



Customs Laboratories  
European Network

## **ILIADe 113:2019 | CLEN Method**

**Community Reference Method for the Determination of the  
Euromarker (Solvent Yellow 124) in Gas Oils and Kerosene**

**Version 12 November 2019**

(compared to the initial version adopted as a CLEN method in February 2017:  
layout harmonisation and addition of the sections 'calculation' and 'expression of results')

# Community Reference Method for the Determination of the Euromarker (Solvent Yellow 124) in Gas Oils and Kerosene

## 1. Scope and field of application

### 1.1. Introduction and references

In the EC Decision 2001/574 of 13 July 2001 a common fiscal marker for gas oils and kerosene has been established.

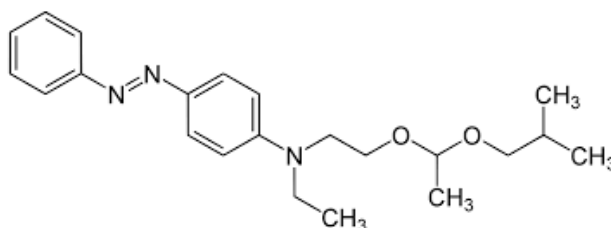
For the proper functioning of the internal market and in particular to prevent tax evasion, Council Directive 95/60/EC of 27 November 1995 has provided for a common marking system to identify gas oils and kerosene, which are subject to a reduced excise duty rate. This publication provides a method for the determination of SY124 in gas oil and kerosene. It shall be applied as a reference method in point of controversy for the examination of marked low tax mineral oils and mixtures with diesel.

The marker is:

Solvent Yellow 124

IUPAC name: N-ethyl-N-[2-(1-isobutoxyethoxy)ethyl]-4-(phenylazo)aniline),

CAS NR: 34432-92-3



The marking level should be between 6 mg and 9 mg of marker per litre of mineral oil.

### 1.2. Scope

This method describes the analysis of Solvent Yellow 124 (Sudan 455) (section 3.1), in the concentration range from the detection limit till 10 mg Solvent Yellow 124 per litre. When the concentration is more than 10 mg/L, a dilution with xylene (3.3) is necessary for the exact determination of the concentration.

## 2. Principle

The sample is put into a sample vial. The product is separated with normal phase (straight) chromatography and UV/VIS detection at 450 nm. Additional information can be obtained by analysing the samples with Diode Array detection at 410 nm in the same run. External calibration is used, the purity of the applied SY124 should be considered.

### 3. Reagents and materials

Use only reagents of acknowledged quality and HPLC grade water (i.e. MilliQ-water).

3.1. Solvent Yellow 124 (purity >98%).

3.2. Toluene, for L.C.

3.3. o-Xylene, p.a.

3.4. Ethyl acetate, p.a.

Use the reagents according to their safety instructions.

### 4. Apparatus

4.1. Standard laboratory glassware. Volumetric flasks (2000ml and 100ml) and pipettes (1ml, 5ml and 10ml) should be B-grade or better.

4.2. HPLC apparatus, equipped with the following:

4.2.1. HPLC-pump, fit for zero pulsation that delivers a constant flow at the rate required.

4.2.2. Sample injector, comprising a loop injector (manual or part of an autosampler) with a capacity of 20 µl.

4.2.3. Column, 5 µm silica length 200- 250 mm, diameter 3.0 to 5 mm ID.  
e.g. Waters Spherisorb 5 µm or Luna 5 µm Silica Phenomenex.

4.2.4. Precolumn, silica e.g. Spherisorb S5W Waters. Use is advised, but not obligatory.

4.2.5. Column oven: should be used when the retention time of the SY124 peak is not stable from run to run. Temperature 40°C.

4.2.6. Detector: UV 450 nm, or diode array both 410 nm and 450 nm.

4.2.7. Integration system, comprising an electronic integrator with calculating and reporting capabilities, compatible with the output of the detector.

### 5. Procedure

#### 5.1. General

Take a representative sample of the product to be analysed.

#### 5.2. Pre-treatment of the sample

Transfer sample to sample vial. Filter the sample when it is dirty through a syringe filter e.g. 0.45 µm PTFE.

#### 5.3. Mobile phase

Eluent: Mix in a 2000 ml volumetric flask, 40 ml ethyl acetate (3.4) and 1960 ml toluene (3.2) and homogenise. The proportions of the two eluents may vary providing that the system check (5.6) conditions are fulfilled.

