

MT Methods

The following is a list of descriptions for CIPAC's MT Methods. For more information, visit the CIPAC website.

International Pesticides Analytical Council (CIPAC) Website:
www.cipac.org

CIPAC F

MT 1 FREEZING POINT

OUTLINE OF METHOD:

The sample is heated to a temperature above its melting point and then allowed to cool in a temperature controlled jacket. The freezing point is taken as that temperature of the material which remains constant to within 0.5 °C for 4 min.

MT 2 MELTING POINT

OUTLINE OF METHOD.

The sample, in a capillary tube, is heated at a controlled rate in a stirred liquid bath, and the temperature observed at which a meniscus is formed on the sample, and/or complete liquefaction of the sample occurs.

MT 3 SPECIFIC GRAVITY, DENSITY, AND WEIGHT PER MILLILITRE

3.1 Hydrometer method

OUTLINE OF METHOD

The sample is brought to the prescribed temperature and transferred to a hydrometer cylinder at approximately the same temperature. The appropriate hydrometer is lowered into the sample and allowed to settle. The hydrometer is read and the temperature of the sample noted. If required, the cylinder and its contents are placed in a constant temperature bath to avoid excessive temperature variation during the test.

3.2 Pyknometer method

OUTLINE OF METHOD In this method the weights of equal volumes of the material and water are compared.

3.2.1 Capillary stoppered pyknometer

SCOPE

The method is suitable for the determination of the specific gravity or density of liquids or solids. It is not suitable for these determinations on highly volatile liquids.

3.3 Density of suspension concentrates

3.3.1 Hydrometer method

OUTLINE OF METHOD

Direct determination of density by hydrometer, density bottle or liquid displacement method has been shown to be unsuccessful because of aeration and viscosity effects. The density at 20 °C of a 1 : 1 aqueous dilution can be readily determined using a hydrometer and hence the actual density of the suspension concentrate can be calculated.

3.3.2 Density bottle method

OUTLINE OF METHOD

A portion of the sample is weighed into a density bottle and diluted with water containing an anti-foam agent, using vacuum, if necessary to remove occluded air. The volume of sample taken is then found by making up to capacity with the anti-foam solution and weighing.

MT 5 MATERIAL SOLUBLE IN ACETONE

SCOPE These methods are intended for materials which are freely soluble in acetone.

5.1 Hot solution

OUTLINE OF METHOD

The sample is refluxed with acetone, the acetone is evaporated, and the residue is dried and weighed.

5.2 Solution at room temperature

OUTLINE OF METHOD The material is shaken with acetone, the insoluble material is filtered off, dried and weighed.

MT 6 MATERIAL SOLUBLE IN HEXANE

SCOPE These methods are intended for materials which are freely soluble in hexane.

OUTLINE OF METHOD

The sample is refluxed with hexane, the hexane is evaporated and the residue dried and weighed.

MT 7 MATERIAL SOLUBLE IN ETHANOL

SCOPE These methods are intended for materials which are freely soluble in ethanol.

7.1 Hot solution

OUTLINE OF METHOD The sample is refluxed with ethanol, the insoluble material is filtered off, dried and weighed.

7.2 Solution at room temperature

OUTLINE OF METHOD The material is shaken with ethanol, the insoluble material is filtered off, dried and weighed.

MT 8 MATERIAL INSOLUBLE IN KEROSENE

OUTLINE OF METHOD

The sample, dissolved in kerosene, is exposed to daylight at room temperature for 10 days. It is examined at intervals for any turbidity and sediment.

MT 9 MATERIALS SOLUBLE IN WATER

SCOPE

The method is intended for materials containing up to 1% water-soluble material.

OUTLINE OF METHOD

The sample is shaken in water until all the soluble material has dissolved. The insoluble matter is filtered off, dried and weighed.

MT 10 MATERIAL INSOLUBLE IN WATER

SCOPE

The method is used for the determination of (i) impurities in water-soluble technical pesticides or (ii) insoluble materials in water-soluble formulations which could cause blockage of sieves or jets in spray machinery.

10.1 Hot solution of the sample

OUTLINE OF METHOD

The sample is dissolved in boiling water; any insoluble matter is filtered off, dried, and weighed.

10.2 Cold solution of the sample

OUTLINE OF METHOD

The sample is dissolved in cold water; any insoluble material is filtered off, dried, and weighed.

10.3 Coarse material insoluble in water

OUTLINE OF METHOD

The material is shaken with water for a given time, then the mixture is sieved, and any residue on the sieve is dried and weighed.

10.4 Materials insoluble in aqueous solutions of pesticides

OUTLINE OF METHOD

The sample is filtered through a sintered glass crucible, the crucible is dried, weighed and hence the insoluble material content is determined.

MT 11 MATERIAL INSOLUBLE IN XYLENE

SCOPE

The method is intended for the determination of insoluble material in aldrin (HHDN) and dieldrin (HEOD).

MT 12 FLASH POINT

INTRODUCTION

Flash points are obtained by measuring the lowest temperature at which the vapour/air mixture over a substance, usually an organic liquid, will ignite. Several tests are used, which do not necessarily give the same measure for a given substance. Even with the strictest attention to detail both with the apparatus and its use, variations between laboratories can amount to several degrees. The tests are, however, very important because they are used in various ways to control the conditions under which substances, potentially dangerous as fire hazards, are stored, used and transported. In the U.K. alone there are six different values which, according to circumstances, categorise a substance and two test methods are required. Before determining a flash point, ensure that the correct method is used. In the U.K., the Abel Method, described in the Petroleum (Consolidation) Act, 1928, is the legal method, where appropriate, for determining flash points. In the USA a flash point of 27 °C (80 °F) by the Tag Open Cup Method is used by the US Interstate Commerce Commission as the minimum value for classifying liquids as non-flammable. The Tag Closed Tester is used by the NFPA (National Fire Protection Association, USA) for their insurance code. The result reported should always specify the method used, e.g. 10 °C (50 °F) Abel Method.

12.1 Abel method

INTRODUCTION

The Act makes no provision for liquids having a flash point below 19 °C (66 °F), consequently, additional methods are given for liquids flashing between 32 and 49 °C (90 and 120 °F) and for liquids flashing between 0 and 18 °C (65 °F).

12.2 Tag closed tester

SCOPE

This method determines the flash point of all mobile liquids flashing below 79 °C (175 °F) except products classified as Grade No 4 or heavier fuel oil (Note 10).

OUTLINE OF METHOD

The sample is placed in the cup of the tester and, with the lid closed, heated at a slow constant rate. A small flame of specified size is directed into the cup at regular intervals. The flash point is taken as the lowest temperature at which application of the test flame causes the vapour above the sample to ignite.

12.3 Pensky-Martens closed tester

SCOPE

This method is intended for determining the closed flash point and the fire point of petroleum and other products having a flash point above 49 °C (120 °F), including fuel oils, viscous materials, and suspensions of solids.

OUTLINE OF METHOD

The sample is heated at a slow constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of the stirring. The flash point is the lowest temperature at which application of the test flame causes the vapour above the sample to ignite.

MT 14 FREEZING MIXTURES

14.1 At - 5 ± 1 °C

14.2 At - 10 ± 1 °C

MT 15 SUSPENSIBILITY OF WETTABLE POWDERS IN WATER

15.1 CIPAC method

DEFINITION

Suspensibility is defined as the amount of active ingredient suspended after a given time in a column of liquid, of stated height, expressed as a percentage of the amount of active ingredient in the original suspension.

OUTLINE OF METHOD

A suspension of known concentration in Standard Water or distilled water is prepared, placed in a prescribed measuring cylinder at a constant temperature, and allowed to remain undisturbed for the specified time. The top 9/10ths are drawn off and the content of active ingredient in the bottom 1/10th determined, so allowing the content of the top 9/10th to be calculated.

SCOPE

The method is suitable for suspensions containing up to 1% active ingredient but is not necessarily suitable for suspensions of higher concentrations.

15.2 AID (Aid for International Development Programme) method

INTRODUCTION

The suspensibility test is carried out on the material as received and/or after accelerated storage. When tested as received, the test is carried out with distilled water, but after accelerated storage, Standard Water is used.

SCOPE

This method has been successfully used with (i) 75% DDT wetttable powders and (ii) malathion wetttable powders, at a concentration of 5 g per 100 ml.

MT 16 MATERIAL INSOLUBLE IN DICHLORODIFLUOROMETHANE

OUTLINE OF METHOD

Based on WHO Method WHO/M/9 in 'Specifications for Pesticides used in Public Health', 4th Ed. 1973.

MT 17 LOSS IN WEIGHT

17.1 Weight loss in an oven for 1 hour

OUTLINE OF METHOD The sample is heated in an oven at the specified temperature for 1 h.

