MERCK

What do you expect from your PESTICIDE STANDARDS?

TraceCERT® Certified Reference Material Mixes
for Pesticide Testing

The Life Science business of Merck operates as MilliporeSigma in the U.S. and Canada.

Supelco®
Analytical Products

*Trace*CERT® Certified Reference Materials for Pesticide Testing

Pesticide testing is conducted to ensure that agricultural products are safe for consumption and that their production processes do not negatively impact the environment. This testing is crucial for detecting and measuring the residues of pesticides, which can have harmful effects on human health if present in high concentrations. Regulatory bodies such as the Environmental Protection Agency (EPA) in the United States, the European Food Safety Authority (EFSA) in the European Union, and other national agencies are responsible for setting the standards and regulations for testing. The methodologies employed, as well as the list of targeted compounds, will vary depending on the sample type and associated regulations.

Testing methods, whether they are standardized or developed in-house, often cover several different pesticide classes. It can be challenging for laboratories to prepare reference materials that cover these analyte lists, which can often be rather rather extensive.

We have developed several new ready to use mixes that cover 8+ different classes of pesticides. Our R&D chemists formulated these mixes for optimized stability from highly characterized starting materials. All are produced and tested at our ISO 17034 and ISO/IEC 17025 accredited facilities and have been thoroughly qualified as certified reference materials (CRMs), which is of critical importance if your laboratory is ISO/IEC 17025 accredited.

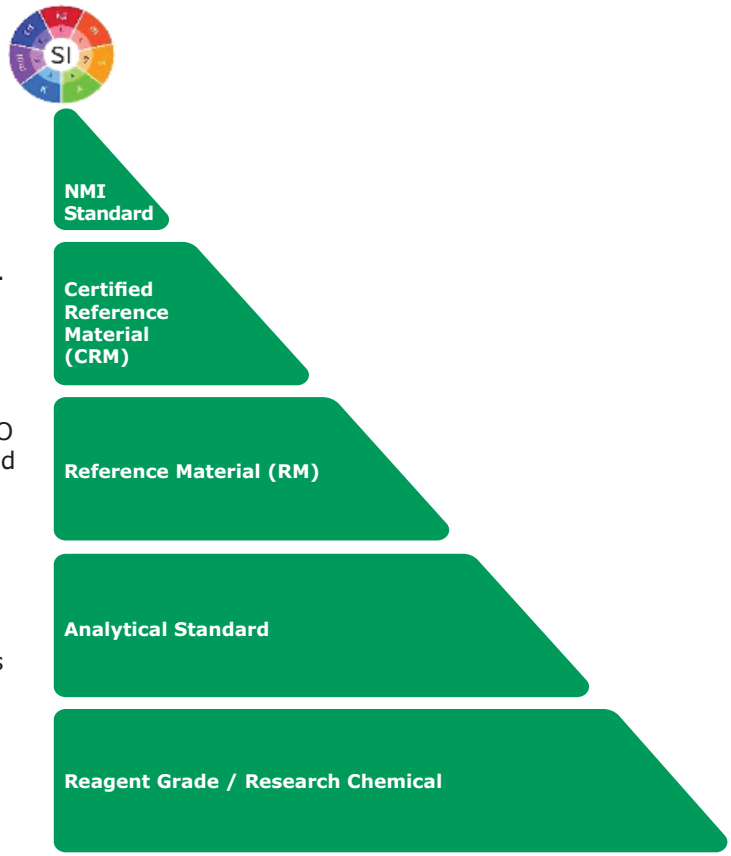
Why is the use of CRMs critical?

- CRMs, when available, are mandatory for ISO/IEC 17025 accredited laboratories.
- They help achieve high precision and reliability with your method.
- When used properly, will ensure accurate quantitative values.

What are CRMs?

