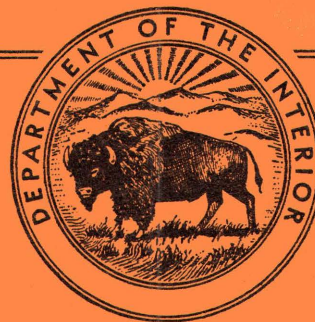

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**FIELD METHOD FOR THE
DETERMINATION OF
ZINC IN PLANTS**

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ABSTRACT

A field method for estimating zinc in fresh plant leaves is described whereby samples are collected with a leaf punch and ashed directly over a flame, the zinc in the ash then being determined with dithizone. Results obtained by the field method compare favorable with those obtained by the more precise laboratory method. Forty or more samples can be tested for zinc in a day.

INTRODUCTION

In further continuation of a study of biogeochemical prospecting for zinc (Robinson, Lakin, Reichen),^{1/} a field test for zinc in plant leaves has been devised that makes possible on-the-spot investigations in mineralized areas. The study of plant tissues offers numerous advantages for geochemical prospecting: Their composition may reflect the composition of the soils on which they grow (Robinson, Edgington, 1942); they may concentrate some elements abnormally (Williams, Lakin, Byers); and their extended root systems often sample large areas not readily studied by sampling the soils (Robinson, Edgington, 1943). Almost always present, vegetation thus offers a means of studying the increasing or decreasing concentration of an element in the soil over extended areas.

To be successful, a field test must be as simple as possible and require a minimum of reagents and apparatus. The usual methods of effecting the solution of vegetation, which require the weighing of air-dried or oven-dried samples and digesting with nitric and perchloric acids (Piper) or ashing at a controlled temperature, are time consuming and impractical for field use. Acids, moreover, are difficult and hazardous to transport. In the field test described below fresh vegetation is used, the sample being measured by leaf area (Harley, Lindner); the material then is ashed in a dish over a direct flame, and the zinc is estimated by an adaptation of a simple field method used for soils (Lakin, Stevens, Almond).

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APPARATUS

In field testing it is desirable to have reagent and equipment kits that contain everything needed yet are easily moved from place to place. The hand kit for estimating zinc in vegetation is shown in plate 1. It contains:

- 20 pyrex test tubes, 18 by 150 millimeters, marked at 3, 10, and 11 milliliters.
- 20 pyrex test tubes, 16 by 150 millimeters, marked at 5 milliliters.
- 1 rack for test tubes.
- 1 250-milliliter pyrex glass-stoppered bottle for dithizone solution.
- 1 250-milliliter pyrex glass-stoppered bottle for buffer solution.
- 1 250-milliliter pyrex glass-stoppered bottle for hydrochloric acid.
- 2 250-milliliter pyrex glass-stoppered bottles for water.
- 1 50-milliliter pyrex glass-stoppered bottle for sodium thiosulfate.

^{1/} A full list of publications cited will be found on p. 4.

- 1 50-milliliter pyrex glass-stoppered bottle for zinc standard B.
 - 1 5-milliliter graduated pipette. fitted with stopcock at upper end.
 - 1 test tube to support graduated pipette.
 - 1 3-milliliter pipette.
 - 1 camel's-hair brush.
 - 10 platinum or nickel crucibles, 4 centimeters in diameter and 2 centimeters high.
 - 1 pair platinum-tipped crucible tongs (if platinum dishes are used).
 - 1 porcelain plate on which to set platinum crucibles after ashing.
 - 1 leaf punch, Fisher Scientific Co. No. 2-846, cutting a disk 1 square centimeter in area.
 - 1 fused-quartz grating to place over burner.
- Corks.

For ashing the samples a Coleman pocket stove is satisfactory. Reserve supplies are transported by truck in a box illustrated in plate 2.

REAGENTS

Water.—Distilled in an all-pyrex still or passed through a resin demineralizer such as the Bantam manufactured by Barnstead Still & Sterilizer Co.

Acetate buffer.—Dissolve 248 grams sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) in 900 milliliters of water. Add 11 milliliters glacial acetic acid and make up to 1 liter. Remove reacting heavy metals by shaking with 0.01-percent dithizone solution.

Sodium thiosulfate.—50 grams $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 100 milliliters of water.

Standard zinc solutions.—Solution A: 0.01 percent in 1N hydrochloric acid. Dissolve reagent-grade 30-mesh zinc in a slight excess of hydrochloric acid and dilute to volume. Solution B: 5 micrograms per milliliter. Add 35 milliliters acetate buffer and 5 milliliters sodium thiosulfate to 2.5 milliliter standard solution A and dilute to 50 milliliters with 1N hydrochloric acid. This solution should be made fresh daily.