17.2 Weight loss under vacuum at temperatures above room temperature

OUTLINE OF METHOD

The sample is heated to constant weight in a vacuum oven at a specified temperature and pressure.

17.3 Weight loss under vacuum at room temperature

OUTLINE OF METHOD

The material is stored for a specified time under reduced pressure in the presence of phosphorus(V) oxide as desiccant. The percentage loss is determined.

17.4 Weight loss at 100 °C for 4 hours

OUTLINE OF METHOD

The material is heated at 100 °C for 4 h, and the loss in weight is determined.

MT 18 STANDARD WATERS

INTRODUCTION

Instructions for the preparation of Standard Waters and of waters of any desired hardness are given in CIPAC Monograph 1. For the Standard Waters A to G, stock solutions of Ca⁺⁺ and Mg⁺⁺ are prepared; the working solutions are then made by dilution of these stock solutions.

18.1 Preparation of Standard Waters A to G (MT 18)

18.2 Preparation of salted waters H and J.

18.3 Non-CIPAC Standard Waters

18.3.1 WHO Standard Hard Water

18.3.2 GB Standard Water

18.3.3 AOAC Standard Water

18.3.4 US Navy Hard Water

18.3.5 Synthetic Nile Water

18.3.6 ASTM Hard Water

18.4 Preparation of Standard Waters of required hardness

CIPAC H

18.5 Simplified method of preparing stock solutions

MT 19 PHOSPHATE BUFFER SOLUTIONS

MT 20 STABILITY OF DILUTE EMULSION

MT 21 SILICA FOR CHROMATOGRAPHY

21.1 Silica

21.2 Sorbisil® M 60

21.3 Florisil

MT 22 VISCOSITY

22.1 Viscosity of transparent and opaque liquids in CGS units

22.2 Redwood method

INTRODUCTION

This method determines the viscosity of an oil as a time of flow in seconds through a Redwood viscometer; it does not measure viscosity in absolute units.

22.3 Viscosity of mineral oil

SCOPE

This method describes a procedure for the determination of the kinematic viscosity of liquid petroleum products, either transparent or opaque, by measuring the time for a volume of the liquid to flow under gravity through a calibrated glass capillary viscometer. The method is intended for liquids which exhibit Newtonian flow

MT 23 MISCIBILITY WITH HYDROCARBON OIL

OUTLINE OF METHOD

The sample is mixed with a suitable oil and is then allowed to stand at 30 °C for 1 h. The solution is examined for layering or separation of solid material.

SCOPE

The test is intended to determine whether a pesticide solution is suitable for application after dilution with oil instead of water.

MT 24 PHOSPHORUS(V) OXIDE

MT 25 SAND FOR GERMINATION TESTS

MT 26 JOHN INNES COMPOST

26.1 Seeding Compost - with fertilizer

26.2 Seeding Compost - without fertilizer

MT 27 MATERIAL INSOLUBLE IN ACETONE

MT 28 DIMEDONE DERIVATIVE

OUTLINE OF METHOD

The aldehyde is heated with dimedone, the condensation product filtered off, and re-crystallized from ethanol. The aldehyde is characterized by the melting point of this derivative.

MT 29 SULPHATED ASH

MT 30 Water

30.1 Karl Fischer method

OUTLINE OF METHOD

The sample is dispersed in methanol, and titrated with standard Karl Fischer reagent of known water equivalent.

30.2 Dean and Stark method

OUTLINE OF METHOD

The water in the sample is determined by forming an azeotropic binary mixture with toluene, or solvent naphtha, and then distilling.

30.3 Free water - 'Speedy' method

30.4 Water in acetone solutions.

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30.5 Karl Fischer method using pyridine-free reagents

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MT 31 FREE ACIDITY OR ALKALINITY

SCOPE

The method is suitable for determining free acidity or alkalinity in technical or formulated pesticides. It does not allow the determination of acids or alkalis which are insoluble in acetone-water mixtures.

OUTLINE OF METHOD

The acidity or alkalinity is determined by titration with standard acid or alkali, in the presence of methyl red. Where this is impracticable, the end point is determined electrometrically.

31.1 Methyl red indicator method

31.2 Electrometric procedure

31.3 Acidity of petroleum products

MT 32 DETERMINATION OF CONDUCTIVITY

MT 33 TAP DENSITY

OUTLINE OF METHOD

The powder is put into a glass measuring cylinder of known mass which is then raised and allowed to fall vertically through a distance of 2.5 cm on to a rubber pad. The operation is repeated 50 times and the final volume of the powder is measured.

MT 34 DUSTABILITY TESTS AFTER TROPICAL STORAGE

MT 35 OIL INSOLUBLE MATERIAL

MT 36 EMULSION CHARACTERISTICS OF EMULSIFIABLE CONCENTRATES

The (existing) methods are not always suitable for emulsifiable concentrates containing solid active ingredients. For these and for products used in very low concentrations alternative methods are under consideration.

36.1 Five per cent v/v oil phase

36.2 1 per cent v/v oil phase

CIPAC K

36.3 Emulsion characteristics and re-emulsification properties

SCOPE

The method is suitable for determining the emulsification stability of emulsion formed by the dispersion of emulsifiable concentrates (EC), or emulsions, oil in water (EW) at dilution rates of 0.1 % to 5 % (Note 1).

OUTLINE OF METHOD

An emulsion of known concentration in standard water is prepared. The stability of this emulsion is then assessed in terms of amounts of free 'oil' and/or 'cream', which separates while the emulsion is allowed to stand undisturbed for 24 h. The ability of the system to re-emulsify at the end of the 24 h period is also determined.

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MT 37 ISOLATION OF ACTIVE INGREDIENT

37.1 Extraction with acetone

37.2 Extraction with petroleum spirit

37.3 Removal of solvents by distillation

MT 38 ORGANIC CHLORINE

38.1 Potassium - xylene method

OUTLINE OF METHOD

The organic chlorine is converted by potassium in xylene to the chloride ion which is then titrated by the silver nitrate/ammonium thiocyanate procedure, or determined electrometrically.

38.2 Stepanov method

38.3 Oxygen flask method

MT 39 STABILITY OF LIQUID FORMULATIONS AT 0°C

39.1 Emulsifiable concentrates and solutions

OUTLINE OF METHOD

A sample is maintained at 0°C for 1 h and the volume of any separated solid or oily matter is then recorded. Storage at 0°C is continued for 7 days, any solid matter is settled by centrifuging and its volume recorded.

39.2 Aqueous solutions

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39.3 Low temperature stability of liquid formulations

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MT 40 WATER CONTENT AND SUSPENDED SOLIDS IN TECHNICAL ESTERS OF PHENOXYALKANOIC ACIDS

OUTLINE OF METHOD The ester is dissolved in toluene. Any insoluble matter is filtered off, dried and weighed.

MT 41 DILUTION STABILITY OF HERBICIDE AQUEOUS SOLUTIONS

MT 42 PARTICLE SIZE OF COPPER AND SULPHUR PRODUCTS

SCOPE

The method is intended for determining the particle size of water insoluble copper compounds and 'micronized' sulphur products.

OUTLINE OF METHOD

The method is based on the rate of settling of particles in suspension in a liquid of known viscosity. A suspension of the sample is successively decanted into a series of beakers. A cumulative curve of particle size is constructed.

42.1 Formulations without carriers

OUTLINE OF METHOD

The sample is made into a suspension of unit particles. This is then successively decanted into a series of beakers.

42.2 Formulations containing carriers

OUTLINE OF METHOD.

A suspension is successively decanted as in MT 42.1. Separate determinations of the total weight (active ingredient plus carrier) and the active ingredient for each successive deposit are made. These determinations give the particle size of the active ingredient and also that of the carrier.

MT 43 PARTICLE SIZE DISTRIBUTION OF DDT WETTABLE POWDERS

OUTLINE OF METHOD.

A modified Andreason method is described in which a uniformly dispersed suspension of the DDT in standard water settles under stable conditions. Samples are withdrawn from a fixed point in the suspension, after given times, and the DDT content of each is then determined (Note 1).

It is assumed that the suspension is sufficiently dilute to allow settling without mutual particle interference and, also, that Stokes' Law is obeyed.

MT 44 'FLOW NUMBER'

The method has not been collaboratively tested, although it has been shown to be useful:

SCOPE

The method is suitable for the determination of flowability (flowing properties) of powders, i.e. mineral carriers, formulated dusts and wettable powders containing pesticides. The method is *not* suitable for:

- (i) seed treatment powders or other powders to which oils have been added to suppress dustiness, or
- (ii) powders which do not form homogeneous mixtures with sand (Note 2). The products to be tested should pass a 250 μm test sieve; products of larger particle size are examined for free flow by visual inspection.

