Potentiometric Determination of Monuron in Herbicide Formulations

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Monuron is extracted from a dispersion of the sample in hydrochloric acid into chloroform and the residue after evaporation of the chloroform is hydrolysed with boiling 24 N sulphuric acid. The liberated dimethylamine is distilled into 2 per cent. boric acid and titrated potentiometrically with standard hydrochloric acid. The method has been applied to technical monuron and aqueous suspension formulations with an error of 0.9 per cent.

Monuron, \(N'-(4\text{-chlorophenyl})-NN\text{-dimethylurea}\), is structurally related to diuron. For the macrodetermination of diuron and monuron, Lowen and co-workers\(^1,^2\) described three titrimetric methods; these methods are time consuming mainly because of the high stability of the herbicides. A rapid method for assaying diuron\(^3\) depends on the liberation of the dimethylamine in boiling 24 N sulphuric acid followed by its distillation and titration with standard hydrochloric acid, with methylene blue - methyl red as indicator. The experimental conditions of this method were found to be equally applicable in the determination of monuron, but the results were over-estimated owing to the obscure end-point. This difficulty was caused by the buffering effect of 4-chloroaniline, which is distilled together with the dimethylamine and is soluble in dilute boric acid solution. The inflection point occurred at \(pH 5.9\) to 6.3, instead of \(pH 5.1\) when dimethylamine alone was titrated. The methylene blue - methyl red indicator (\(pH 5.0\) to 5.3) was therefore unsuitable and is used only for determining the reagent blank. Several other indicators were tried without success. However, the end-point was satisfactorily located potentiometrically and was evaluated by calculating the first and second derivatives of the potential, \(dV\) and \(d^2V\), as a function of volume,\(^4\) with the equivalence point occurring at the maximum of the \(dV\) graph.

**Method**

**Apparatus—**

Steam-distillation apparatus.

\(\text{pH meter—A direct-reading pH meter, equipped with a glass and a saturated calomel electrode and a magnetic stirrer, was used.}\)

**Reagents—**

\(\text{Hydrochloric acid, 4 N.}\)
\(\text{Sulphuric acid, 24 N.}\)
\(\text{Sodium hydroxide solution, 10 N.}\)
\(\text{Boric acid solution, 2 per cent.}\)
\(\text{Mixed indicator—Mix equal volumes of aqueous solutions containing 0.4 per cent. of water-soluble methyl red and 0.2 per cent. of methylene blue.}\)
\(\text{Standard hydrochloric acid, 0.05 N.}\)

**Procedure—**

Weigh accurately a sample containing 0.3 to 0.4 g of monuron into a 250-ml separating funnel, add 100 ml of 4 N hydrochloric acid, extract the mixture successively with three 50-ml portions of chloroform, by shaking the funnel for 1 minute each time, and collect the extracts in a 250-ml boiling flask. Evaporate off the solvent at a temperature of 40 to 50 \(^\circ\text{C}\) under reduced pressure with a rotary evaporator, add 30 ml of 24 N sulphuric acid and boil the solution under reflux for 30 minutes. Add cautiously 100 ml of water to the cooled solution, transfer the contents to a 500-ml Kjeldahl flask, cool again, then add 85 ml of

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10 N sodium hydroxide solution. Distil the solution into a 500-ml conical flask containing 50 ml of 2 per cent. boric acid solution until 150 ml of the distillate have been collected. Transfer the contents of the flask into a 600-ml beaker and titrate them potentiometrically with 0.05 N hydrochloric acid.

Carry out concurrently a determination on the reagents used, detecting the end-point visually with the mixed indicator.

One millilitre of 0.05 N hydrochloric acid is equivalent to 9.935 mg of monuron (relative molecular mass 198.7).

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\text{Monuron content of sample, per cent. } m/m = \frac{0.9935V}{\text{Amount of sample in grams}}
\]

where \( V \) ml is the volume of 0.05 N hydrochloric acid used (corrected for the blank).

**RESULTS AND DISCUSSION**

Monuron Col is an aqueous suspension containing 50 per cent. of active ingredient together with surfactants. To establish the accuracy of the method, analyses were carried out on 0.3-g portions of pure monuron alone and in the presence of an equal amount of blank Col formulation, which contained all of the components except the active ingredient.

The recovery of monuron, based on fourteen determinations, averaged 99.5 per cent. with a coefficient of variation of 0.9 per cent., which is considered to be the error of the method. The precision of the method applied to various aqueous formulations was found to be acceptable, with agreement between duplicates within 0.3 per cent. for samples containing 35 to 60 per cent. of monuron.

The method is not affected by the presence of ammonium ions and free amines, but any volatile bases liberated from other components of the formulation interfere. Both diuron and fenuron are determined as monuron, but diuron can be distinguished by the presence of insoluble 3,4-dichloroaniline in the distillate, while with monuron the distillate is clear. Linuron and monolinuron are hydrolysed to yield methoxymethylamine, which is partially distilled into the boric acid solution. Other herbicides, such as bipyridylium compounds, triazines, halogenated pyridines and phenoxyacetic acids, have no effect.

**REFERENCES**


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