Refinery Stream Composition Data—Update to Speciation Data in API 4723

API PUBLICATION 4723-A
DECEMBER 2018

AMERICAN PETROLEUM INSTITUTE

Executive Summary

The Petroleum Environmental Research Forum (PERF) completed a project in the 1990s to create a compilation of refinery process stream speciation data, which was later published as American Petroleum Institute Publication 4723 (API 4723). The refining industry has routinely used these data for various permitting and reporting purposes, such as estimating hazardous air pollutant (HAP) emissions from equipment fugitives, storage tanks, and loading operations; estimating emissions from miscellaneous process vents; and preparing Toxic Release Inventory (TRI) reports.

Since API 4723 was published, new regulatory requirements (e.g. Mobile Source Air Toxics rule, reformulated gasoline standards, lower fuel sulfur requirements) have resulted in refinery process changes that potentially altered the concentrations of species in process streams. Changing feedstocks, new process additives, and new catalysts may also have affected what species are present in specific process streams.

Therefore, PERF initiated a project to evaluate more recent process stream speciation data from several oil companies' refineries. The project results are provided in this report. Data were compiled for 68 refinery process streams using an expanded list of chemical species. The chemical species selected are those that can be found in refinery process streams and identified in hazardous air pollutant (HAP), persistent bioaccumulative toxic, or TRI lists. For a given process stream, up to 75 chemical species were targeted for inclusion to capture a wider range of volatile, semi-volatile, and metal HAP compounds, compared to the 24 species in the original study. Some concentration data were reported for additional species beyond the targeted list, such that data for a total of 89 different species are reflected in the project results. Most of the new species are metal HAP and heavier semi-volatile compounds.

Updates to laboratory methods have generally improved method accuracy and provide for lower method detection limits (MDLs) than were possible for the original PERF project. The lower detection limits contributed to an increase in the number of chemical species identified in various analytical test methods. The lower limits also allow for lowering the floor that was used in the original study—a default MDL that was set at 0.01 weight percent. By contrast, for the current study, the lowest MDL was for benzo(a)pyrene at 1E-08 weight percent in a coke record.

Based on the more recent data, this report provides updated most likely values (MLVs) associated with 68 refinery process streams. Many process streams had decreases in chemical species MLVs versus the original study. Some process streams had increases, but these results were generally supported by larger datasets. More chemical species may have been identified in a given process stream compared to the original study due to the expanded list of species or due to improved laboratory methods providing lower MDLs.

The material contained in this report will be of use in estimating the emissions of specific chemical species, preparing permit applications, and performing other environmental assessments. API, PERF, and the project participants make no claims as to the suitability or acceptability of the stream composition data reported herein for specific reporting or regulatory purposes.

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Acronyms

API	American Petroleum Institute
CAS #	Chemical Abstracts Service number
CAT	catalytic
H/C	hydrocracker or hydrocrackate
HAP	hazardous air pollutant
LPG	liquefied petroleum gas
Max	maximum
MDL	method detection limit
Min	minimum
MLV	most likely value
ND	non-detectable or non-detect
PAH	polycyclic aromatic hydrocarbons
PERF	Petroleum Environmental Research Forum
TRI	Toxic Release Inventory
US EPA	United States Environmental Protection Agency

Definitions

Dataset: Set of records for a given process stream and chemical species combination

MDL: Each analytical method has a lower concentration limit that can be measured and reported with 99 % confidence that the chemical species is present. This concentration is the method detection limit for determining that the chemical species is present in the mixture.

ND: Non-detect is the result provided in an analytical test for a chemical species that cannot be determined to be present at or above the MDL. If the chemical species is expected to be present in the mixture, the concentration is below the MDL. If the chemical species is not expected to be present, a zero may be substituted for a ND result.

Number of analyses: Number of measurements used to calculate the annual average concentration for a record.

N Data: Number of records; also equal to N_{Obs}.

N_{Obs}: Number of records, also equal to N Data.

N Quantified: Number of records that have quantified values—i.e. values reported at or greater than the method detection levels.

R (R Code): An integrated suite of software facilities for data manipulation, calculation, and graphical display. The software provides a wide variety of statistical (linear and nonlinear modeling, classical statistical tests, time-series analysis, classification, clustering, etc.) and graphical techniques.

Record: A row in the database providing all data associated with a submission of an annual average concentration (number of analyses, number of ND, test method, minimum value, maximum value, MDL, etc.).

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1 Introduction

Passage of the Clean Air Act Amendments of 1990 created a number of new compliance challenges for the United States refining industry. To provide improved approaches to meeting these challenges and allow leveraging of research expenditures, a number of the members of the Petroleum Environmental Research Forum (PERF) formed the Cooperative Air Program (CAP). The CAP consisted of a number of individual research projects, including a project to develop industry-representative concentration profiles for refinery process streams. This effort was undertaken to improve emissions estimates for regulatory applicability determinations, operating permits, risk assessments, and other applications. The results of the CAP work were published as API Publication 4723, *Refinery Stream Speciation* [1].

The refinery stream speciation profiles presented in API 4723 were developed from available stream sampling data from participating PERF companies. Most of these data were collected in the 1980s and 1990s. The speciation profiles were based on analyses from 31 refineries, over 20 different process units, and 65 refinery process streams. One of the most significant observations was the wide range of the reported concentrations for some of the chemical species. Since process units usually monitor and control operations based on physical properties such as temperature or pressure, the range of compositions in a specific process stream may vary widely depending on the product slate, processing severity, and other factors.

Since the publication of API 4723 in 2002, new regulatory requirements have resulted in many changes in refinery processes that may have altered process stream compositions. Changing feedstocks, new process additives, and new catalysts may also have affected the concentrations of chemical species present in specific process streams.

Based on an assessment of the range and depth of more recent stream speciation data, PERF elected to update the stream speciation profiles using more recent composition sampling. The updated profiles are provided in this report. PERF members believe that the newer data are more representative due to improved sampling and analytical techniques and that these newer analyses better reflect changes in refinery operations over recent years.

A large database of records was collated for the current study, representing information from 25 refineries. Each record includes the annual average concentration of a chemical species in a given process stream for a given refinery. For this report, *dataset* refers to a collection of records for a given process stream and chemical species combination.

The original study reported on 24 chemical species and the current study provides data on 89 species. The original study reported on 65 refinery process streams and the current project provides data on 68 process streams.

The process units and streams considered are shown in Table 1.

This report is divided into a number of sections that describe the data collection and analysis procedures, contain tables of stream compositions, and provide a graphical presentation of the data.

Section 2 provides a summary of the data gathering methodology. It contains a list of the process units and streams, and the chemical species included in the study.

Section 3 provides the data analysis methodology, including summaries of data quality and quantity.