MT 45 REMOVAL OF DYES

OUTLINE OF METHOD

The sample, dissolved in petroleum spirit, is chromatographed on a column of alumina, Brockmann activity III.

MT 46 ACCELERATED STORAGE PROCEDURE

SCOPE

The objective is to accelerate the ageing of a product by heating.

No evidence is available to indicate that a product which has failed this test has a satisfactory shelf life (of at least 2 years) either in the tropics or in temperate zones. The test thus provides a useful guide on performance after storage in hot or temperate climates. However, a product may pass the test and yet be unsatisfactory in the field.

46.1 General method

As this is intended as a model procedure, temperature and times specified are examples only since the parameters will normally be given for individual pesticide formulations. However, as the factors involved in storage are numerous, several accelerated storage procedures are described.

46.2 AID methods

CIPAC J

46.3 Accelerated storage procedure (combined method)

SCOPE

The objective is to simulate the normal long-term ageing of a formulation by heating. Although actual data from a product in sales packs and stored in e.g. warehouses is preferable, the accelerated storage test provides useful guidance on performance after storage since many formulations that perform poorly in the accelerated test do not have satisfactory shelf lives (of at least 2 years) in hot or temperate climates.

OUTLINE OF METHOD

A sample is placed in a glass bottle (or another suitable container), which is subsequently closed and placed in an oven at a specified temperature for a defined period of time.

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MT 47 PERSISTENT FOAMING

MT 48 STABILITY OF TAR OIL PRODUCTS

48.1 Undiluted miscible type

OUTLINE OF METHOD

The product is stored at -10°C for 16 h and is examined for the presence of cloudiness and deposits. It is then warmed to 0°C and rapidly poured into ice-cold, distilled water. The mixture is allowed to stand at room temperature for 4 h and is examined for the separation of oil, then poured through a sieve and the sieve examined for any material retained e.g. crystalline or slimy deposits.

48.2 Stock emulsion type

OUTLINE OF PROCEDURE

A sample is cooled to -5°C for 48 h and is then examined for traces of separated oil and sediment. It is then heated to 20°C for 1 h, poured into distilled water at the same temperature, and allowed to stand for 4 h. The amount of oil that has separated is noted. The mixture is then poured through a sieve which is examined for any material retained e.g. crystalline or slimy deposit.

MT 49 STABILITY OF TAR AND PETROLEUM PRODUCTS - DILUTED

49.1 Tar oils - miscible and stock emulsion type

OUTLINE OF METHOD

The sample is added to GB Standard Water, stirred, allowed to stand for 4 h and, after gentle stirring, poured through a sieve which is then examined for traces of separated oil.

49.2 Petroleum oil - miscible type

MT 50 ALUMINA

MT 51 STABILITY OF UNDILUTED PETROLEUM - TAR AND PETROLEUM OIL PRODUCTS

51.1 Miscible type

OUTLINE OF METHOD

A sample is cooled to $-5 \pm 1^{\circ}\text{C}$ and is then examined for cloudiness. It is warmed to 0°C , poured rapidly into ice-cold, distilled water and stirred vigorously. After standing at room temperature for 4 h, it is then examined for oil.

MT 52 STABILITY OF DILUTED PETROLEUM - TAR AND PETROLEUM OIL PRODUCTS

52.1 Miscible type

OUTLINE OF METHOD

The product is added to vigorously stirred GB Standard Water and allowed to stand for 4 h. It is then examined for traces of oil.

MT 53 WETTABILITY

53.1 Wetting time of a standard tape

OUTLINE OF METHOD

A weighted length of cotton tape is dropped into a tall cylinder containing an aqueous solution of a wetting agent. The time required for the thread connecting the weight and the tape to relax is recorded as the sinking time. Concentrations of wetters requiring a sinking

time of 15 sec are compared. The test may be used on formulated pesticides but it does not necessarily apply to cationic wetters.

53.2 Wetting of leaf surfaces

OUTLINE OF METHOD

A freshly picked leaf is immersed in a solution of wetting agent under standardized conditions and a visual examination of the area wetted is made.

53.3 Wetting of wettable powders

SCOPE

The method describes a procedure for the determination of the time of complete wetting of wettable powders.

OUTLINE OF METHOD

A weighed amount of the powder is dropped on water in a beaker from a specified height. The time for complete wetting is determined.

MT 54 STABILITY OF UNDILUTED PETROLEUM OIL FORMULATIONS, INCLUDING THOSE CONTAINING DNOC AND TAR PRODUCTS

OUTLINE OF METHOD

The product is cooled, examined for separation of free oil, heated and then poured into distilled water. After standing, it is examined for traces of free oil.

MT 55 STABILITY OF AQUEOUS DILUTIONS OF PETROLEUM OIL FORMULATIONS, INCLUDING THOSE CONTAINING DNOC AND TAR PRODUCTS

55.1 Petroleum oil and tar products

OUTLINE OF METHOD

The sample is added to GB Standard Water, mixed thoroughly, and allowed to stand for 4 h; the amount of free oil is noted.

55.2 Petroleum Oil Formulations, including those containing DNOC.

55.3 Petroleum oils for orchard use.

55.4 Petroleum oils for glasshouse use.

MT 56 VOLATILITY OF NEUTRAL OIL

56.1 Preliminary examination

56.2 Full method.

MT 57 UNSULPHONATED RESIDUE OF NEUTRAL OIL

MT 58 DUST CONTENT AND APPARENT DENSITY OF GRANULAR PESTICIDE FORMULATIONS

58.1 Sampling

58.2 Preparation of sample.

58.3 Sieve analysis

58.4 Apparent Density after compaction without pressure

MT 59 SIEVE ANALYSIS

OUTLINE OF METHOD

Sieve analysis consists of the quantitative separation of a powder into fractions with different ranges of particle size by use of an appropriate sieve or sieves.

Sieving is carried out either *(i)* dry, by a process of shaking, tapping and brushing; or *(ii)* wet, by washing the material on the sieve with a stream of water. Treatment of the sample with a wetting agent is used, where necessary, to assist the sieving process. The specification or the method of analysis for the material under test gives directions as to whether dry or wet sieving is to be applied.

Where more than one nominal aperture size is specified, the sample is first sieved on the smallest aperture sieve. This removes most of the very fine particles which tend to clog the sieves and may interfere with quantitative separation of the larger particles. The sieves are stacked in order of aperture size with the largest at the top; the retained material is transferred to the largest aperture sieve, and sieving continued until passage of undersize material through each sieve is substantially complete.

The residue on each sieve is finally transferred to a dish, dried if wet sieving has been used, and weighed.

59.1 Dry sieving - dusts

59.2 Granular products. See MT 58

59.3 Wet sieving

MT 60 SOLUBILITY OF THE ALKALI METAL SALTS OF PHENOXYALKANOIC ACID HERBICIDES AND THEIR SOLID FORMULATIONS

MT 61 DISTILLATION RANGE OF NEUTRAL OIL

MT 64 HYDROLYSABLE ORGANIC CHLORINE

64.1 HCH technical

64.2 HCH dusts and dispersible powders

64.3 HCH emulsifiable concentrates and solutions

64.4 DDT technical

64.5 DDT dusts and wettable powders

64.6 DDT emulsifiable concentrates and solutions

MT 65 ORGANIC CHLORINE IN PESTICIDES IN AQUEOUS EMULSIONS

OUTLINE OF METHOD

The pesticide is absorbed on granulated carbon, which is then extracted with hydrocarbon-alcohol solvent mixture. The extracted material is reacted with sodium and the chloride ion produced is determined by potentiometric titration with standard silver nitrate solution.

SCOPE

The method is suitable for aqueous emulsions produced from emulsion concentrates of HCH, lindane, DDT, endrin, HEOD, and HHDN. It is probably suitable for other organochlorine pesticides.

MT 66 FREE ACIDITY OF PHENOXYALKANOIC ESTERS

OUTLINE OF METHOD

The material is dissolved in ethanol, cooled and the free acid titrated with standard sodium hydroxide.

MT 67 FAT EXTRACTION APPARATUS

MT 68 TOTAL CHLORIDES

68.1 Chlorides in phenoxyalkanoic acids

OUTLINE OF METHOD

The material is dissolved in ethanol, diluted with water, and the chloride determined by titration with silver nitrate.

68.2 Chlorides in technical mercurial compounds

OUTLINE OF METHOD

Heat the sample with sodium hydroxide and zinc metal, filter off the liberated mercury as a zinc amalgam, and determine the chloride in the filtrate by the Volhard method.

SCOPE

The method is suitable for the determination of the total chloride in technical mercurial chlorides, e.g., mercury(II) chloride, phenylmercury(II) chloride, etc.