#### 5.4. Reference stock solution

Make a reference stock solution of SY124 of 100 mg/L by weighing the amount of Solvent Yellow (3.1) needed in a 500 ml volumetric flask and by making up with xylene (3.3) to volume at a temperature of 20± 1°C. Record the weight to four decimal places. The purity of the applied SY124 should be considered. Mix thoroughly and allow to stand for one night. Then thoroughly mix again and prepare the calibration solutions.

## 5.5. Calibration solution

Concentration	Volume reference stock solution	Final volume volumetric flask
Ca. 10 mg/L	10 ml	100 ml
Ca. 5 mg/L	5 ml	100 ml
Ca. 1 mg/L	1 ml	100 ml

## 5.6. System check

The stability of the HPLC system, the retention time of the SY124 and the isolation of the peak of SY124 have to be checked before analysing the samples.

Inject the calibration solution of 10mg/L or your laboratory reference solution, three times. The relative standard deviation of the peak area of the three injections should be less than 1%. The relative standard deviation of the retention time of SY124 should be less than 2%. If retention time is too short or too long the eluent has to be adapted. Addition of ethyl acetate to the eluent results in a shorter retention time.

## 5.7. Determination

Samples and the calibration solutions are analysed in duplicate.

Commence with the three calibration solutions or laboratory reference solutions (from certified reference material). Maximum twelve samples can be measured in duplicate before a new calibration has to be performed. The sequence ends with the three calibration solutions or the laboratory reference solution (or certified reference material). The calibration curve is forced through zero. If the correlation coefficient of the linear regression of all the calibration points is more than 0.999 the calibration is adequate. If the correlation coefficient is less than 0.999 the system performance has to be checked and if possible improved.

## 6. Calculation

$$A_c = \frac{o_m - K_c}{K_b} \times XF$$

Where:  $A_c$  = concentration SY124 in mg/L

$o_m$  = peak area in counts

$XF$  = dilution factor

$K_c$  = constant from calibration curve  $y = (K_b \times X) + K_c$

$K_b$  = slope from calibration curve  $y = (K_b \times X) + K_c$

## 7. Expression of the results

Lower than 0.02mg/L, report as “below LOD” (<0.02mg/L);

From  $\geq 0.02$  mg/L to <0.07 mg/L (LOQ): report as “detected but below LOQ”

$\geq 0.07$  mg/L (i.e.  $\geq$ LOQ): result rounded on 0.1 mg/L.

Note: should a laboratory have its own LOQ lower than 0.07 mg/L, the laboratory can adapt the above expression of the results to its own LOQ.

## 8. Precision

### 8.1. Detection limit

The detection limit in gas oil and kerosene is 0.02 mg/L.

### 8.2. Quantification limit

The quantification limit in gas oil and kerosene is 0.07 mg/L.

### 8.3. Repeatability

The difference between the results of two single determinations, carried out in rapid succession by the same operator under the same conditions on identical test material, shall not exceed the values in 95 % of the analyses, for samples with a content of:

Range	Repeatability
0.1 – 0.3 mg/L	0.03 mg/L
4 - 10 mg/L	0.16 mg/L

These repeatability values have been evaluated from the CLEN ring tests, cf. annex B.

### 8.4. Reproducibility

The difference between the results of two single and independent determinations, obtained by two operators working in different laboratories under different conditions on identical material, shall not exceed in 95 % of the analyses, for samples with a content of:

Range	Reproducibility
0.1 – 0.3 mg/L	0.05 mg/L
4 - 10 mg/L	0.10 X where X is the mean of the two results

These reproducibility values have been evaluated from the CLEN ring tests, cf. annex B.