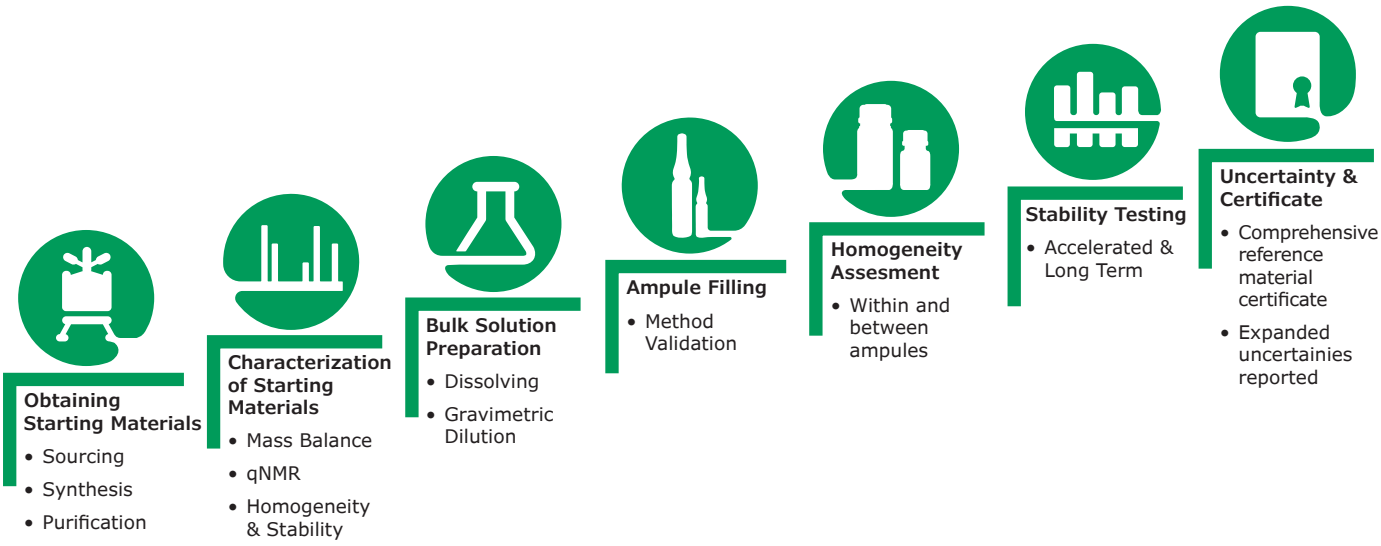
Reference materials are classified into five major categories based on their quality grades, with the highest grade being primary reference materials from national metrology institutes followed by Certified Reference Materials (CRMs), Reference Materials (RMs), analytical standards, and the lowest being research grade or research chemicals. The certification and traceability requirements increase as you move up the pyramid.

The top-level is given standardization by national governments, whereas specific ISO guidelines provide standardization for CRMs and RMs. These ISO requirements include ISO 17034, ISO/IEC 17025, and ISO Guide 31. Reference material producers must meet these ISO requirements to manufacture CRMs or RMs. For CRMs, a Reference Material Certificate (formerly referred to as a “certificate of analysis” or “COA”) must be provided, and the information contained within is defined by the earlier mentioned ISO guidelines. By contrast, the quality specifications for analytical standards and reagent grade/research chemicals are outlined by each independent producer rather than by a national government or ISO guidelines.



Why choose *Trace*CERT® pesticide reference material mixes?

Your success in the laboratory is our goal, and our commitment is reflected in the quality of these reference materials. Many rigorous characterization and testing steps were included in the development and production of these pesticide mixes.



Sourcing & Characterization of Starting Materials – The Advantage of qNMR

The first step in developing these pesticide mixes was obtaining starting materials of each pesticide as a neat compound. Sourcing and procurement was done from trusted suppliers, and the highest purity (>99%) obtained. In the case of several compounds, external sourcing was not possible so a synthetic and/or purification process was developed in-house.

Next, the starting materials were characterized. In addition to chromatographic techniques, we employ quantitative nuclear magnetic resonance (qNMR) to determine content and homogeneity of each material. In qNMR, the signal area is directly proportional to the number of nuclei in the compound that contribute to the resonance. This makes the method suitable for quantification since it enables the comparison of two different molecules in one measurement. This is an advantage over other ways of detection.