MT 69 FREE PHENOLS

69.1 2,4-D

OUTLINE OF METHOD

The absorbance of an ethanolic-ammonia solution of the sample is determined, after adding 4-aminophenazone and potassium hexacyanoferrate(III) solutions

69.2 MCPA

69.3 2,4-DB

69.4 Dichlorprop

69.5 MCPB

69.6 Mecoprop

MT 71 SOLUBILITY IN SODIUM HYDROXIDE

71.1 Phenoxyalkanoic acids

71.2 Cresols

71.3 Bromoxynil and Ioxynil

OUTLINE OF METHOD

The material is dissolved in sodium hydroxide and the insoluble material is determined by sieving.

MT 73 HARDNESS OF WATER

MT 74 NEUTRALITY

OUTLINE OF METHOD

The sample is shaken with distilled water to which an acid-base indicator has been added. The colour of the aqueous layer is compared with that of a neutral solution of the indicator.

MT 75 DETERMINATION OF pH VALUES

75.1 General method

OUTLINE OF METHOD

The pH value of a liquid is determined by means of a pH meter and a glass electrode.

75.2 pH of aqueous dispersions

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75.3 Determination of pH values (revised method)

OUTLINE OF METHOD

The pH value of a mixture of a sample with water or of an undiluted aqueous formulation is determined by means of a pH meter and an electrode system.

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MT 76 SOLUBILITY IN AQUEOUS TRIETHANOLAMINE

MT 77 DETERMINATION OF 1-CHLORO-2,3-EPOXYPROPANE

OUTLINE OF METHOD

The 1-chloro-2,3-epoxypropane is reacted with trimethylamine hydrochloride, and the liberated trimethylamine is titrated with perchloric acid.

MT 78 HYDROGEN SULPHIDE AND THIOLS

MT 79 ACID WASH

OUTLINE OF METHOD

Equal volumes of the sample and sulphuric acid (95% m/m) are shaken together. The colour of the acid is compared with solutions of standard colour

MT 80 RESIDUE ON EVAPORATION

80.1 Low boiling products

OUTLINE OF METHOD

Seventy five per cent of the sample is distilled. The residue in the flask is transferred to a weighed dish, and the evaporation completed on a water bath; the residue remaining on completion of the test is determined by weighing.

80.2 Cresols

OUTLINE OF METHOD

The weight of residue is determined after evaporation of the sample, first on a boiling water bath and then in an oven at 105°C.

MT 81 SOLUBLE ALKALINITY

OUTLINE OF METHOD

The sample is boiled with water, the mixture is filtered, and the filtrate is titrated with sulphuric acid to a methyl red end point.

MT 82 SOLUBLE CHLORIDES

OUTLINE OF METHOD

The solution retained from MT 81 is titrated with silver nitrate, using potassium chromate as indicator.

MT 83 SEED ADHESION TEST FOR POWDERS FOR SEED TREATMENT

83.1 Cereal seeds

OUTLINE OF METHOD

The seed is shaken with the powder under standard conditions. The amount of pesticide on the seed is determined.

83.2 Pea seeds

OUTLINE OF METHOD

The seed is treated with the specified amount of powder at a specified application rate under standardized conditions similar to those in a simple tumbler seed treatment machine. The amount of pesticide is then determined.

MT 84 IGNITION TESTS

Assessment of the spontaneous ignition potential of dithiocarbamates

OUTLINE OF METHOD

Hot air is passed over the sample until ignition takes place. The temperature of the air stream on either side of the sample is noted, and also the time taken for ignition to occur. The nature of burning is noted.

MT 86 KIESELGUHR

86.1 For GLC

OUTLINE OF METHOD

Neutral kieselguhr is prepared by treatment first with acid and then with alkali. The material is then dried and sieved to size.

86.2 For Partition Chromatography

MT 87 MATERIALS SOLUBLE IN CHLOROFORM

OUTLINE OF METHOD

The sample is extracted with hot chloroform, the chloroform is evaporated and the residue is dried and weighed. Alternatively the sample is shaken with cold chloroform, filtered, and the residue is dried to constant weight.

SCOPE

The methods are suitable for samples which are freely soluble in chloroform.

87.1 Hot solution

87.2 Cold solution

MT 90 MATERIALS SOLUBLE IN TOLUENE

SCOPE

The method is suitable for samples which are freely soluble in toluene.

OUTLINE OF METHOD

The sample is shaken with toluene, the suspension is centrifuged and the residue, after removal of the solution, is dried and weighed.

MT 92 DETERMINATION OF LEAD

92.1 Dithizone general method

OUTLINE OF METHOD

After destruction of organic matter and separation from interfering substances, lead is extracted with a solution of 1,5-diphenyl-3-thiocarbazone (dithizone) at pH 9.0 to 9.5, and determined absorptiometrically as the pink complex.

92.2 Dithizone alternative method

MT 93 DETERMINATION OF MANGANESE

INTRODUCTION

Two methods for determining manganese are given. The first, the bismuthate method, is preferred and can be applied to all samples. The second, an EDTA titration, is quicker and suitable for technical materials. It can give erroneous results for certain formulations due to the presence of interfering substances.

93.1 Bismuthate Method

OUTLINE OF METHOD

The sample is dispersed in nitric acid, the mixture is boiled, and insoluble material is filtered off. Sodium bismuthate is added, the excess is filtered off, and the filtrate is treated with a measured excess of *diammonium iron(II) sulphate* solution. The residual iron(II) sulphate is titrated with potassium permanganate.

93.2 EDTA Method

OUTLINE OF METHOD

The material is dissolved in a known excess of EDTA solution. The mixture is gently boiled, cooled, and ascorbic acid and ammonia buffer solution are added. The excess EDTA is titrated with magnesium sulphate using mordant black 11.

MT 94 DETERMINATION OF ZINC

94.1 Zinc dithiocarbamates

OUTLINE OF PROCEDURE

The dithiocarbamate is decomposed with sulphuric acid and nitric acid, *disodium disulphite* is added to reduce any iron, and then mercury(II) thiocyanate solution is added. The resulting complex is filtered off, dried and weighed.

MT 95 DETERMINATION OF IRON

95.1 Total iron

95.1.1 *Oxidation of divalent iron*

OUTLINE OF METHOD

The iron present is reduced to divalent iron with a silver reductor, and divalent iron is titrated with cerium(IV) sulphate using ferroin sulphate as indicator.

95.1.2 *Reduction of trivalent iron.*

OUTLINE OF METHOD

The divalent iron present is oxidized with an excess of potassium permanganate and the solution is boiled to destroy the excess. The solution is then titrated with titanium(III) sulphate using ammonium thiocyanate as indicator.

95.1.3 *EDTA*

OUTLINE OF METHOD

The iron is titrated with EDTA using salicylic acid in acetone as indicator.

95.2 **Divalent iron**

OUTLINE OF METHOD

The divalent iron is titrated with cerium(IV) sulphate solution using ferroin sulphate as indicator.

95.3 **Trivalent iron**

As for 95.1.2 except that the oxidation of the divalent iron with potassium permanganate is omitted.

MT 97 SEPARATION AND IDENTIFICATION OF HERBICIDES

SCOPE

The method is suitable for the separation and identification of the following herbicides: MCPA, MCPB, 2,4-D, 2,4-DB, 2,4,5-T, DNOC, dinoseb, dalapon either alone or in mixtures of technical and formulated materials.

MT 98 WATER-SOLUBLE COPPER

98.1 **Colorimetric method**

OUTLINE OF METHOD

The water soluble copper is extracted and reduced to the Cu^+ state. Bathocuproine is added and the absorbance of the coloured copper complex formed is measured at 465 nm.

SCOPE

The method is suitable for the determination of water-soluble copper in copper oxychloride and other water-insoluble copper fungicides.

98.2 **Atomic absorption spectrophotometric method**

OUTLINE OF METHOD

The sample is dispersed in de-ionized water. The mixture is centrifuged, filtered and the copper determined by means of an atomic absorption spectrophotometer.

MT 99 DETERMINATION OF ARSENIC

OUTLINE OF METHOD

The arsenic is reduced with zinc in hydrochloric acid to yield arsine, which is absorbed in a solution of silver diethyldithiocarbamate in quinoline. The purplish-red colour produced is measured by the colloiddally dispersed silver photometrically at 540 nm.

MT 100 TOTAL CHLORIDES

100.1 In mercurials

SCOPE

The method is suitable for the determination of chloride in technical mercurial chlorides, e.g. phenylmercury(II) chloride.

OUTLINE OF METHOD

The sample is heated with sodium hydroxide and excess of zinc, the liberated mercury is filtered off as a zinc amalgam, and the sodium chloride in the filtrate is determined by the Volhard method.

MT 101 HEPTANE-INSOLUBLE MATERIALS IN ALDRIN

OUTLINE OF METHOD

A prescribed amount of sample is dissolved in heptane. Any residue is filtered off, dried and weighed.

