A Method of Estimating 6-Chloropicolinic Acid in Soil

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Introduction

In a study of the fate of 2-chloro-6-(trichloromethyl)pyridine, the active ingredient in N-SERVE® nutrient stabilizer, Redemann and co-workers (3) found that this compound underwent hydrolysis in soil to 6-chloropicolinic acid. In another study (2), it was shown that crop plants can absorb this hydrolysis product from soil and that 6-chloropicolinic acid is the residue most apt to be found following agricultural application of N-SERVE. Because of these facts, it is desirable to have a chemical method of estimating 6-chloropicolinic acid in soil.

The analytical method described is based on ultraviolet absorption spectroscopy. It utilizes the method of Morton and Stubbs (1) for correction of "irrelevant absorbance". It has given excellent results with soil samples containing between 1 and 10 ppm. 6-chloropicolinic acid. Presumably, the range could be extended to lower concentrations by increasing the thickness of the spectrophotometer cuvette.

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Procedure

A 50-gram sample of soil is mixed well with 1 gram of calcium sulfate and packed into a 3/4-inch, inside-diameter chromatographic adsorption tube, supported on a plug of glass wool.

Water is permitted to leach through the soil until 60 ml. of effluent has collected. The effluent is adjusted to pH 2.2 with dilute hydrochloric acid, and the 6-chloropicolinic acid is extracted into 3 successive 65-ml. portions of ethyl acetate. The ethyl acetate extracts are then combined and shaken out with 3 successive 25-ml. portions of 1.5N ammonia.

The ammonia extracts are combined, diluted to 100 ml. with a saturated solution of ethyl acetate in 1.5N ammonia, and the absorbance is measured in a 1-cm. silica cell at 255, 273 and 284.5 mu.

N, the micrograms of 6-chloropicolinic acid in the soil sample, is given by the formula:

$$N = 5228\ A_{273} - 3192\ A_{284.5} - 2035\ A_{255}$$

where the A terms are the absorbances at wavelengths denoted by the subscripts.

Recoveries

The recoveries of 6-chloropicolinic acid from a typical Southern California sandy loam are shown in Table 1. These indicated recoveries have not been corrected for the small negative blank.

TABLE 1

Recovery of 6-Chloropicolinic Acid from Soil A_1

Micrograms Added to 50 gm. Soil	Micrograms Found	Recovery, Percent
0	0	-
0	-16	-
50	36	72
50	48	96
100	88	88
100	88	88
200	204	102
200	176	88
500	508	101
500	468	94

Discussion

Calcium sulfate is added to the soil to act as a source of bivalent ions, thereby minimizing soil colloid peptizing by the leach water.

The absorption spectrum of the ammonium salt of 6-chloropicolinic acid in 1.5N ammonia shows a maximum absorbance at 273 mu and equal absorbances at 284.5 mu and at 255 mu. The solutions obey Beer's Law at each of these wavelengths. Moreover, the "blank" absorbance of most soils extracted and cleaned up by the recommended method is a linear function of wavelength. These observations form the rationale for the application of Morton and Stubb's correction method.

The recoveries listed in Table 1 illustrate the fact that this method has performed satisfactorily with at least one soil. The analytical procedure described should prove useful for studying the persistence of residues of 6-chloropicolinic acid in a wide range of soils and a variety of environments.

Acknowledgment

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References

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