For example, UV detectors produce signal when molecules absorb UV radiation, which in turn, results in promotion of electrons to a higher energy state. The optimized wavelength for this to occur will vary depending on a molecule's structure – and in some cases (such as hydrocarbons) no signal is possible. In the case of GC-FID, signal is produced by ions that are formed when a compound burns in a hydrogen/air flame, with intensity being greater for structures containing more C-H bonds. By contrast, qNMR is directly measuring the resonating protons and or other NMR active nuclei e.g. carbon, phosphorus, fluorine within a molecule. qNMR is a relative primary method, and when an appropriate internal standard is measured with the sample compound, the ratio of signals between the two enables the content determination of the sample as a mass fraction. In addition, traceability to the SI can be established by using a primary reference material for comparison. The content can therefore be measured with high precision and low measurement uncertainty. qNMR can also be used during stability studies to measure content over a given time.

As an example of how this is done, let's look at one of the components in Pesticide Mix 4 (36082) – imidacloprid. **Figure 1** shows an HPLC-UV purity determination of the starting material used in the mix. By comparing the signals of the main peak to the smaller impurity peaks, a purity was calculated at 99.8%. The goal of the purity determination is to measure the amount of imidacloprid present in the starting material relative to other components (i.e., impurities). In this HPLC-UV test, signal intensity is related to compound structure, specifically, UV-absorbing chromophores. Chromophores are organic structures which absorb light, and in this case the detector is measuring UV light of a specific wavelength that can be absorbed by molecules. If an impurity is present that does not have a chromophore, it will not produce a signal. The structure of imidacloprid is shown with the chromatogram, and the groups acting as chromophores are indicated with arrows.

HPLC-UV Analysis of impurities in imidacloprid

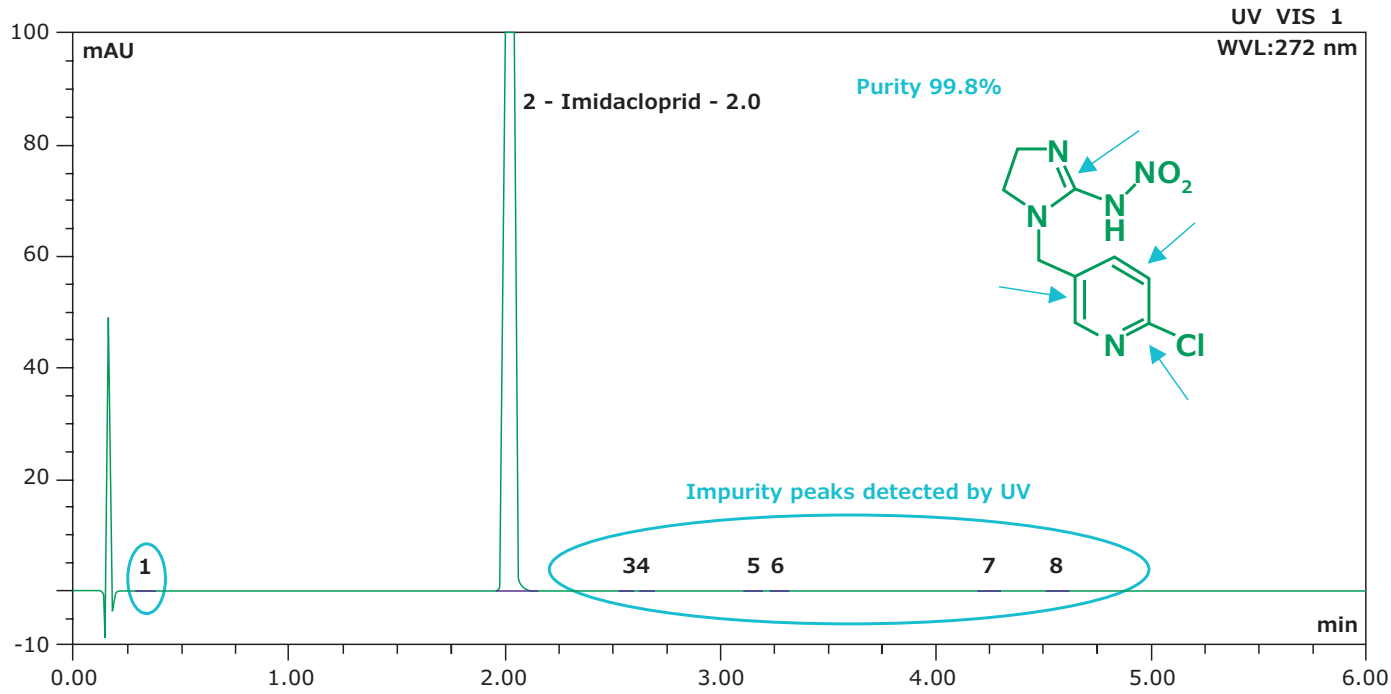
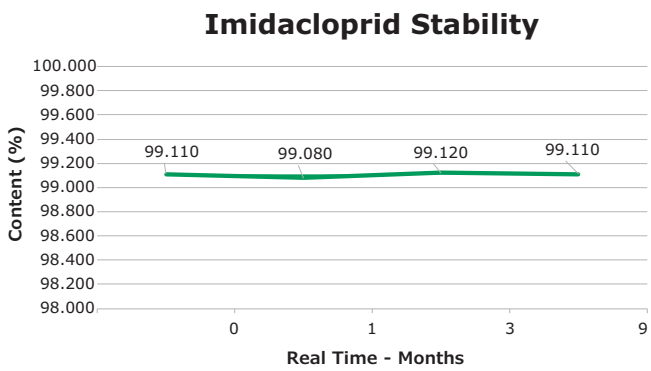