MT 104 IDENTIFICATION OF MERCURIAL COMPOUNDS

104.1 Organomercury compounds

OUTLINE OF METHOD

Portions of the material are dissolved in (i) acetone, and (ii) acetone/aqueous sodium chloride, and spotted onto a silica gel thin layer plate, which is then developed with cyclohexane/acetone mixture. The plate is sprayed with copper(II) sulphate and potassium iodide/sodium sulphite solutions. The spots produced are compared with those produced in a similar manner from a mixed solution of standard mercury compounds in acetone.

MT 105 PREPARATION OF NITROGEN COMPLEXES OF NITRO COMPOUNDS

105.1 Technical compounds

OUTLINE OF METHOD

The nitron complex of the compound is prepared and its melting point is determined by a conventional method e.g. MT 2.

105.2 Esters

OUTLINE OF METHOD

The ester is converted to the corresponding phenol with butylamine and hydrochloric acid. The phenol is extracted with petroleum spirit, the solvent is evaporated, and the nitron complex is prepared.

MT 107 AMMONIA-AMMONIUM CHLORIDE BUFFER SOLUTION-pH 10

MT 108 DINITRO COMPOUNDS - SOLUBILITY OF SALTS AND MATERIALS INSOLUBLE IN ALKALI

108.1 Ammonium salt

OUTLINE OF METHOD

The technical material is dissolved in methanol, the appropriate base is added and, the solution is diluted with Standard Water. Any insoluble matter is filtered off and weighed.

108.2 Sodium salt

108.3 Triethanolamine salt.

MT 109 ACID CONTENT OF DINITRO COMPOUNDS

OUTLINE OF METHOD

The material is extracted with a known amount of standard hydrochloric acid. The extract is titrated with standard sodium hydroxide solution and the free acidity is calculated.

MT 110 MERCURIAL IMPURITIES IN TECHNICAL AND FORMULATED MERCURIALS

INTRODUCTION

The methods are intended for the determination of mercurial impurities which are pesticidally inactive, phytotoxic, or are present in large amounts in the named compound thus giving a poor quality product.

110.1 General TLC method for samples containing more than 1% of inorganic mercury

SCOPE

The method is suitable for the determination of 1 to 14% inorganic mercury salts in technical and formulated organomercury(II) compounds.

OUTLINE OF METHOD

The sample is dissolved in acetone/aqueous sodium chloride or dioxane/ aqueous sodium chloride. The solution is spotted on to a silica gel TLC plate, developed with carbon tetrachloride/acetone, and sprayed with copper(II) sulphate and potassium iodide/sodium sulphite solutions. The resulting spots are compared with standard spots from pure mercury(II) chloride to give the inorganic mercury content of the sample.

110.2 Gravimetric method

SCOPE

The method is suitable for the determination of inorganic mercury, in phenylmercury(II) acetate, chloride and nitrate.

OUTLINE OF METHOD

Inorganic and any organic mercury compounds soluble in acetic acid are extracted from the sample by stirring it with hot acetic acid. The mixture is filtered, the filtrate is neutralized with ammonia, and potassium iodide is added to precipitate phenylmercury(II) compound as phenylmercury(II) iodide which is filtered off. The filtrate is heated with bis(ethylenediamine) copper(II) sulphate solution to form an insoluble mercury complex [bis(ethylenediamine)mercury(II) sulphate] which is then filtered off, and weighed.

- 110.3 **Sulphide colorimetric method**
- 110.4 **2-Ethoxyethylmercury(II) and 2-methoxyethyl(II) chlorides** - Determination of the mercury content of materials insoluble in sodium hydrogen carbonate solution
- 110.5 **Mercurial seed treatments containing mercury(II) chloride and/or iodide** - Determination of free mercury and mercury from mercury(I) salts
- 110.6 **Phenyl mercury(II) chloride** - Determination of water-soluble inorganic and/or organic mercury compounds

MT 113 SILANIZATION OF GAS CHROMATOGRAPHIC COLUMNS

- 113.1 **Off column**
- 113.2 **On column**

MT 114 CORRECTIONS FOR INTERFERING PEAKS

INTRODUCTION

This is a correction for peaks from the active ingredients which interfere with peaks from the internal standards or vice versa. It is applicable to gas liquid and high performance liquid chromatography methods. It is not applicable where both the active ingredient peak and the internal standard peak mutually interfere. *This should be avoided if at all possible by careful selection of the internal standard.*

MT 116 MERCURY(II) SALTS - CHARACTERISTIC REACTIONS

- 116.1 **Precipitation of sulphide**
- 116.2 **Deposition of mercury on copper**
- 116.3 **Reduction with tin(II) chloride**
- 116.4 **Precipitation of mercury(II) iodide**
- 116.5 **Precipitation of mercury(II) oxide with sodium hydroxide**
- 116.6 **Precipitation of ammonium mercury(II) chloride with ammonia solution**

MT 117 TEST FOR CHLORIDE

- 117.1 Liberation of chlorine
- 117.2 Precipitation of silver chloride
- 117.3 Formation of chromyl dichloride (CrOCl_2)

MT 118 TESTS FOR IODIDES

- 118.1 Liberation of iodine
- 118.2 Precipitation of silver iodide
- 118.3 Liberation of iodine
- 118.4 Precipitation of mercury(II) iodide
- 118.5 Precipitation of copper(I) iodide

MT 120 TESTS FOR PHOSPHATES

Phosphate	ortho-	Meta-	Pyro-
Test 1	yellow ppt	white ppt	white ppt
Test 2	white ppt	no ppt	white ppt
Test 3	canary-yellow ppt	canary-yellow ppt	canary-yellow ppt
Test 4	blue colour	blue colour	blue colour

MT 121 TESTS FOR SILICATES

- 121.1 Preparation of sample
- 121.2 Precipitation of silicic acid and evaluation of ammonia
- 121.3 Formation of silicic acid gel
- 121.4 Precipitation of silver silicate

MT 126 EXTRACTABLE ACIDS

OUTLINE OF METHOD

A solution of the formulation as specified in the appropriate monograph is prepared, and acidified with hydrochloric acid. The precipitated acids are extracted with diethyl ether. The ether is removed by evaporation and the residue is dissolved in neutral ethanol. This solution of the acids is titrated with sodium hydroxide, using the specified indicator

MT 127 MELTING POINT OF EXTRACTABLE ACIDS

OUTLINE OF METHOD

The solution is acidified and the liberated acids are extracted with diethyl ether. The ether solution is dried with anhydrous sodium sulphate and evaporated to dryness. The melting and mixed melting points of the acids are then determined.

MT 129 GAS LIQUID CHROMATOGRAPHY OF PHENOXYALKANOIC AND OTHER HERBICIDES

SCOPE

The method provides a suitable basis for the determination of the active ingredient(s) in the technical material and in most formulations containing the ionic salts of bromoxynil, 2,4-D, 2,4-DB, dichlorprop, fenoprop, MCPA, MCPB, mecoprop, 2,4,5-T and 2,3,6-TBA.

OUTLINE OF METHOD

The herbicides are precipitated from alkaline solution with hydrochloric acid, extracted with diethyl ether and converted to their methyl esters or ethers with *either* diazomethane *or* methanol + sulphuric acid. The esters of ethers are separated by gas liquid chromatography on a column of Chromosorb G (AW, DMCS) *or* Chromosorb W (AW, DMCS) coated with Apiezon L, and the active ingredient determined, preferably by flame-ionization detection, using an internal standard. Duplicate sample solutions are prepared by the method given in the monograph for the active ingredient. Two portions of each solution are methylated and duplicate chromatograms are prepared for each, i.e. a total of eight chromatograms from the sample.

For schematic flow sheet of methods of analysis see Fig. 38. For routine purposes only one portion of each solution need be used, i.e. a total of four chromatograms from the sample.

129.1 Preparation of solutions for methylation

129.2 Methylation of acids

129.3 Gas chromatography

MT 130 COLORIMETRIC TESTS FOR IDENTIFYING CERTAIN ALKYLENE-BIS(DITHIOCARBAMATES) IN TECHNICAL MATERIAL AND FORMULATED PRODUCTS

OUTLINE OF METHOD AND PRINCIPLES INVOLVED

Aqueous dispersions of the unknown sample and the standard reference dithiocarbamates are spotted systematically on to the filter paper and allowed to dry. Different spots from sample and standards are treated with (i) acid dithizone (ii) sodium hydroxide and (iii) sodium hydroxide and acid dithizone. The colours produced due to the metallic moieties present in the central powder spot and annulus are compared with those from the standards and this enables the sample to be categorised and sometimes positively identified. Supplementary tests are used to indicate the presence of water soluble or insoluble zinc salts such as sulphate or carbonate.

