

Manual of Petroleum Measurement Standards Chapter 19.4

Evaporative Loss Reference Information and Speciation Methodology

FOURTH EDITION, OCTOBER 2023



Special Notes

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed. The use of API publications is voluntary. In some cases, third parties or authorities having jurisdiction may choose to incorporate API standards by reference and may mandate compliance.

Neither API nor any of API's employees, subcontractors, consultants, committees, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication. Neither API nor any of API's employees, subcontractors, consultants, or other assignees represent that use of this publication would not infringe upon privately owned rights.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to ensure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be used. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

All rights reserved. No part of this work may be reproduced, translated, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 200 Massachusetts Avenue, NW, Suite 1100, Washington, DC 20001-5571.

Foreword

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

The verbal forms used to express the provisions in this document are as follows.

Shall: As used in a standard, “shall” denotes a minimum requirement to conform to the standard.

Should: As used in a standard, “should” denotes a recommendation or that which is advised but not required to conform to the standard.

May: As used in a standard, “may” denotes a course of action permissible within the limits of a standard.

Can: As used in a standard, “can” denotes a statement of possibility or capability.

This document was produced under API standardization procedures that ensure appropriate notification and participation in the developmental process and is designated as an API standard. Questions concerning the interpretation of the content of this publication or comments and questions concerning the procedures under which this publication was developed should be directed in writing to the Director of Standards, American Petroleum Institute, 200 Massachusetts Avenue, NW, Suite 1100, Washington, DC 20001. Requests for permission to reproduce or translate all or any part of the material published herein should also be addressed to the director.

Generally, API standards are reviewed and revised, reaffirmed, or withdrawn at least every five years. A one-time extension of up to two years may be added to this review cycle. Status of the publication can be ascertained from the API Standards Department, telephone (202) 682-8000. A catalog of API publications and materials is published annually by API, 200 Massachusetts Avenue, NW, Suite 1100, Washington, DC 20001.

Suggested revisions are invited and should be submitted to the Standards Department, API, 200 Massachusetts Avenue, NW, Suite 1100, Washington, DC 20001, standards@api.org.

Contents

	Page
1	Scope..... 1
2	Normative References 1
3	Symbols 1
4	Variables 3
4.1	Meteorological Data 3
4.2	Stock True Vapor Pressure P_V 3
4.3	Component Saturated Vapor Pressure P_i^o 7
4.4	Stock Liquid Molecular Weight M_L 7
4.5	Stock Vapor Molecular Weight M_V 8
4.6	Component Molecular Weight M_i 8
4.7	Concentrations for Selected Compounds in Petroleum Liquids 20
4.8	Tank Solar Absorptance α 23
5	Speciation Methods 23
5.1	Speciation Based on Liquid Profiles 23
5.2	Speciation Based on Vapor Profiles 25
6	Speciation Example 26
7	Speciation Theory 31
7.1	Introduction 31
7.2	Raoult's Law 31
7.3	Precision, Accuracy, and Variability of Methods 32
7.4	Common Mistakes 35
Annex A (informative)	Validity of Raoult's Law 36
Annex B (informative)	Vapor Pressure by Antoine's Equation 47
Annex C (informative)	Comparison of Molecular Weight, Normal Boiling Point, and Blending RVP for Selected Hydrocarbons and Oxygenates 51
Annex D (informative)	Vapor Pressure by Maxwell-Bonnell Correlations 55
Annex E (informative)	Vapor Pressure by the HOST Test Method 59
Annex F (informative)	EPA Categories of POM/PACs/PAHs 61
Annex G (informative)	Properties of Heavy Fuel Oil 64
Annex H (informative)	Derivations of Speciation Equations 77
Annex I (informative)	Storage Tank Liquid Bulk, Liquid Surface, and Vapor Space Temperatures 83
Annex J (informative)	SI Units 121
Bibliography 122

Contents

Page

Figures

C.1	Normal Boiling Point (NBP) Versus Molecular Weight.....	53
C.2	Pure Substance Vapor Pressure at 100 °F Versus Molecular Weight.....	54
E.1	EPA Approval Letter and Approved Method.....	60
I.1	Heat Transfer Model.....	90
I.2	Insulation.....	91
I.3	Bulk Temperature vs Time.....	107

