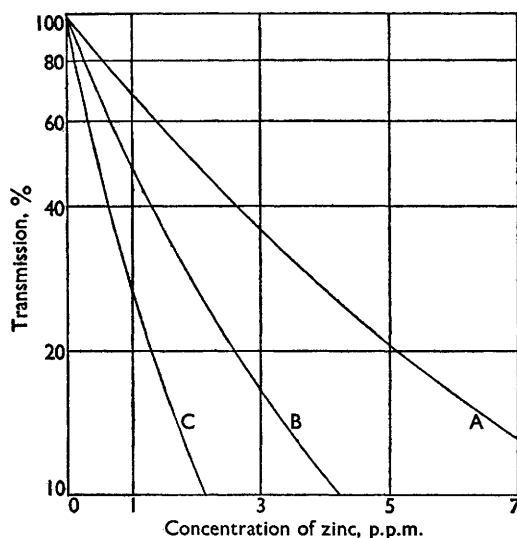

Fig. 1.   Absorption for zinc measured at 2138·6 A :
curve A, in aqueous solution; curve B, in 40 per cent.
acetone; curve C, in isobutyl methyl ketone

With both types of lamp, a "warming-up" period of 30 to 60 minutes was necessary before maximum intensity was attained.   Both lamps gave results similar in sensitivity and reproducibility, but that having the brass cathode had the longer life.   The operating currents used were the minimum necessary to ensure that full-scale readings were attainable, and, with both lamps, reduction of current to below the values mentioned above led to a rapid decrease in intensity.

The burner used provided a flame 12 cm in length and has been described by Clinton[4]; the atomiser was of the Lundegårdh type, modified to aspirate solutions directly from a beaker. The zinc line at 2138·6 A was used for all measurements, this being the only line in the zinc spectrum that gives measurable absorption.

SENSITIVITY—

The sensitivity attainable with this equipment when aqueous solutions were sprayed into an air - acetylene flame is shown by curve A in Fig. 1.   Linearity and sensitivity depend to some extent on the particular lamp used, and this curve is an approximate average of results obtained over 3 years, which in the extremes gave transmissions of 20 per cent. for 3 and 7 p.p.m. of zinc.   The sensitivity is about four times that reported by Gidley and Jones and about ten times that reported by David, and, although most of this increase in sensitivity is due to the longer flame used, some contribution may have come from the atomiser.   When a coal-gas flame is used, the sensitivity is increased by about 20 per cent., but there is no increase with a fuel-rich flame, indicating that the dissociation of zinc into atoms is virtually complete.

USE OF ORGANIC SOLVENTS—

The effect of spraying an organic rather than an aqueous solution has been discussed in detail elsewhere.[5] Curves B and C in Fig. 1 were plotted from the results obtained with solutions made up in 40 per cent. acetone and isobutyl methyl ketone, respectively. Ammonium pyrrollidine dithiocarbamate was used to form a complex with the zinc before extraction into the latter solvent, as this complex is readily soluble in esters and ketones, which are particularly suitable for spraying into flames.

The effect of pH on the extraction has been investigated. To a 10-ml portion of each of a series of sodium acetate - hydrochloric acid solutions, containing from 1 to 20 μg of zinc, were added 1 ml of a 1 per cent. aqueous solution of amonium pyrrollidine dithiocarbamate and 10 ml of isobutyl methyl ketone. The mixture was shaken, and, after the layers had separated, the zinc content of each layer was determined. The percentages of zinc extracted into the organic layer from solutions of pH 1·5, 2·1 and 2·5 to 5·0 were, respectively, 67, 95 and 100.

Somewhat surprisingly, it was found that the organic solvents used (isobutyl methyl ketone, ethyl pentyl ketone and ethyl acetate) frequently contained traces of zinc; however, these solvents could readily be purified by washing with 2 per cent. hydrochloric acid.