Following the step-wise procedure, elimination of the various possible dithiocarbamates from the sample is progressively achieved until finally, spots derived from a chloroform dispersion of the sample and mancozeb standard, and to which neutral dithizone is added, distinguish between mancozeb, and a mixture of maneb and zinc sulphate or other water soluble zinc salts. These are indistinguishable in aqueous suspension, and the non-aqueous neutral conditions are deliberately chosen to suppress ionization of the zinc salts or zinc oxide. Mancozeb therefore gives a noticeably different colour response, and this is believed to be due to the co-ordinately bound zinc having sufficient ionic character in chloroform to form rapidly the zinc dithizone complex. Test 7 (see *p.* 324) briefly describes the response from mancozeb as a bright pink "flash" and that from the other products as being slower, duller and

more feeble. It is important to note that the 'flash' collectively describes three processes occurring in *rapid sequence* at the powder spot on adding the dithizone reagent, i.e. (i) The appearance of a bright pink colour.

(ii) The transient existence of the colour due to migration of the material on the filter paper which is quickly transferred to the outer edge of the powder spot, forming a halo. Traces of ethanol in the chloroform are responsible for the effect.

(iii) The re-appearance of the background colour of the powder spot as process (ii) takes place. This gives the illusion of the spot emerging from the surface of the paper. These processes are repeatable by over-spotting with reagent.

MT 133 DETERMINATION OF NITROPHENOLS - TITANIUM(III) CHLORIDE METHOD

OUTLINE OF METHOD

The nitro groups are reduced with a known excess of titanium(III) chloride and the excess is titrated with standard iron(III) chloride solution.

MT 134 PREPARATION OF 2-PYRIDYLAMINE (2-AMINOPYRIDINE) COMPLEXES OF NITRO COMPOUNDS

134.1 Technical nitrophenols

134.2 Technical nitrophenol esters

OUTLINE OF METHOD

The ester is converted with butylamine and hydrochloric acid to the phenol. The phenol is extracted with hexane and the 2-pyridylamine complex prepared as in MT 134.1.

MT 137 IDENTIFICATION OF UREA HERBICIDES

OUTLINE OF METHOD

The urea herbicides present in both technical materials and dispersible powders are distinguished and identified by reverse phase TLC separation of the active ingredient, using paraffin impregnated silica gel plates and developing with ethanol + water. Alternatively, or for confirmation of identity, the separation may be performed on silica gel plates with chloroform + acetone or chloroform + ethyl acetate as developing solvents.

MT 139 POUR POINT OF MINERAL OIL

SCOPE

The test for pour point is intended for use on any petroleum oil (Note 1).

OUTLINE OF METHOD

After preliminary heating the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the oil is observed is recorded as the pour point.

MT 141 DETERMINATION OF FREE AMINES IN UREA HERBICIDES

OUTLINE OF METHOD

The herbicide is dispersed in hydrochloric acid and extracted with chloroform, the free amines being retained in the acid layer. The free aromatic amines are determined by bromination and the free aliphatic by distillation into hydrochloric acid, which is back titrated with standard sodium hydroxide.

MT 142 DETECTION AND IDENTIFICATION OF IMPURITIES IN SUBSTITUTED PHENYLUREA HERBICIDES

OUTLINE OF METHOD

The phenylurea herbicides are separated from impurities by thin layer chromatography and the impurities are estimated by visual comparison with standards on the same plate.

MT 145 ACTIVE INGREDIENTS CONTAINING PHOSPHORUS

Spectrophotometric determination as molybdovanadophosphate after TLC separation

OUTLINE OF METHOD

The method is applicable only if the substance to be determined can be separated from other components of the sample by TLC in such an amount that the area of the silica gel layer used for the determination contains approximately 200-400 µg of phosphorus. The substance to be determined is separated from manufacturing impurities and added modifying agents by TLC on aluminium foils coated with silica gel. The area containing the active ingredient is cut out and the active ingredient is converted to inorganic phosphate with sulphuric acid and hydrogen peroxide. The phosphate formed is determined colorimetrically as the molybdovanado complex.

MT 146 'OIL CONTENT' OF EMULSIFIABLE PESTICIDE CONCENTRATES

OUTLINE OF METHOD

The weighed sample is eluted through a mixed bed of macro reticular anion and cation exchange resins with pentane as solvent. The eluate is evaporated free of solvent, and the residue is expressed as a percentage of the original sample.

MT 147 RETENTION TEST FOR SEED TREATMENT POWDERS USED ON CEREAL SEEDS

OUTLINE OF METHOD

The seeds are treated with the seed treatment powder by the adhesion test (MT 83). The treated seeds are then dropped down a cylinder of specified height on to a sieve. This is repeated five times and the active ingredient remaining on the seeds is determined.

MT 148 POURABILITY OF SUSPENSION CONCENTRATES

OUTLINE OF METHOD

The suspension concentrate is allowed to stand for a definite time and the amount remaining in the container after a standardized pouring procedure is determined. The container is rinsed and the amount then remaining is determined.

CIPAC J

148.1 Pourability of suspension concentrates (revised method)

CIPAC F

MT 149 PACKING COLUMNS FOR GAS CHROMATOGRAPHY

MT 151 DETERMINATION OF TCDD IN 2,4,5-T 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin

151.1 TCDD in 2,4,5-T technical

OUTLINE OF METHOD

TCDD is extracted from 2,4,5-T constituents with hexane and cleaned up by liquid chromatography. It is subsequently separated by capillary gas chromatography with detection by low resolution mass spectrometry.

151.2 TCDD in 2,4,5-T technical esters

OUTLINE OF METHOD

The TCDD is separated from 2,4,5-T ester constituents by liquid chromatography and is subsequently determined by capillary gas chromatography with detection by low resolution mass spectrometry.

MT 152 IDENTIFICATION OF AMINES

OUTLINE OF METHOD

Sodium hydroxide is added to the acidic residue in the flask, after determination of the dithiocarbamate content, and the mixture is distilled. The first fraction is collected for colour tests for the presence of dimethylamine. Similar tests are applied to the alkaline residue in the flask for the presence of ethylenediamine and propylenediamine.

MT 153 QUALITATIVE PROCEDURE FOR CONFIRMATION OF THE PRESENCE OF A DITHIOCARBAMATE OR THIURAM DISULPHIDE

OUTLINE OF METHOD

The presence of a dithiocarbamate and/or a thiuram disulphide, e.g. thiram, is confirmed by the evolution of carbon disulphide when the sample is decomposed with sulphuric acid.

153.1 Liquids

153.2 Solids

MT 154 IDENTIFICATION OF DITHIOCARBAMATE ANIONS

154.1 Zinc dithiocarbamates - Identification by TLC

OUTLINE OF METHOD

The dithiocarbamate is decomposed by alkaline EDTA. The anions are separated on silica gel and visualized as their copper complexes.

MT 155 ANALYTICAL HPLC METHOD FOR DETERMINATION OF PHENOLIC IMPURITIES IN PHENOXYALKANOIC HERBICIDES

155.1 Ultraviolet Detector Method

OUTLINE OF METHOD

The phenolic impurities are separated on a reverse phase (μ Bondapak C18) column using methanol/acetate buffer solution 45 + 55 as mobile phase. Detection is performed by ultraviolet absorption at 280 nm. The determination is carried out by an external standard technique. The identification of the chlorinated phenols is verified by separating samples and spiked samples with eluant(s) of varying pHs.

155.2 Electrochemical Detector Method

OUTLINE OF METHOD

The phenolic impurities (and the active ingredients) are separated on a reverse phase column using methanol/acetonitrile/buffer as mobile phase. Phenolic impurities are detected with an electrochemical detector at +0.9 V. Determination is carried out by using 4-bromo-2-chlorophenol as internal standard. Identification of the impurities is confirmed by spiking, and/or analyzing samples and spiked samples with eluant(s) of alternative pH value(s) (See CIPAC 1C pp. 2091 and 2160). Determination of active ingredients can also be done by UV-detection at 280nm using 2-(2,4-dibromo-phenoxy)propionic acid as internal standard.

MT 157 WATER SOLUBILITY

OUTLINE OF METHOD

At the test temperature a saturated aqueous solution of the test substance is prepared, and the mass concentration is determined using a suitable analytical method.

157.1 Preliminary Test

157.2 Column Elution Method (Solubility less than 10^{-2} g/l)

OUTLINE OF METHOD

This method is based on the elution of the test substance with water at constant temperature from a column charged with the substance which is finely distributed on an inert support material. The flow rate of the water should be adjusted so that a saturated solution leaves the column. Saturation is achieved when, in consecutive fractions of the eluate at different flow rates, the mass concentration - determined by a suitable method - is constant. This is shown by a plateau when the concentration is plotted against time or eluted volume.