Carbon tetrachloride.—Purify reagent-grade carbon tetrachloride by distillation in an all-pyrex still.

Hydrochloric acid.—Prepare 1N hydrochloric acid from constant boiling hydrochloric acid distilled in an all-pyrex still.

Dithizone solution.—0.0025 percent (weight per volume) in pure carbon tetrachloride.

PROCEDURE

Collect 20 disks (20 square centimeters) from the leaves of the plant with the leaf punch. Place these disks in a platinum (or nickel) dish and ash directly over the flame of the Coleman pocket stove, heating only long enough to burn the samples completely. Transfer the ash to a test tube (18 by 150 millimeters) with a camel's-hair brush and rinse the dish with a little 1N

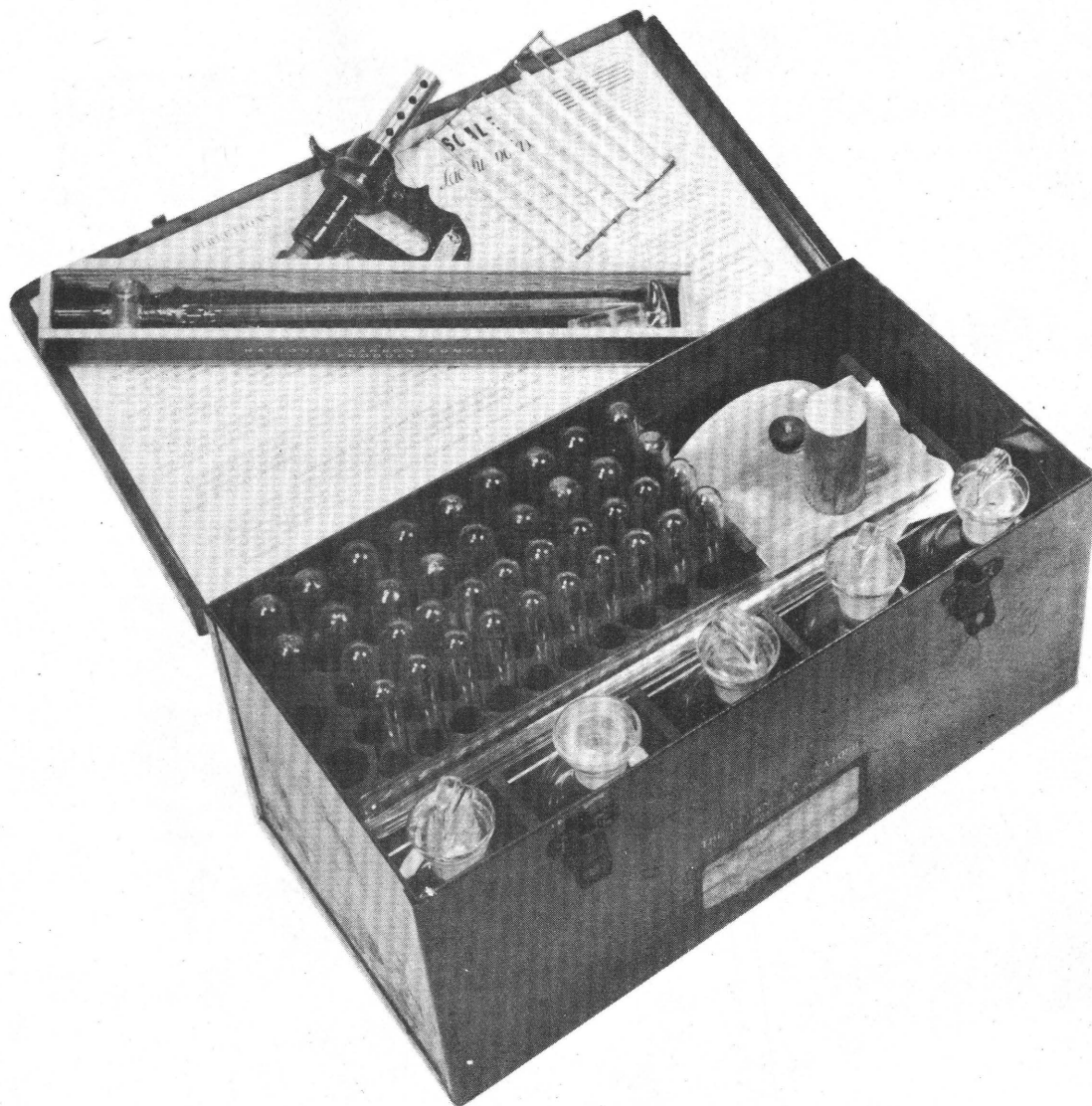


Plate 1.--Hand kit for field determination of zinc in plants.