REPRODUCIBILITY—

Reproducibility was determined by repeatedly measuring the absorptions of a series of solutions containing 0·4, 1·6, 4·0 and 8·0 p.p.m. of zinc. At these concentrations, the coefficients of variation of the apparent zinc content, calculated from twenty-one sets of measurements, were 3·1, 2·5, 1·8 and 3·0 per cent., respectively.

With adequate control over hollow-cathode current, photomultiplier voltage, air pressure and flow of gas, reproducibility depends largely on the stability of the hollow-cathode lamp. In my experience, the above results are fairly average; on occasions, better have been obtained, and, with some lamps, worse. That Gidley and Jones obtained a coefficient of variation of 3·5 per cent. after integration for 30 seconds reflects the fact that at present not all hollow-cathode lamps are equally good.

INTERFERENCE—

David's observation[1] that none of the elements present in plant digests interferes with the determination of zinc has been confirmed. Likewise, to judge from the results in Table II (p. 533), none of the elements present in soil or fertiliser solutions causes any interference, provided always that the total concentration of salt and acid is not sufficiently great to alter the physical properties of the solution to an extent such that atomisation is affected. The

TABLE I

EFFECTS OF DIFFERENT ACIDS ON ZINC ABSORPTION

Zinc present, p.p.m.	Galvanometer reading for solution in—			
	hydrochloric acid	sulphuric acid	nitric acid	perchloric acid
0·0	100	100	100	100
0·3	88·3	88·5	88·5	87·0
0·6	78·5	79·0	79·0	79·0
1·2	64·0	64·5	64·7	64·8
3·0	35·5	35·5	35·5	34·5
6·0	18·5	18·5	18·5	18·3

plant-digest solutions used contained about 2 ml of 72 per cent. perchloric acid in 20 ml of solution; this was sufficient to cause results for zinc to be low by some 5 to 7 per cent. unless standards containing approximately the same amount of acid were used.

The effects of various acids on measurement of the zinc absorption were tested by using a series of solutions containing up to 6 p.p.m. of zinc, prepared in 0·5 N hydrochloric, sulphuric, nitric and perchloric acids. For these experiments the apparatus was set to give 100 per cent. transmission when distilled water was sprayed into the flame. The results obtained with an air - acetylene flame are shown in Table I, from which it can be seen that no acid itself caused any absorption and that, within the experimental error of reading the galvanometer, zinc absorption was the same in the four acids. Similar results were obtained with air - coal-gas and air - propane flames.

The observation by Gidley and Jones[2] that an absorption band was produced when halogen acids were sprayed into the flame and interfered with measurement of zinc absorption led to experiments in which it was established that the presence of hydrochloric acid caused no difference in the absorption at 2138 A under a wide variety of flame conditions and in presence of a number of compounds that could conceivably occur in flames in some circumstances. It was concluded that Gidley and Jones's results were caused by contamination from a brass burner giving rise to the zinc line at 2138 A and the copper lines at 2165, 2178 and 2183 A, which have been shown[6] to absorb strongly. This conclusion was reached by Gidley and Jones in a Note[7] that appeared after this paper had been submitted.

ANALYTICAL APPLICATIONS

The methods used and the results obtained for the determination of zinc in various agricultural materials are briefly described below.

FERTILISERS—

A suitable weight of sample was boiled with 3 N hydrochloric acid, the solution was evaporated to dryness, the residue was dissolved in 0·5 N hydrochloric acid, and this solution was diluted to 100 ml. Recoveries and results for different weights of sample are shown in Table II.

TABLE II
ZINC FOUND IN FERTILISERS, SOIL AND SOIL EXTRACT

Sample	Amount of sample taken	Zinc added, μg	Zinc found per g of sample, μg	
Fertiliser A*	1·0 g	—	294	Average 293
	0·25 g	—	292	
	0·25 g	100	692	(Expected 693)
	0·25 g	200	1084	(Expected 1093)
Fertiliser B†	1·0 g	—	485	Average 487
	0·25 g	—	488	
	0·25 g	100	892	(Expected 887)
	0·25 g	200	1280	(Expected 1288)
Soil	4·0 g	—	84‡	
	2·0 g	—	89	
	1·0 g	—	90	Average 90
	1·0 g	100	188	(Expected 190)
	1·0 g	200	295	(Expected 290)
Soil extract	10 ml undiluted	—	10·3	
	5 ml diluted to 10 ml	—	10·4	Average 10·5
	2·5 ml diluted to 10 ml	—	10·8	
	5 ml diluted to 10 ml	6·25	11·4	(Expected 11·5)

    * Superphosphate.
    † Proprietary fertiliser consisting essentially of lime, superphosphate, limonite and small amounts of various salts, including zinc sulphate.
    ‡ Low result probably due to decrease in efficiency of atomiser.