157.3 Flask Method (Solubility above 10^{-2} g/l)

OUTLINE OF METHOD

The test substance is thoroughly distributed in water at 20°C. In a fraction of the suspension, any suspended particles are separated and the concentration of the test substance in the clear solution is determined, using a suitable analytical procedure. Saturation is attained when no significant difference in concentration is found in consecutive tests, and after doubling the time intervals used for the adjustment of equilibrium.

MT 158 DETERMINATION OF MERCURY ON TREATED SEEDS

OUTLINE OF METHOD

The organic matter is destroyed by wet oxidation and the mercury is determined colorimetrically with dithizone.

MT 159 POUR AND TAP BULK DENSITY OF GRANULAR MATERIALS

OUTLINE OF METHOD

A known weight of sample is put into a glass measuring cylinder and its volume measured. The cylinder is then raised and allowed to fall vertically through a distance of 25 mm on to a rubber pad. The volume is measured again after 100 'taps'.

MT 160 SPONTANEITY OF DISPERSION OF SUSPENSION CONCENTRATES

OUTLINE OF METHOD

The method is broadly similar to that used to determine the suspensibility of concentrates (MT 161), except that it employs only one inversion and a 5 min standing time. It involves preparing 250 ml of a mixture of formulation and water, mixed with only one inversion of the measuring cylinder. After standing under defined conditions the top nine-tenths is removed, and the remaining tenth assayed chemically, gravimetrically or by solvent extraction. The spontaneity of dispersion is readily calculated.

MT 161 SUSPENSIBILITY OF AQUEOUS SUSPENSION CONCENTRATES

OUTLINE OF METHOD

The method is broadly similar to previously published methods for determining the suspensibility of wettable powders (e.g. MT 15.1). It involves preparing 250 ml of diluted suspension, allowing it to stand in a measuring cylinder under defined conditions, and removing the top nine-tenths. The remaining tenth is then assayed either chemically, gravimetrically or by solvent extraction, and the suspensibility calculated.

MT 162 DETERMINATION OF ETHYLENETHIOUREA (ETU) (IMIDAZOLIDINE-2-THIONE)

162.1 HPLC method (Referee method)

OUTLINE OF METHOD

The ETU is extracted from the sample with methanol. An aliquot of the methanolic solution is evaporated to dryness and the residue is dissolved in water. The solution is filtered and diluted, if necessary, and injected on to a column of Nucleosil C₁₈ or Spherisorb ODS. The ETU is eluted with water containing tetrahydrofuran and detected at 233 nm (Note 1).

162.2 Paper chromatographic method

OUTLINE OF METHOD

The ETU is extracted from the sample with methanol. Portions of the sample and standard solutions are spotted on to filter paper and developed with butan-1-ol + ethanol + water. The chromatogram is sprayed with pentacyanoaminoferroate [PCAF] reagent which produces a blue spot with ETU. The ETU content of the sample is determined by comparing the spot with those from the standards.

MT 163 IDENTITY TESTS FOR PERMETHRIN, CYPERMETHRIN AND FENVALERATE

OUTLINE OF METHOD

The identity of the active ingredient is established by comparison with the equivalent authentic standard (Note 1) using at least two of the following techniques, one of which is must be spectroscopic: GLC, HPLC, IR, ¹³C-NMR, ¹H-NMR or MS.

**MT 164 IDENTITY TESTS FOR PIRIMICARB, BUPIRIMATE, ETHIRIMOL,
PIRIMIPHOS-METHYL AND PIRIMIPHOS-ETHYL**

OUTLINE OF METHOD

The identity of the active ingredient is established by a comparison with the equivalent authentic standard by at least two of the following techniques, one of which must be spectroscopic: GLC, TLC, IR, ¹H-NMR.

**MT 165 ULTRAVIOLET ABSORPTION TEST FOR EVALUATION OF
ETHYLENEBIS(DITHIOCARBAMATE)**

OUTLINE OF METHOD

The ultraviolet spectrum is recorded in the range of 200-400 nm on the filtrate of an ethylenebis(dithiocarbamate) water dispersion. Absorbance values are measured at 280-285 nm for the EBDC anion, using a linear baseline procedure.

Zineb, mancozeb, and mixtures of maneb and water-soluble zinc salts give an absorbance not exceeding 0.05 absorbance units, whereas maneb, and mixtures of maneb with zineb or insoluble zinc salts give an absorbance higher than 0.05 absorbance units (typically in the range of 0.1 to 0.7 absorbance units).

MT 166 SAMPLING OF WATER DISPERSIBLE GRANULES

OUTLINE OF METHOD

Water dispersible granules (WG) may have a relatively broad particle spectrum so that segregation into different particle sizes may occur during transportation or handling of the products.

It is, therefore, essential to divide samples with great care. This may be achieved by using a dividing apparatus or by standardized manual dividing.

**MT 167 WET SIEVING AFTER DISPERSION OF WATER
DISPERSIBLE GRANULES
(See CIPAC MT 59.3)**

OUTLINE OF METHOD

A sample of water dispersible granules is dispersed in water and the suspension is transferred to a sieve and washed. Determination of the weight of the residue on the sieve is done according to MT 59.3 which has been adapted to the requirements of testing water dispersible granules.

MT 169 TAP DENSITY OF WATER DISPERSIBLE GRANULES

1 Standard-method (See CIPAC MT 58.4 and MT 33)

OUTLINE OF METHOD

The granules are put into a glass measuring cylinder of known weight which is then raised and allowed to fall vertically through a distance of 2.5 cm on to a rubber pad; the operation is repeated 50 times and the final volume of powder is measured.

2 Method with dry substance jolting volumeter

OUTLINE OF METHOD

The tap density is determined with a Dry Substance Jolting Volumeter according to DIN 53194 (Note 1).

MT 170 DRY SIEVE ANALYSIS OF WATER DISPERSIBLE GRANULES

OUTLINE OF METHOD

Sieve analysis consists of the quantitative separation of water dispersible granules into fractions of different particle size ranges by use of the modified method MT 58.3 (machine sieving described under A). If the apparatus required is not available, a simple method (hand sieving described under B) can be used.

MT 171 DUSTINESS OF GRANULAR PRODUCTS

DEFINITION

Dustiness in this method is defined as the property of a granular product to liberate dust into the air when handled under specified conditions. These conditions are related to typical handling in agricultural practice (i.e. measuring out and pouring the product into the spray tank).

OUTLINE OF METHOD

The determination of the dustiness of a granular product involves two operations. Firstly, a weighed amount of a granular product is allowed to fall under standard conditions in a test chamber, thus releasing dislodgeable dust. The second operation is the collection and/or assessment of the amount of airborne dust. This can be achieved by a gravimetric method, in which the generated dust is removed by an airflow, collected on a filter and weighed, or by an optical method in which the obscuration of a light-beam by the airborne dust is measured.

MT 172 FLOWABILITY OF WATER DISPERSIBLE GRANULES AFTER HEAT TEST UNDER PRESSURE

OUTLINE OF METHOD

After the accelerated storage test according to MT 46.1, the amount of granules remaining on a sieve is determined without any mechanical disturbance, and afterwards with a standardized tapping.

MT 173 COLORIMETRIC METHOD FOR DETERMINATION OF THE STABILITY OF DILUTE EMULSIONS

OUTLINE OF METHOD

A dye is dissolved in the emulsifiable concentrate formulation (EC). A sample of the dyed EC is added to a standard water to obtain an aqueous emulsion. At the end of a specified time an aliquot is withdrawn from the emulsion, and transferred to a flask to which propan-2-ol is added to clarify the emulsion. Then the absorbance of the dyed solution is measured in a spectrophotometer and compared to the absorbance of a similar aliquot taken under the same conditions but at t_0 (initial emulsion).

MT 174 DISPERSIBILITY OF WATER DISPERSIBLE GRANULES

OUTLINE OF METHOD

A known amount of a water dispersible granule (WG) is added to a defined volume of water and mixed by stirring to form a suspension. After standing for a short period, the top nine-tenths are drawn off and the remaining tenth dried and determined gravimetrically. The method is virtually a shortened test of suspensibility and is appropriate for establishing the ease with which a WG dispersed uniformly in water.

MT 175 DETERMINATION OF SEED-TO-SEED UNIFORMITY OF DISTRIBUTION FOR LIQUID SEED-TREATMENT FORMULATIONS.

OUTLINE OF THE METHOD

High quality seed (certified seed) of cereals is treated with liquid seed treatment formulations in a laboratory seed treatment machine which utilises a rotary atomiser to atomise the formulation. The uniformity of the distribution of the formulation from seed to seed is determined colorimetrically. The dye present in the formulation being extracted individually from 100 seeds.

MT 176 DISSOLUTION RATE OF WATER SOLUBLE BAGS

OUTLINE OF METHOD

An aqueous suspension of the test powder is prepared. A piece of the bag is immersed in the suspension for a certain period of time and finally stirred together with the suspension. The suspension is then passed through a filter and the flow time is measured or any blockage of the filter is observed.