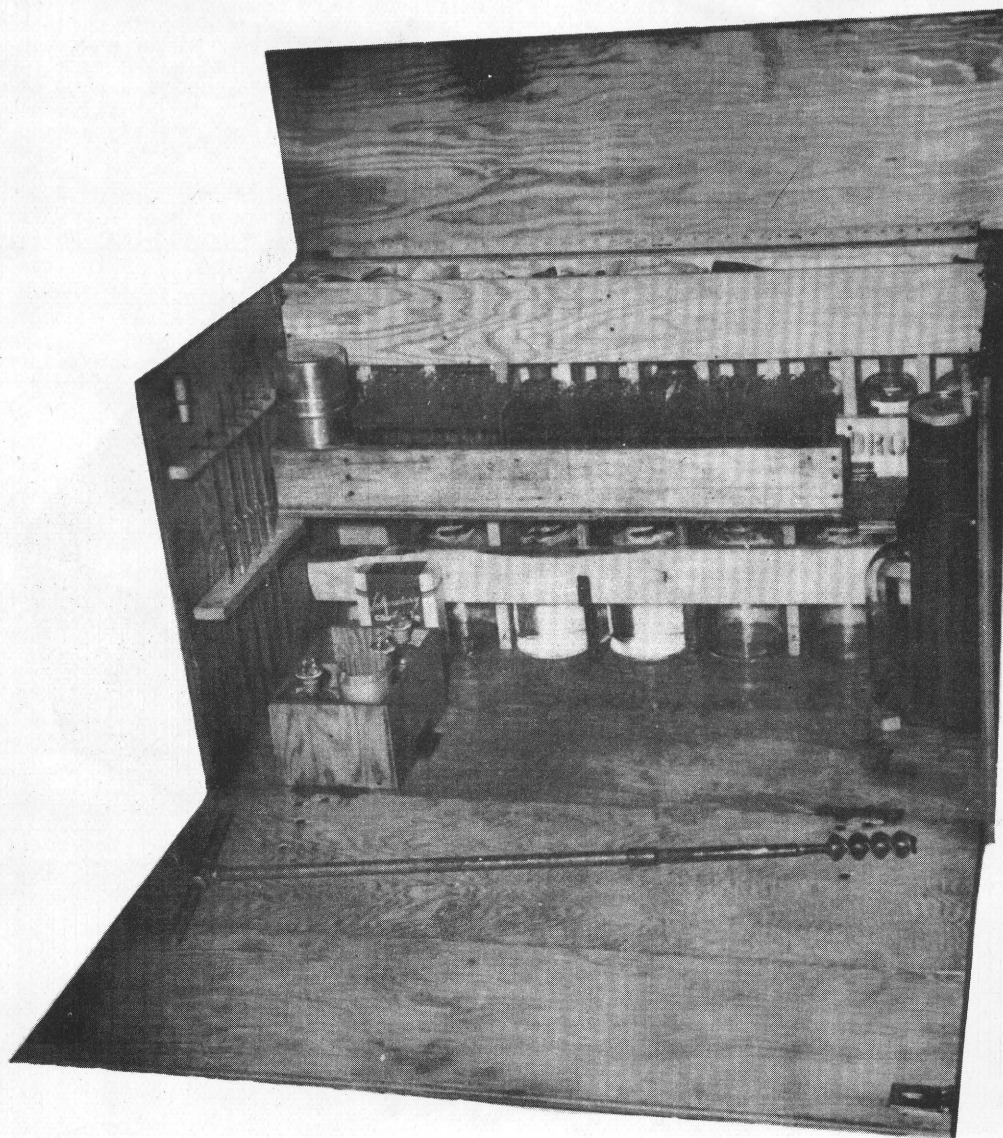


Plate 2.--Box for transporting reserve supplies by truck in field determination of zinc in plants.

hydrochloric acid. Dilute to 3 milliliters with 1N hydrochloric acid, add 7 milliliters acetate buffer and 1 milliliter sodium thio-sulfate, stopper with a clean cork, and mix by shaking.

Prepare a standard by shaking for 1 minute 1 milliliter of standard solution B (5 micrograms of zinc) with 5 milliliters of the dithizone solution in a test tube (16 by 150 millimeters). The standard must be prepared frequently because the color fades.

Put 5 milliliters of the dithizone solution in another test tube and add the sample solution in increments of 1 milliliter, shaking vigorously for 1 minute after each addition until the color of the carbon tetrachloride layer matches as nearly as possible that of the standard. If less than 1 milliliter of sample solution is needed to match the standard, dilute 1 milliliter of sample solution tenfold with water and determine the volume of this diluted solution needed to match the standard.