SOILS—

Various amounts of soil were digested with nitric and perchloric acids, silica was removed with hydrofluoric acid, and the solution was evaporated to dryness; the residue was dissolved in 5 per cent. perchloric acid, and the solution was diluted to 50 ml. Results for soils are also shown in Table II. The low result for the most concentrated solution was probably caused by a decrease in the efficiency of the atomiser owing to the high salt content. A similar effect occurred when these solutions were analysed for copper by the same method. For most soils, 1- to 2-g are sufficient.

SOIL EXTRACTS—

A 2-g sample of a peat soil was shaken with 20 ml of a 1 per cent. aqueous solution of disodium ethylenediaminetetra-acetate (a commonly used extractant for "available" zinc) for 2 hours, and the mixture was then filtered. Various aliquots of the filtrate were diluted to 10 ml, and the solutions were analysed for zinc; standards made up with 0·1 N hydrochloric acid were used. The results are also shown in Table II.

PLANTS—

Triplicate samples of various sizes were digested with 20 ml of a nitric - perchloric acid mixture (17 ml of concentrated nitric acid and 3 ml of 72 per cent. perchloric acid). After the solutions had cleared, each was concentrated to about 2 ml, transferred to a 20-ml calibrated flask, diluted to the mark with water and filtered. The filtrates were analysed for zinc, standards made up in 10 per cent. perchloric acid being used. The results are shown in Table III; each represents a single determination, and sample heterogeneity and chance contamination may have contributed to the variation between replicates.

TABLE III

ZINC FOUND IN APPLE AND GRASS

Sample	Weight of sample taken, g	Zinc added, µg	Zinc found per g of oven-dried sample, µg	
Apple	1·0	—	2·8, 3·1, 2·9 (mean 2·93)	Average 3·00
	2·0	—	3·1, 3·1, 3·0 (mean 3·07)	
	1·0	4·8	7·7, 7·4, 7·9 (mean 7·7; expected 7·8)	
Grass	0·5	—	42·0, 39·0, 40·0 (mean 40·3)	Average 39·9
	1·0	—	39·5, 40·5, 39·5 (mean 39·8)	
	2·0	—	39·8, 40·5, 38·8 (mean 39·7)	
	1·0	37·5	76·5, 78·0, 78·3 (mean 77·6; expected 77·4)	

CONCLUSION

The determination of zinc by atomic-absorption spectrophotometry compares more than favourably with other methods in simplicity, speed, reproducibility and accuracy. In a recent review of chemical methods for determining trace amounts of zinc, Margerum and Santacana[8] stated that their preferred method had an operating range of 3·3 (coefficient of variation 6·1 per cent.) to 32·7 µg of zinc (coefficient of variation 1·93 per cent.). The determination of zinc by neutron-activation analysis has also been described[9,10]; with this technique the ultimate sensitivity was 0·04 µg of zinc, and reliable determinations were possible on samples containing 0·3 µg of zinc.

In the proposed method, the limit of sensitivity (99 per cent. transmission) for an aqueous solution is 0·025 p.p.m. of zinc, which, when 2 ml of solution are used for a determination, amounts to 0·05 µg, and determinations of reasonable accuracy (coefficient of variation of, say, 5 per cent.) can be carried out on a solution containing 0·2 p.p.m. of zinc, i.e., 0·4 µg per 2 ml. When it is convenient to extract the zinc into an organic solvent, these figures are decreased to about one-fifth.

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