

**Detection of CIBA Irgamet 39® in insulating mineral oil****Index**

<b>1. Scope</b>	<b>2</b>
<b>2. Principles</b>	<b>2</b>
2.1 Summary	2
2.2 Significance and use	2
2.3 Interferences	2
2.3.1 Co-eluting compounds	2
2.3.2 UV-adsorbing interfering compounds	3
<b>3. Equipment</b>	<b>3</b>
3.1 Apparatus	3
3.2 Reagents and Materials	3
3.2.1 Purity of Reagents	3
3.2.2 Required reagents	3
3.2.3 Standard materials	4
3.2.4 Standard solutions	4
<b>4. Sampling</b>	<b>4</b>
<b>5. Analytical procedure</b>	<b>4</b>
5.1 Preparation of Apparatus	4
5.1.1 Instrument	4
5.1.2 Separation conditions	4
5.1.3 UV detection	5
5.2 Calibration	6
5.2.1 Calibration procedure	6
5.3 Analysis	6
5.3.1 Sample pre-treatment by SPE	6
5.3.2 HPLC analysis	6
5.4 Calculations	6
5.5 Report	6
<b>6. Analytic recovery yield</b>	<b>7</b>
6.1 Adsorption yield	7
6.2 Elution yield	7
<b>7. Precision data</b>	<b>7</b>
7.1 Detection limit	7
7.2 Repeatability	7
7.3 Reproducibility	7

## 1. Scope

This test method covers the determination of passivator CIBA Irgamet® 39 in insulating mineral oils, used and unused.

**Note** This method is based on an existent method for determination of another passivator, BTA (Benzotriazole), which can be detected in the same chromatographic run of Irgamet 39, as described.

This test method uses the commercial product Irgamet 39, produced by CIBA, for calibration. Its inherent uncertainty is related to its purity degree as supplied.

## 2. Principles

### 2.1 Summary

A weighted portion of the sample oil is diluted with pentane and passed under vacuum through a silica gel SPE cartridge, previously rinsed with methanol and pentane. The residue of non-polar oil constituents retained by the solid phase is then eluted with a further volume of pentane and discarded. The cartridge is then dried by flushing it with air under vacuum.

The analytes are eluted with a known volume of methanol and filtered through a 0,45 • m PTFE filter.

The solution is injected into a HPLC system equipped with a reverse-phase column, and Irgamet 39 detected with a UV detector at a wavelength 260 – 270 nm.

### 2.2 Significance and use

This test method covers the determination of Irgamet 39 for routine analysis.

Irgamet 39 is a toluitriazole amminic derivate, liquid at room temperature, added in mineral insulating oils mainly as a metal passivator, for its capability to inhibit the corrosive reactions involving copper (and other metals) surface and metal-reactive compounds present in the oil. Irgamet 39 is usually added to mineral oils in concentrations 0,005 – 0,02 %.

Other triazole derivates are used in insulating mineral oils as BTA (benzotriazole) and TTA (toluitriazole), having a lower solubility in oil. BTA is more widely used then TTA, mainly to modify the electrical behaviour of copper surfaces.

Irgamet 39 is a mixture of 2 isomers: N,N-bis(2-ethylesil)-4-methyl-1H-benzotriazol-1-methylamine and N,N-bis(2-ethylesil)-5-methyl-1H-benzotriazol-1-methylamine. The two isomers are not usually separated in the conditions described in this method, but they may give two partially overlapping peaks if a high efficiency column is used (C18, 250 mm); in this case the total area of two peaks must be considered.

Heavily oxidized oils may partially affect the analysis, giving relevant interferences from UV-absorbing polar compounds. In the case of doubts the standard addition method can be used for more accurate determinations.

This method can be used for monitoring Irgamet 39 content in passivated insulating mineral oils, used and unused.

**Note** In order to obtain the optimal separation and detection condition with individual chromatographic systems this method allows a large flexibility in choice of stationary phase and mobile phase separation.

### 2.3 Interferences

#### 2.3.1 *Co-eluting compounds*

TTA was found to co-elute with Irgamet 39 in the conditions described in this method.

The same Irgamet 39 seems to decompose to TTA during some stage of the chromatographic run, being the UV spectra of the two compounds (recorded from the chromatogram) identical.