Volumes of sample solution needed to match the standard correspond with the following zinc values for the sample:

Table 1.—Zinc contents corresponding to various volumes of sample solution

Milliliters required for closest matching of standard	Zinc content	
	Micrograms per 100 square centimeters fresh material	Approximate micrograms per gram air-dry weight (parts per million)
Original sample solution		
5	50	100
4	60	120
3	80	160
2	125	250
1	250	500
Diluted sample solution		
6	400	800
5	500	1,000
4	600	1,200
3	800	1,600
2	1,250	2,500
1	2,500	5,000

"Micrograms per area" is a comparatively unfamiliar manner of expressing trace-element content of plant material. For orientation purposes, therefore, these calculations are given both in micrograms per gram (parts per million) and in micrograms per 100 square centimeters. Because of the variation in the leaf-structure density of different kinds of plants, no accurate conversion from area to weight basis can be made; however, it has been found that multiplying the micrograms per 100 square centimeters by 2 will give the approximate micrograms per gram.

EXPERIMENTAL

To determine the loss of zinc in ashing the plant material over a direct flame,

leaves were decomposed both by ashing and by wet oxidation with nitric and perchloric acid, and the zinc in each was then determined by the Holmes dithizone method (Holmes). Table 2 shows comparative data by wet oxidation and by ashing in platinum dishes, of samples of weighed, finely ground, air-dried plant material.

Table 2.—Loss of zinc by volatilization in air-dried plant material

Plant and sample number	Zinc content (parts per million)		
	After wet oxidation	After dry ashing	Percent zinc lost
Ragweed (1)	2,100	1,800	14
Ragweed (2)	40	27	23
Poplar (1)	1,800	1,500	16
Poplar (2)	140	120	14
Horsetail (1)	5,300	3,400	36
Horsetail (2)	70	18	72

Table 3 shows comparative data by wet oxidation and by ashing in both platinum and nickel dishes, of samples of fresh green leaves.

Table 3.—Comparison of results by wet oxidation and dry ashing of fresh vegetation.*

Plant	After wet oxidation	After dry ashing	
		In platinum	In nickel
Micrograms Zn in 5 gm. fresh material			
Zinc weed	44	52, 56, 38	--
Maple	58	66, 56, 60	--
Chrys- anthe- mums	40	35, 27, 41	--
Micrograms Zn per 100 sq. cm.			
Dog- wood	50	50-	50-, 50-
Hick- ory	160	125	100
Pop- lar	110	100	80, 80

* The figures in horizontal rows represent determinations made on separate replicate samples.

Platinum dishes are not ideal equipment for a field test because of the initial expense and the possibility of loss. Good results were obtained with nickel (table 3), inasmuch as the oxide coating formed during the ashing seems to prevent the nickel, which would interfere with the dithizone estimation of zinc, from being dissolved by the hydrochloric-acid rinse. Ashing in nickel takes longer, however, and because of greater volatilization may account for the slightly lower zinc content indicated for the samples ashed in nickel. Porcelain dishes are not satisfactory because of heat transfer and consequent slower burning, and pyrex test tubes are unsuitable in

that they do not allow free access of oxygen.

The loss of zinc through volatilization is not considered sufficiently large to affect the geochemical pattern of zinc content.

In table 4 the results of the field method performed in the field are composed with the laboratory analyses of duplicate samples using nitric-perchloric acid digestion and determination of zinc by the Holmes method. The laboratory "micrograms per gram" were calculated from the air-dry weight of the 20-square centimeter sample and the "micrograms per 100 square centimeters" directly from the area of the sample. The weight of the duplicate samples was assumed to be the same, and the field "micrograms per gram" were calculated from the air-dry weight of the corresponding sample used for laboratory analysis.

Table 4.—Comparison of laboratory and field results on fresh willow leaves

Sample	Micrograms per gram (parts per million)		Micrograms per 100 sq. cm.	
	Laboratory	Field	Laboratory	Field
1	370	190	120	60
2	230	180	105	80
3	210	170	105	80
4	320	310	130	125
5	270	210	160	125
6	230	190	150	125
7	780	630	310	250
8	900	1,100	260	300
9	470	530	310	300
10	870	750	480	400
11	750	1,000	300	400
12	950	1,200	380	500
13	930	1,000	560	625
14	900	1,800	320	625
15	1,100	1,300	780	830
16	2,400	2,300	1,300	1,250

Examination of table 4 indicates that the errors involved in the field test are not sufficiently large to obscure the basic geochemical pattern. It is felt, therefore, that the test may prove useful in biogeochemical prospecting.

A discussion of the sampling of plant material for purposes of biogeochemical prospecting and an application of the field method for zinc will be published later.

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