MT 177 SUSPENSIBILITY OF WATER DISPERSIBLE POWDERS (Simplified method)

OUTLINE OF METHOD

A suspension of known concentration in standard water or distilled water is prepared, placed in a prescribed measuring cylinder at a constant temperature, and allowed to remain undisturbed for a specified time. The top 9/10ths are removed and the content of active ingredient in the top 9/10ths is determined.

CIPAC H

MT 178 ATTRITION RESISTANCE OF GRANULES

OUTLINE OF METHOD Prior to the test the granule is sieved on a 125 µm sieve in order to remove fine particles. A known amount of this dust free granule is transferred to a glass bottle and is then subjected to a rolling movement with an equal amount of glass beads. After rolling for a specified period of time the attrition resistance is determined by sieving again on a 125 µm sieve and weighing the material remaining on the sieve.

CIPAC K

178.2 Attrition resistance of dispersible granules

OUTLINE OF METHOD Prior to the test the granules are sieved on a 125 µm sieve in order to remove fine particles. A known amount of this dust free granules is transferred to a glass bottle and is then subjected to a rolling movement. After rolling for a specified period of time the attrition resistance is determined by sieving again on a 125 µm sieve and weighing the material remaining on the sieve.

CIPAC H

MT 179 DISSOLUTION DEGREE AND SOLUTION STABILITY

SCOPE The method is intended for the determination of the degree of dissolution and the stability of solution of water soluble granules.

OUTLINE OF METHOD The SG formulation is dissolved in Standard water in a graduated 250 ml cylinder at 25 °C. After 15 inversions and a standing time of 5 minutes, the contents are poured over a 75 µm sieve. The residue on the sieve is quantified. The stability of the solution is checked by allowing the filtrate to stand for a period of 18 hours and filtering it again through a 75 µm sieve.

MT 180 DISPERSION STABILITY OF SUSPO-EMULSIONS

OUTLINE OF METHOD

A dispersion of prescribed concentration in Standard Water is prepared and aliquots are placed in two graduated emulsion tubes, which are then allowed to remain undisturbed for specified time in a upright and inverted positions at a constant temperature. The dispersion characteristics are observed immediately after the preparation of the dispersion, after a specified time, and after re-dispersion.

MT 181 SOLUBILITY IN ORGANIC SOLVENTS

OUTLINE OF METHOD

The solubility - within predefined ranges - of a test substance in organic solvents is determined by adding measured volumes of solvent to a known mass of test substance until complete dissolution is observed.

A preliminary test is employed to determine the approximate solubility of the test substance. The results of the preliminary test are used to select the most appropriate mass of test substance for the test.

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MT 182 WET SIEVING USING RECYCLED WATER

SCOPE

This procedure is applicable for determining the amount of non-dispersible material in water dispersible granules.

OUTLINE OF METHOD

An aqueous dispersion of the test sample is prepared, poured through a 75 µm sieve, and rinsed using a low volume of water from a re-circulation reservoir. The residue remaining on the sieve is quantified.

MT 183 THE USE OF THE AGROCHEMICAL EMULSION TESTER (AET) FOR THE DETERMINATION OF THE STABILITY OF DILUTE EMULSIONS

SCOPE

The method is suitable for determining the emulsion stability of dilute emulsions at a dilution rate of 1 %.

OUTLINE OF METHOD

An appropriate aliquot amount of the agrochemical emulsion or emulsifiable concentrate is dispersed in CIPAC Standard Hard Water, to provide 250 ml of dilute emulsion. The dilute emulsion is then allowed to flow under gravity through the instrument cell, under controlled conditions, and instrument readings are taken initially and over a 30 minute period. Instrument readings are dependent on variations in droplet size as the dilute emulsion flows through the cell. Low readings, (typically <1) and stable over time, are indicative of fine uniform droplets, and good emulsion stability. Higher initial readings, (typically >1), which change with time, are indicative of coarse, non-uniform droplets and poor emulsion stability.

MT 184 SUSPENSIBILITY OF FORMULATIONS FORMING SUSPENSIONS ON DILUTION WITH WATER

OUTLINE OF METHOD

A suspension of known concentration in CIPAC Standard Water is prepared, placed in a prescribed measuring cylinder at a constant temperature, and allowed to remain undisturbed for a specified time. The top 9/10ths are drawn off and the remaining 1/10th is then assayed either chemically, gravimetrically, or by solvent extraction, and the suspensibility calculated. If the formulation (e.g. WP) is packed in water soluble bags, the suspensibility tests should be performed in presence of dissolved water soluble bag material.

MT 185 WET SIEVE TEST

SCOPE The method is suitable for the determination of the amount of non-dispersible material in formulations, that are applied as dispersions in water.

OUTLINE OF METHOD A sample of the formulation is dispersed in water and the suspension formed is transferred to a sieve and washed. The amount of the material retained on the sieve is determined by drying and weighing.

MT 186 BULK DENSITY

OUTLINE OF METHOD A known weight of a solid material is placed in a glass measuring cylinder and its volume measured (to determine the 'pour density'). The cylinder is then raised and allowed to fall vertically through a distance of 25 mm on to a rubber pad (50 times) or this is carried out using a Dry Substance Jolting Volumeter ISO 787 (Note 1). The volume is measured again (to determine the 'tap density').

MT 187 PARTICLE SIZE ANALYSIS BY LASER DIFFRACTION

SCOPE

This method provides guidance on the measurement of particle size distributions of crop protection formulations, for example granules, powders, suspensions and emulsions, through analysis of their angular light scattering patterns. Detailed descriptions for the use of laser diffraction methods are given in ISO 13320-1.

OUTLINE OF THE METHOD

A representative sample, dispersed at an adequate concentration in a suitable liquid or gas, is passed through the beam of a monochromatic light source, usually a laser. The light scattered by the particles at various angles is measured by a multi-element detector and numerical values relating to the scattering pattern are then recorded for subsequent analysis. These numerical scattering values are then transformed, using an appropriate optical model and mathematical procedure, to yield the proportion of total volume to a discrete number of size classes forming a volumetric particle size distribution.

MT 188 DETERMINATION OF FREE PARATHION-METHYL IN CS FORMULATIONS

The method is suitable for determining free parathion-methyl (up to 100 % free active ingredient relative to the total active ingredient content) in CS formulations up to 400 g/kg.

OUTLINE OF METHOD

A known amount of capsule suspension is mixed with a defined volume of an aqueous solution containing a non-ionic surfactant. The mixture is stirred for a defined period at a defined temperature. After two centrifugation steps the active ingredient content is determined in the supernatant.

MT 189 DETERMINATION OF FREE LAMBDA-CYHALOTHRIN IN CS FORMULATIONS

SCOPE

This method is intended for use only with lambda-cyhalothrin CS formulations for public health applications.

OUTLINE OF METHOD A known quantity of the capsule suspension is transferred to a glass bottle and is then subjected to a rolling movement with a specified amount of hexane with an internal standard. After rolling for a specified period the concentration of lambda-cyhalothrin in the hexane layer is determined.

MT 190 DETERMINATION OF RELEASE PROPERTIES OF LAMBDA-CYHALOTHRIN CS FORMULATIONS

SCOPE

This method is intended for use only with lambda-cyhalothrin CS formulations for public health applications.

OUTLINE OF METHOD A known quantity of the capsule suspension is transferred to a glass bottle and is then subjected to a rolling movement with a specified amount of a hexane-ethanol mixture with an internal standard. After rolling for three specified periods the concentrations of lambda-cyhalothrin in the hexane-ethanol layer are determined.

MT 191 ACIDITY OR ALKALINITY OF FORMULATIONS

SCOPE

The method is suitable for determining the acidity or alkalinity of formulated pesticides.

OUTLINE OF METHOD

The acidity or alkalinity is determined by titration with standard acid or alkali using electrometric end point determination. The titration is carried out in water.

MT 192 VISCOSITY OF LIQUIDS BY ROTATIONAL VISCOMETRY

SCOPE

This method is intended for characterising the flow behaviour of liquid crop protection formulations. The measurement of non-Newtonian liquids is best carried out by rotational viscosimeters.

OUTLINE OF METHOD A sample is transferred to a standard measuring system. The measurement is carried out under different shear conditions and the apparent viscosities are determined. During the test the temperature of the liquid is kept constant.

MT 193 FRIABILITY OF TABLETS

SCOPE

The method is suitable for determining the friability of non-coated tablets under defined conditions. Friability is defined as change of the tablet surface and the refraction by jarring impact.

OUTLINE OF METHOD The tablets are circulated/turned around in a rotating dish with a build-in, bow-shaped baffle.