Figure 1

In contrast, when this same starting material of imidacloprid was tested using qNMR, the content was determined as 92.4%. qNMR only measured what was actually present as imidacloprid, or in other words, the "content" of the starting material. This warranted purification of the imidacloprid, which was then retested using qNMR and determined to be 99.1%. Of course, other tests such as residual solvents, water, and inorganics can be used to determine the presence of impurities not detected by HPLC-UV. Combining these results is referred to as a "mass balance" approach to purity analysis. Mass balance is a much more comprehensive approach than chromatographic purity alone and can be considered as complementary to qNMR for purity analysis. The disadvantage of this technique over qNMR is that with each of these tests comes some uncertainty, which when combined, will be much higher overall than a single qNMR test.

Returning again to the imidacloprid example, after purification and qNMR testing, the material was subjected to a 9 month stability study, and qNMR was used to measure if any change occurred over time in the amount present. The high accuracy of qNMR will be able to detect any small changes that occur, and in this case, the imdacloprid was very stable over the course of the study. If HPLC-UV had been used for measuring amount, and degradants formed with weak or no UV signals, an inaccurate stability profile would have resulted.



After characterization and certification testing has been completed on the starting materials, a mix is formulated. Our R&D scientists determine the best formulations for multi-component mixes based on known chemical characteristics of the starting materials. For example, acidic and basic compounds will often not be put together in the same mix. Next, preliminary experiments are done to determine specific weighing and dilution steps to be used in preparation of a bulk solution. Different solvents are tested for both solubility of the starting materials and loss due to volatility during the solution packaging process.

The certified value of each pesticide in the mix is confirmed using isotope dilution GC-MS and LC-MS. The testing on packaged mix is done on multiple ampules sampled throughout the packaging of the entire batch.

Stability Testing – Determination of Shelf Life

Two types of stability testing are conducted on the ampulized mixture:

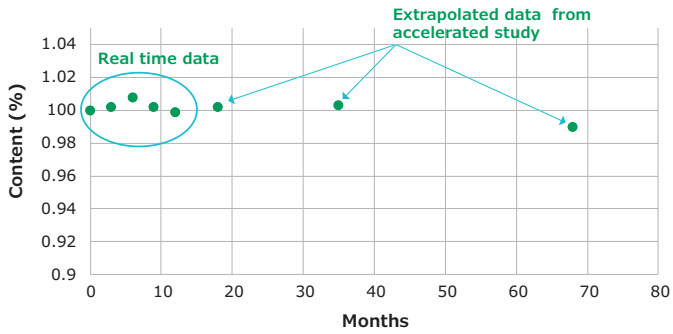
- Accelerated Stability Testing
- Long Term Stability Testing

Accelerated stability testing involves exposing the samples to elevated temperatures to determine the final storage conditions required for a specific shelf life (which translates into the expiration date). Next, long term stability testing is conducted at the final storage conditions to verify the shelf life indicated from the accelerated study. In both types of testing, the certified values of the mix are determined at specific intervals. Changes in concentrations detected in the stability testing are incorporated into the uncertainty values reported for each compound on the final reference material certificate.