Being the two compounds added to oil for the same purposes, and considering the relatively low diffusion of TTA, it can be acceptable to quantify as Irgamet 39 both the compounds, if present in the

same sample.

**Note** It is recommended to verify the effective co-elution of Irgamet 39 and TTA under the selected separation conditions. TTA can be purchased from CIBA as Irgamet® TTZ.

### 2.3.2 *UV-adsorbing interfering compounds*

Heavily oxidized oils may contain UV-adsorbing compounds showing retention times close to Irgamet 39. For the same reason, a relevant background noise may be encountered.

In these cases, when the integration of the peak is difficult, or an overlapping peak appears, the standard addition method should be used for quantification.

## 3. Equipment

### 3.1 Apparatus

#### **Balance**

Top loading, with automatic tare, capable of weighing to 0.001 g, capacity of 100 g. minimum.

#### **Vacuum manifold for SPE**

For vacuum elution of Silica cartridges.

#### **Silica SPE cartridges**

Sorbent substrate: Silica; Sorbent weight: 500 to 1000 mg; pH range: 2 – 8; Particle size: 20 – 200 • m

**Note** The choice of the sorbent weight should be carefully correlated with the weight of sample analyzed and to the load capacity of the cartridge. While optimizing the method a check for analyte recovery is recommended.

#### **PFTE filters**

0,45 • m, fitting Luer plug.

#### **HPLC system**

Equipped with:

- a pumping device suitable for at least two solvents
- an injection device suitable for injection of 10 – 100 • l (automatic injection is preferable)
- RP column, C8 or C18, end-capped, suitable for mobile phase with pH 2 – 8

**Note** The choice of the length of the column and particles diameter may vary, and it's up the laboratory applying this method. Good analytical results were obtained with 150 to 250 mm columns, particles Ø 3,5 to 5 • m, column diameter 4,6 mm.

- RP pre-column, with the same stationary phase
- UV detector (a diode array detector is preferable, to record UV spectra)
- Data acquisition device

### 3.2 Reagents and Materials

#### 3.2.1 *Purity of Reagents*

Reagent grade chemicals shall be used in all tests.

All solvents used for chromatographic elution shall be HPLC grade.

#### 3.2.2 *Required reagents*

##### **Methanol for HPLC**

##### **HPLC grade water**

##### **Pentane**

##### **Toluene**

### 3.2.3 *Standard materials*

#### **Irgamet® 39**

Irgamet® 39, as supplied by CIBA, shall be used as standard for calibration.

**Note** Commercially available products, obtained by dilution of Irgamet 39 in mineral oil or other suitable solvents, shall not be used for calibration, even if the Irgamet 39 content is known.

#### **TTA (Irgamet® TTZ)**

TTA of analytical grade, or CIBA Irgamet® TTZ.

#### **Blank oil**

A mineral insulating oil, free from Irgamet 39, for dilution.

**Note** for the reasons reported in § 2.3.1, the blank oil for dilution shall be also TTA free.

### 3.2.4 *Standard solutions*

#### 3.2.4.1 *Stock solution*

A concentrated mg/kg solution of Irgamet 39 in toluene. It is recommended to prepare a fresh stock solution each 3 months, and to store it in dark bottles at room temperature.

**Note** 1000 mg/kg stock solutions were found to be stable for at least 3 months. If an higher lasting is desired, the stability shall be checked by comparison with a fresh solution.

#### 3.2.4.2 *Standard solutions*

From the stock solution, at least 5 diluted solutions should be prepared for calibration.

The solutions are prepared fresh each calibration stage, by diluting the stock solution with blank oil.

The standard solution should cover the range of 5 – 500 mg/kg.

## 4. **Sampling**

The objective of sampling is to obtain a representative test specimen. Thus, take laboratory samples in accordance with IEC 60475. The specific sampling technique can affect the accuracy of this test method.

## 5. **Analytical procedure**

### 5.1 **Preparation of Apparatus**

#### 5.1.1 *Instrument*

Design differences between instruments, columns and detectors make it impractical to detail the operating conditions. Consult the manufacturer's instructions for operating the instrument, accordingly with the selected separation and detection conditions.

#### 5.1.2 *Separation conditions*

Both C8 and C18 end-capped RP columns were found suitable for separation of Irgamet 39. Good separation can be carried out either with isocratic or gradient elutions, with mobile phase water/methanol; the solvent ratio may be 50% / 50% (with C8 columns) to 20% water / 80% methanol (with C18 columns).

