



BSI Standards Publication

**Liquid petroleum products —  
Determination of hydrocarbon  
types and oxygenates via  
multidimensional gas  
chromatography method —  
Round Robin research report**

### **National foreword**

This Published Document is the UK implementation of CEN/TR 15745:2015. It supersedes PD CEN/TR 15745:2008 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/15, Natural Gas and Gas Analysis.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

© The British Standards Institution 2015.

Published by BSI Standards Limited 2015

ISBN 978 0 580 88362 0

ICS 75.160.20

**Compliance with a British Standard cannot confer immunity from legal obligations.**

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 31 May 2015.

### **Amendments/corrigenda issued since publication**

<b>Date</b>	<b>Text affected</b>
-------------	----------------------

---

English Version

Liquid petroleum products - Determination of hydrocarbon types  
and oxygenates via multidimensional gas chromatography  
method - Round Robin research report

Produits pétroliers liquides - Détermination des groupes  
d'hydrocarbures et de la teneur en composés oxygénés par  
méthode par chromatographie multidimensionnelle en  
phase gazeuse - Rapport de recherches interlaboratoires

Flüssige Mineralölerzeugnisse - Bestimmung der  
Kohlenwasserstoffgruppen und sauerstoffhaltigen  
Verbindungen mit multidimensionalen  
gaschromatographischen Verfahren - Round Robin  
Forschungsbericht

This Technical Report was approved by CEN on 24 February 2015. It has been drawn up by the Technical Committee CEN/TC 19.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

**CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels**

## Contents

Page

Foreword.....	4
Introduction .....	5
1 Scope .....	6
2 Normative references .....	6
3 Participating laboratories .....	6
4 Sample set .....	7
5 Results from the round robin test.....	8
5.1 Sample 1 .....	8
5.2 Results sample 2.....	9
5.3 Results sample 3.....	11
5.4 Results sample 4.....	13
6 Review of the data .....	14
6.1 MTBE.....	14
6.2 Methanol .....	16
6.3 t-Butanol .....	16
6.4 i-Propanol .....	17
6.5 i-Butanol .....	19
7 Results and conclusions .....	20
Annex A (normative) Round Robin Report 2010 - 688.....	22
A.1 General.....	22
A.2 Motivation .....	22
A.2.1 General.....	22
A.2.2 Remarks .....	22
A.3 Test Procedure and Protocol.....	23
A.3.1 General.....	23
A.3.2 Participating Laboratories Method A.....	23
A.3.3 Samples .....	23
A.3.4 Results and Precision Evaluation .....	24
A.4 Essential RRT Details Methods B, C, D .....	38
A.4.1 Test Procedure and Protocol.....	38
A.4.2 Participating Laboratories Method B, C and D .....	38
A.4.3 Samples .....	38
Annex B (normative) Round Robin Report 2010 - 689.....	43
B.1 Methods and laboratories used.....	43
B.2 Samples .....	44
B.3 Results received .....	44
B.3.1 General.....	44

<b>B.3.2</b>	<b>Conclusions .....</b>	<b>44</b>
<b>B.3.3</b>	<b>Overview results received .....</b>	<b>45</b>
<b>B.4</b>	<b>Graphs .....</b>	<b>52</b>
	<b>Bibliography .....</b>	<b>56</b>

## **Foreword**

This document (CEN/TR 15475:2015) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes CEN/TR 15745:2008.

The second edition of this document includes Round Robin data generated in 2012 that led to revision of EN ISO 22854.

## Introduction

In 2004, the company AC Analytical Controls<sup>1)</sup> conducted a Performance Monitoring Program on the AC Reformulyzer™. This is a kind of crosscheck program where customers analyse samples distributed by the company and then report the analysis results. The company checks the analytical performance of the instruments, keeping in mind the possible analytical errors that can occur. Because raw data are reported (chromatogram and data for each carbon number/group), a detailed review can be made. The company informs a customer when the instrument performance is inadequate and where possible provides information and instructions to improve the performance.

The intention was to get a precision statement for oxygenates that were not included in EN 14517 [2], but that are listed in EN 228. Besides this, the performance for other properties (aromatics, olefins, benzene) has been determined.

More information on the review of the data is available from the monitoring, but this technical report focuses on oxygenates. Results for other properties (aromatics, olefins, benzene) are listed in the tables but are not discussed in detail here. Also the evaluation for outliers is done on oxygenates only, not on the other properties.

The precision data obtained from this program were used to develop the EN ISO 22854 method which was published in 2008 [3].

In 2010 another Round Robin was organized to establish a test method to determine the oxygenated components in ethanol automotive fuel (E85). Components such as ethers, C3-C5 alcohols and ethanol could be made part of an E85 specification.

Four methods were tested:

- A. EN ISO 22854 modified (with sample dilution)
- B. EN 1601 modified (with sample dilution)
- C. Capillary column method (2 columns in series, UNGDA method)
- D. Capillary column method (2 separate columns, Suedzucker method)

Only method A with sample dilution had enough participants to derive a precision statement. The dilution step was needed to lower the ethanol content in the sample to values below 20 % (V/V).

The Round Robin was carried out by TC 19/WG 9 and the results were evaluated conform EN ISO 4259. As methods B, C and D did not get enough participants a 2nd ILS was carried out to see if more data could be obtained for these methods. The details of these Round Robin Tests are added as Appendix A and B to this Research Report.

---

<sup>1)</sup> Postal address: AC Analytical Controls, Innsbruckweg 35 3047 AG Rotterdam, The Netherlands, E-mail:sales.netherlands@pacpl.com, Web: www.pacpl.com.

## 1 Scope

This Technical Report presents the study on the application of EN 14517 [2] to other oxygenates. This report supports an extension of the scope of the method, which has been explicitly requested by ISO/TC 28 at the time of revision of EN 14517 and was agreed to result in the parallel Standard EN ISO 22854 [3].

This Technical Report is published as background information to judge the approval of the use of the method for the determination of all oxygenates as mentioned in the European Fuels Directive. This Technical Report should also support the use of multidimensional chromatography as the method for disputes on oxygenates in EN 228 [1].

NOTE For the purposes of this document, the term “% (V/V)” is used to represent the volume fraction.

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259)*

## 3 Participating laboratories

Laboratories that have participated in the 2005 to 2006 Round Robin work are mentioned in Table 1.

**Table 1 — Participating laboratories**

Company / lab	Country	Company / lab	Country
Umweltbundesamt	Austria	MOL	Hungary
Total Raffinaderij	Belgium	ENI Gela	Italy
BRC	Belgium	ENI, Euron	Italy
Statoil Kalundborg	Denmark	ENI Agip Roma	Italy
Fortum	Finland	ENI Agip	Italy
ExxonMobil	France	ENI Agip Sanazzaro	Italy
Total CReG	France	ENI R&M Livorno	Italy
Shell Petit-Couronne	France	SGS Spijkenisse	Netherlands
PCK	Germany	Nerefco	Netherlands
BP Gelsenkirchen	Germany	Total	Netherlands
Total Leuna	Germany	Shell Pernis	Netherlands
SGS Speyer	Germany	Slovnaft	Slovak Republic
Bayernoil	Germany	Repsol	Spain
BP	Germany	BP Castellon	Spain
Opel	Germany	ConocoPhillips	UK
Shell Heide	Germany	Intertek Sunbury	UK
Hellenic Petroleum	Greece	Total	UK
MOL RT	Hungary	Shell Global Solutions	UK

Laboratories that have participated in the second RR work are presented in Annex B.