When developing these Pesticide Mixes, the goal was a 24-month shelf life. With this in mind, accelerated stability studies were conducted at elevated storage temperatures. From this, it was possible to calculate the required storage conditions for a 24-month shelf life to be -20 °C. A long-term stability study (24 months at -20°C) was then conducted to verify the shelf life indicated by the accelerated study.

As an example, let us look at the stability testing data for the pesticide malathion that is a component of Pesticide Mix 6.

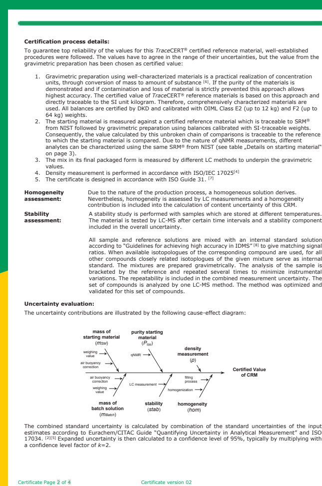
Malathion stability determination in Pesticide Mix 6

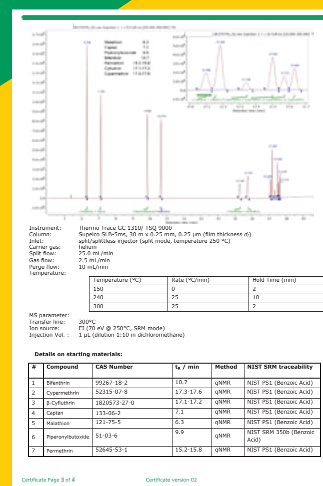


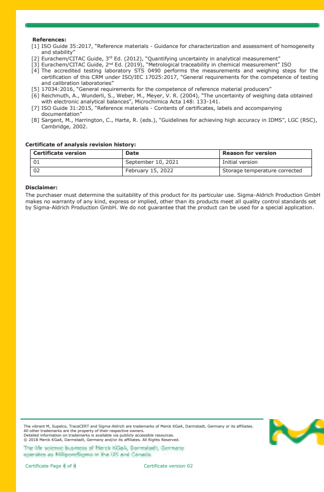
The above graph shows data points collected during the long-term stability study on malathion in the pesticide mixture over the course of 12 months real time, under storage conditions of -20°C . Three additional points past 12 months were extrapolated using data from the accelerated stability study. This was done for each pesticide in all mixes to ensure stability of the product and to include as part of the uncertainty calculated and reported for each compound.

The Reference Material Certificate

A comprehensive reference material certificate (previously referred to as a “certificate of analysis” or “COA”) is included with each pesticide mix.







Page 1

Contains information on:

- Storage conditions
- Expiration date
- Lot number
- Certified values of concentrations and expanded uncertainties
- Handling instructions

The expiration date reflects shelf life of an unopened ampule stored under the conditions specified. Once the ampule is opened, the laboratory should conduct their own assessment to determine how long the standard can be used.

Page 2

Shows a description of the certification process used to establish traceability to an SI unit.

Also included on this page are general descriptions of:

- Homogeneity testing
- Stability testing
- Calculation of uncertainty (including all the contributing factors) that is reported with the certified value on page 1.

Page 3

Shows the test conditions used for the final mix. In this case, GC-MS/MS was the testing method. The conditions shown can be useful as a starting point if you are developing your own test method. Also included is a summary table of the testing details for the starting materials used to make the mix. The constituents in this mix were characterized using qNMR with traceability established by using a CRM as an internal standard that was certified using a NIST primary standard (benzoic acid in this case).

Page 4

Lists references for the different methods and processes described in the certificate as well as a record of any revisions that were made to the document.

*Trace*CERT® Certified Reference Materials for Pesticide Testing

Now available are *Trace*CERT® pesticide mix sets formulated to cover 104 pesticides of 8+ different classes, including carbamates, organophosphorus, pyrethroids, neonicotinoids, fungicides, growth regulators, and synergists. Included are separate CRM solutions of Spinetoram and Pyrethrum extract, and the latter is supplied with a breakdown of the isomeric composition.