A flow rate 0,5 to 1 ml/min is suitable.

The following table reports some experimental conditions as a guide, but each laboratory should optimize its own separation parameters.

A good separation is obtained if a sharp, shoulder-less peak is obtained, with no overlapping with BTA peak.

**Note** In some cases, to have a better separation and to avoid peak tailing, it is preferable to use a buffer instead of pure water in the mobile phase. Acetic buffer were used at pH 3 (concentration between 50 and 80 mM), increasing

the quality of the separation. In case of use of buffers, check for absorbance spectrum of Irgamet®39, since it may vary with pH.

**Table 1:** examples of separation condition

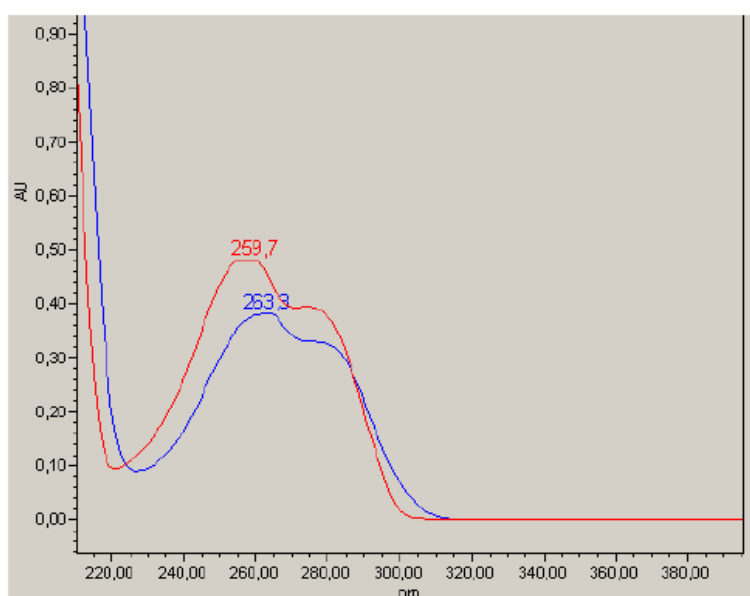
Column	Separation conditions	Timetable			Irgamet 39 RT	(BTA RT)	Notes
		time (min)	% H <sub>2</sub> O	% Met			
C18, 250 mm	Isocratic, 1 ml/min	0:00	30	70	3,5 to 4,5 min	2,5 to 3 min	
		20:00	30	70			
C18, 250 mm	Gradient, 1 ml/min	0:00	30	70	3,5 to 4,5 min	2,5 to 3 min	The step with 100% methanol provide column clean up
		4:00	30	70			
		6:00	0	100			
		10:00	0	100			
		14:00	30	70			
C18, 150 mm	Gradient, 0,5 ml/min	0:00	50	50	8 to 9 min	5 to 6 min	
		15:00	50	50			
		20:00	0	100			
		45:00	0	100			
		50:00	50	50			
C18, 150 mm	Gradient, 1 ml/min	0:00	80	20	6 to 7 min	5 to 6 min	
		7:30	0	100			
		14:00	50	50			
		18:00	80	20			
C8, 150 mm	Isocratic, 0,5 ml/min	0:00	50	50	3,5 to 4,5 min	2,5 to 3 min	
		20:00	50	50			

**Note** A clean up step with pure methanol or acetonitrile should be always used, to avoid accumulation of oxidized compounds which may interfere with the following determinations.

### 5.1.3 UV detection

UV detection of Irgamet 39 can be set at wavelengths of 264 nm, corresponding to the maximum absorbance (see figure 1).

**Figure 1:** UV spectra of Irgamet 39 (in blue) and BTA (in red)



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## 5.2 Calibration

The linear range must be established for the particular instrument being used and the selected separation procedure. The method should show a linear response in a concentration range 5 – 500 mg/kg.

### 5.2.1 *Calibration procedure*

Prepare at least 5 standard solutions by diluting the stock solution (3.2.4.1) with mineral blank oil. The standard solution shall be prepared fresh each calibration.

Extract the blank oil and each standard solution following the procedure in § 5.3.1. Run in triplicate at least the two external points (the minimum and the maximum).