### 8.5. Measurement uncertainty

Relative measurement uncertainty can be estimated from the reproducibility data after having conformed that one's laboratory performs equally well as those laboratories participating in the validation study. These reproducibility data do not comprise uncertainty of the calibration. This uncertainty has to be added. The uncertainty is then estimated as:

$$U = k \cdot c \sqrt{u_R^2 + u_{st}^2}$$

U expanded uncertainty

K coverage factor (for 95% confidence interval choose k=2)

C concentration for which the uncertainty should be evaluated

$u_R$  relative uncertainty due to reproducibility

$u_{st}$  relative uncertainty of the calibration standard (mainly purity).  $u_{st}$  can be ignored if it is <1/3  $u_R$

For  $c = 0.12 \text{ mg/L}$ :  $u_R = 13 \%$

For  $c > 4 \text{ mg/L}$ :  $u_R = 3.5 \%$

## 9. Literature

9.1. EC Directive 95/60 of 27 November 1995, establishing a common fiscal marker for gas oils and kerosene.

9.2. Quantitative testing of Sudan Marker 455 liquid (Solvent Yellow) in Mineral Oils by means of liquid chromatography (HPLC), Joint Research Centre Ispra 1999.

9.3. T. Linsinger, G. Koomen, H. Emteborg, G. Roebben, G. Kramer, A. Lamberty (2004) Validation of the Draft Community Reference Method for the determination of Solvent Yellow 124 in gas oil (Euromarker). EUR 21195 EN, ISBN 92-894-7873-X

## Annex A

(informative)

- *Results of interlaboratory test*

An interlaboratory test, carried out in 2004, by the European Commission, DG-JRC Institute for reference materials and measurements and the Dutch customs Laboratory. Report number: EUR 21195 EN, ISBN 92-894-7873-X, gave statistical results (evaluated in accordance with ISO 5725-2) shown in Table A.1.

Table A.1 - Precision Data

Sample	2	3	4	5	6	7	9	10	11	12
Number of laboratories that reported results	20	20	20	20	20	20	20	20	20	20
Number of accepted test results	19	17	17	18	18	19	15	18	20	19
Mean SY124 content mg/L	6.04	0.12	0.27	5.99	9.05	4.78	6.10	7.13	5.87	6.01
Repeatability standard deviation. $s_r$	0.041	0.007	0.014	0.033	0.064	0.049	0.079	0.070	0.061	0.032
Repeatability coefficient of variation. %	0.68	5.83	5.19	0.55	0.71	1.03	1.30	0.98	1.04	0.53
Repeatability limit. $r$ ( $2 \cdot \sqrt{2} \times s_r$ )	0.116	0.020	0.040	0.093	0.181	0.139	0.223	0.198	0.173	0.091
Reproducibility standard deviation. $s_R$	0.231	0.016	0.020	0.225	0.279	0.153	0.278	0.210	0.189	0.196
Reproducibility coefficient of variation. %	3.82	13.33	7.41	3.76	3.08	3.20	4.56	2.95	3.22	3.26
Reproducibility limit. $R$ ( $2 \cdot \sqrt{2} \times s_R$ )	0.653	0.045	0.057	0.636	0.789	0.433	0.786	0.594	0.535	0.554

Annex B

(informative)

- *Evaluation of repeatability and reproducibility 2016*

The values of repeatability and reproducibility measured in proficiency tests in CLEN Action 2 (all test until 2016 included) in measuring ranges from 0.1 - 0.3 mg / L and 4-10 mg / L have been evaluated. The results are gathered in tables B.1 and B.2. Only 1 of the values failed the statistical F-test. Thereby the values of repeatability and reproducibility are stated valid.

Table B.1. - Evaluation of repeatability

Range 0,1-0,3 mg/L	r	result F-test	critical value F-test
reference value 2004	0,03		
measured 2008	0,021	0,15	2,35
measured 2016	0,022	0,2	2,29

Range 6-9 mg/L	r	result F-test	critical value F-test
reference value 2004	0,16		
measured 2008	0,119	0,28	2,35
measured 2010	0,088	0,15	2,29
measured 2013	0,09	0,16	2,29
measured 2016 (heating oil)	0,064	0,08	2,29
measured 2016 (MDO)	0,056	0,06	2,29

Table B.2. - Evaluation of reproducibility

Range 0,1-0,3 mg/L	R	result F-test	critical value F-test
reference value 2004	0,05		
measured 2008	0,085	2,89	2,35
measured 2016	0,075	2,25	2,29

Range 6-9 mg/L	R	result F-test	critical value F-test
reference value 2004	0,10 . X		
measured 2008	0,11 . X	1,18	2,35
measured 2010	0,08 . X	0,82	2,29
measured 2013	0,10 . X	1,05	2,29
measured 2016 (heating oil)	0,11 . X	1,69	2,29
measured 2016 (MDO)	0,14 . X	2,09	2,29