Tables

1	Typical Properties of Selected Petroleum Liquids.....	5
2	Properties of Selected Petrochemicals (See Table Footnote a).....	9
3	Concentrations (Weight Percent) of Selected Components in Selected Petroleum Liquids.....	20
4	Concentrations (Weight Percent) of Selected Components in No. 6 Fuel Oil.....	21
5	Concentrations of PAHs in Selected Petroleum Liquids (See NOTE 1).....	22
6	Solar Absorptance α for Selected Tank Surfaces.....	23
7	Vapor Profile for Simulated Gasoline.....	26
8	Speciation Example Worksheet.....	29
9	Speciation Example Summary.....	31
A.1	Summary of Results for Summer Blend Unleaded Gasoline.....	36
A.2	Summary of Results for Winter Blend Unleaded Gasoline.....	37
A.3	Compounds Selected for Speciation.....	38
A.4	GC Analysis Concentrations Using Average Response Factors (ARF) and Linear Regression (LR) for Liquid Phase Samples (Concentrations in $\mu\text{g/mL}$).....	39
A.5	GC Analysis Concentrations Using Average Response Factors (ARF) and Linear Regression (LR) for Vapor Phase Samples (Concentrations in $\mu\text{g/mL}$).....	40
A.6	Comparison of Predicted Vapor Concentrations Using the Response Factor Analytical Data.....	42
A.7	Comparison of Predicted Vapor Concentrations Using the Linear Regression Analytical Data.....	43
B.1	Variables in Antoine's Equation.....	47
C.1	Molecular Weight, Normal Boiling Point, and Blending RVP for Selected Hydrocarbons and Oxygenates.....	52
F.1	Comparison of TRI and NTI POM/PAH.....	63
G.1	No. 6 Fuel Oil—True Vapor Pressure (psia) versus Temperature (°F).....	65
G.2	No. 6 Fuel Oil—True Vapor Pressure (psia) versus Temperature (°F).....	66
G.3	Vacuum Residual Oil—True Vapor Pressure (psia) versus Temperature (°F).....	67
G.4	No. 6 Fuel Oil Liquid Phase Speciation Profile.....	68
G.5	No. 6 Fuel Oil Liquid Phase Speciation Profile—Metals.....	69
G.6	No. 6 Fuel Oil Liquid Phase Speciation Profile.....	70
G.7	Key to Sample IDs.....	71
G.8	No. 6 Fuel Oil Vapor Pressure by Isoteniscope (ASTM D2879).....	71
G.9	Cutter Stock Vapor Pressure by Isoteniscope (ASTM D2879).....	72
G.10	Vacuum Residual Vapor Pressure by Isoteniscope (ASTM D2879).....	72
G.11	Vapor Pressure by HOST Method.....	73
G.12	API Gravity.....	73
G.13	Metal Concentrations (ppmw).....	74
G.14	Organic Compounds Concentrations (ppmw).....	75
I.1	Annex I Symbols, Description, and Units.....	85

Contents

	Page
I.2	Difference Between Bulk and Ambient Temperatures: $T_B - T_{AA}$ (°F) 89
I.3	Conducted and Radiant Energy Equations..... 99
I.4	Difference Between Equilibrium Bulk Temperature T_{BE} and Ambient Temperature T_{AA} (°R) 107
I.5	Difference Between Liquid Surface Temperature and Ambient Temperature (temperatures converted from °R to °F)..... 114
I.6	Liquid Surface Temperature T_{LA} (Temperatures Converted from °R to °F)..... 115
I.7	Effect on Emissions for Fixed Roof Tanks – True Vapor Pressure P_{VA} (psia) 115
I.8	Effect on Emissions for Floating Roof Tanks: Vapor Pressure Function P^* 115
I.9	Effect on Emissions for Floating Roof Tanks: Vapor Pressure Function P^* % Difference..... 116
I.10	Effect on Emission Estimates: Good ($\alpha = 0.17$) vs. Average ($\alpha = 0.25$) Solar Absorptance 116
I.11	Conductance c (Btu/(hr °F ft ²))..... 117
I.12	Fraction of Insolation Transmitted f 118

Evaporative Loss Reference Information and Speciation Methodology

1 Scope

This standard provides methodology to estimate emissions of individual hydrocarbon species using the total emissions of multicomponent hydrocarbon mixtures (such as crude oils and gasoline) estimated from API *MPMS* Chapter 19.1 for fixed-roof tanks, API *MPMS* Chapter 19.2 for floating-roof tanks, API *MPMS* Chapter 19.5 for marine vessels, and other methods used for total hydrocarbon emission estimates. This process is referred to as speciation.

Speciation of emissions from hydrocarbon mixtures accounts for the higher evaporation rate of the more volatile components, resulting in a different composition of the mixture in the vapor phase than in the liquid phase. The methodology presented in this standard assumes that there is sufficient liquid present such that the chemical composition at the liquid surface may be considered to not change as a result of the evaporative loss.

This standard also contains reference information used for estimating emissions in accordance with API *MPMS* Chapter 19.1, API *MPMS* Chapter 19.2, and API *MPMS* Chapter 19.5.

The methodology in this standard applies to:

- a) liquids with vapor pressure that has reached equilibrium with ambient conditions at a true vapor pressure less than the ambient atmospheric pressure (i.e. not boiling);
- b) liquids for which the vapor pressure is known or for which sufficient data are available to determine the vapor pressure;
- c) liquid mixtures where Raoult's Law can be used to describe the vapor phase equilibria.

This methodology does not apply to:

- a) emissions that result from leaks from piping components (e.g. valves, flanges, pumps, connectors);
- b) liquid mixtures where Raoult's Law cannot be used to describe the vapor phase equilibria (e.g. mixtures in which hydrocarbons are dissolved in water, or mixtures of hydrocarbons with alcohols).

2 Normative References

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

API *Manual of Petroleum Measurement Standards (MPMS)* Chapter 19.1, *Evaporative Loss from Fixed-Roof Tanks*, Fourth Edition, 2012

API *MPMS* Chapter 19.2, *Evaporative Loss from Floating-Roof Tanks*, Third Edition, 2012

API *MPMS* Chapter 19.5, *Atmospheric Hydrocarbon Emissions from Marine Vessel Transfer Operations*, First Edition, September 2009

3 Symbols

The following symbols, units, and source applies to this document.

NOTE Symbols used in [Annex I](#) are listed in [Section I.1](#).