Plot the peak area against concentration and calculate the regression model ( $y=bx+m$ ) as calibration curve. A correlation factor higher than 0,99 may be considered acceptable. The intercept  $m$  should be very close to the origin, verify that  $|m/b| < 1$ .

Recalibration each 6 months is recommended. Control sample of known concentration should be tested periodically to verify method's stability.

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## 5.3 Analysis

### 5.3.1 *Sample pre-treatment by SPE*

Using a vacuum manifold, slowly rinse a SPE Silica cartridge with ~5 ml of methanol, then condition it by passing ~10 ml of pentane.

Weigh to the nearest 0,01 g a sample portion of 0,5 – 2 g.

**Note** The weight of sample must be optimised in connection to the sorbent material mass in the cartridge. An excessive weight of sample may overload the sorbent and affect the linearity of the method, underestimating the highest concentrations.

Dilute it with 10 ml pentane and pass the solution through the pre-conditioned cartridge at a maximum rate 3 ml/min. Discard the eluate.

Rinse the cartridge with 20 ml fresh pentane at a maximum rate 3 ml/min, to remove the non-polar oil constituents adsorbed by the Silica. Discard the eluate.

Dry the sorbent material by flushing it under vacuum for 5-10 minutes.

Slowly elute the cartridge (in the same vacuum manifold or manually, with a syringe) with methanol, collecting the first 5,00 ml into a volumetric flask.

**Note 1** The elution may be done with a different solvent, e.g. with the chromatographic mobile phase. Check for the solubility of Irgamet 39 if an alternative solvent is used.

**Note 2** A different volume of solvent can be used if the requirements of analytic recovery (§ 6) are satisfied.

### 5.3.2 *HPLC analysis*

With a precision syringe inject into the HPLC a portion of the last eluate collected into the 5 ml flask. The injection volume depends on the sensitivity of the instrument and on the weight of oil analysed: usually 10 to 100 •l are suitable.

Run the chromatogram and record the area of the peak corresponding to Irgamet 39 retention time.

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## 5.4 Calculations

Being  $y=bx+m$  the model obtained during the calibration, calculate the result as:

$$\text{mg/kg (Irgamet 39)} = [(\text{Peak Area}) - m] / b.$$

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## 5.5 Report

Report the concentration of Irgamet 39 in mg/kg to three significant figures.

## 6. Analytic recovery yield

### 6.1 Adsorption yield

Verify the adsorption yield of the silica SPE cartridges as following:

- put 2 cartridges in series in the vacuum manifold
- pass a standard sample (200 mg/kg) through both cartridges as described in § 5.3.1, then separate the two cartridges and elute them separately with 5 ml methanol each one.
- analyze the two samples, and record the results as  $X_1$  (concentration found in the upper cartridge) and  $X_2$  (concentration found in the lower cartridge)
- check that  $\frac{X_1}{X_1 + X_2} \geq 0,98$ .

### 6.2 Elution yield

Verify the elution yield from the silica SPE cartridges as following:

- pass a standard sample (200 mg/kg) through a cartridges as described in § 5.3.1
- elute the cartridge firstly with 5 ml methanol, the elute it again with a second aliquot of 5 ml methanol
- analyze the two samples separately, and record the results as  $X_1$  (concentration found in the first elution) and  $X_2$  (concentration found in the second elution)
- check that  $\frac{X_1}{X_1 + X_2} \geq 0,98$ .

## 7. Precision data

### 7.1 Detection limit

In the condition prescribed in this method a detection limit of < 5 mg/kg is expected. Each laboratory should estimate its own detection limit.

### 7.2 Repeatability

Duplicate determinations carried out by one laboratory should be considered suspect at the 95% confidence level if they differ by more than the value reported in Table 2 (expressed in percentage of the average value).

**Table 2:** Repeatability

Concentration	r (repeatability)
10 mg/kg	10 %
> 50 mg/kg	5 %

### 7.3 Reproducibility

Duplicate determinations carried out by different laboratory should be considered suspect at the 95% confidence level if they differ by more than the value reported in Table 3 (expressed in percentage of the average value).

**Table 3:** Reproducibility

Concentration	r (repeatability)
10 mg/kg	15 %
> 50 mg/kg	8 %