***Trace*CERT® Quality**

- Certified content by quantitative NMR (qNMR)
- Manufactured under ISO 17034 and tested under ISO/IEC 17025 accreditation
- Highest level of accuracy, calculated uncertainties, lot-specific values, and traceability
- Comprehensive documentation delivered with the product according to ISO Guide 31

Multiresidue Pesticide Standard Mix #1

19349 – 1 mL
100 µg/mL in acetonitrile

Thiacloprid
Fipronil
Methiocarb
Chlorfenapyr
Fenoxycarb
Imazalil
Propoxur
Carbofuran
Daminozide
Aldicarb

Multiresidue Pesticide Standard Mix #2

29985 – 1 mL
100 µg/mL in acetonitrile

Coumaphos
Parathion-methyl
Mevinphos
Paclobutrazol
Spiroxamine
Ethoprophos/Ethoprop
Chlordane
Etofenprox
Chlorpyrifos
Dichlorvos
Pentachloronitrobenzene or Quintozene

Multiresidue Pesticide Standard Mix #3

30176 – 1 mL
100 µg/m in acetonitrile

Azoxystrobin
Tebuconazole
Myclobutanil
Pyridaben
Hexythiazox
Spinosad (Spinosyn A & D)
Acetamiprid
Fenpyroximate
Trifloxystrobin
Acequinocyl
Bifenazate
Clofentazine
Etoxazole
Fenhexamid
Flonicamid
Propiconazole
Abamectin
Fludioxonil
Boscalid
Kresoxim-methyl
Dimethoate

Multiresidue Pesticide Standard Mix #4

36082 – 1 mL
100 µg/mL in acetonitrile

Oxamyl
Carbaryl
Methomyl
Dimethomorph
Metalaxyl
Imidacloprid
Thiamethoxam
Chlorantraniliprole

Multiresidue Pesticide Standard Mix #5

30639 – 1 mL
100 µg/mL in acetonitrile

Acephate
Dibrom® (Naled)
Diazinon
Spirotetramat
Spiromesifen
Phosmet
Prallethrin

Multiresidue Pesticide Standard Mix #6

36471 – 1 mL
500 µg/mL in acetonitrile

Permethrin
Malathion
Captan
Cypermethrin
β-Cyfluthrin
Bifenthrin
Piperonylbutoxide

Multiresidue Pesticide Standard Mix #7

56519 – 1 mL
100 µg/mL in acetonitrile

Ancymidol
Chlormequat chloride
Ethephon
Flurprimidol
Phosmet oxon

Multiresidue Pesticide Standard Mix #8

56908 – 1 mL
100 µg/mL in MTBE

Endosulfan sulfate
Alpha endosulfan
Beta endosulfan
Etridiazole
Fenvalerate
Kinoprene-S
MGK-264

Multiresidue Pesticide Standard Mix #9

57999 – 1 mL
100 µg/mL in acetonitrile

Chlothianidin
Dinotefuran
Novaluron
Tebufenozide
Teflubenzuron
Thiophanate-methyl

Multiresidue Pesticide Standard Mix #11

62045 – 1 mL
400 µg/mL in acetonitrile

Aldicarb
Chlorfenapyr
Spiromesifen

Pyrethrum Extract Solution

CRM42339
1 mg/mL in acetonitrile

Spinetoram Solution

43065-1mL
100 µg/mL in acetonitrile

Multiresidue Pesticide Standard Mix #10

61092 – 1 mL
100 µg/mL in acetonitrile

Allethrin
Benzovindiflupyr
Buprofezin
Cyantraniliprole
Cyprodinil
Deltamethrin
Dodemorph
Fensulfothion
Fenthion
Fluopyram
Iprodione
Methoprene
Phenothrin
Pirimicarb
Pyraclostrobin
Resmethrin
Spirodiclofen
Tetrachlorvinphos
Tetramethrin

We Can Provide Everything You Need for Your Pesticide Testing Workflow

In addition to certified reference materials, we can provide solutions for sample preparation and chromatographic analysis of pesticides in a variety of matrices.

Click on the links below to learn more.

Applications

- Pesticides in Hemp by SPE & LC-MS/MS, GC-MS/MS
- Glyphosate, AMPA and glufosinate in oat-based cereals
- Fipronil in eggs

Sample Preparation

- QuEChERS & Solid phase extraction
- Solvents
- Vials
- Pipettes & Pipettors
- Millex® Syringe Filters

Chromatographic Analysis

- HPLC Columns
- GC Columns & Accessories
- Solvents

Quantitation

- *Trace*CERT® certified reference materials
- Pestanal® reference materials

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