

# PAMSGRAM

**Volume 5**  
March 4, 1997

*This PAMSGRAM is a FAXED notice for State and Local air pollution control agencies which highlights issues meriting attention by PAMS monitoring staff.*

## **NEW PARAMETER CODE ESTABLISHED FOR THE SUM OF THE PAMS TARGET COMPOUNDS**

### **Summary:**

The PAMS Technical Assistance Document (TAD, currently in draft form as Appendix N of the *Photochemical Assessment Monitoring Stations Implementation Manual*) calls for the reporting of "Total Non-Methane Organic Compounds" or TNMOC. However, the abbreviation associated with this compound in AIRS was "TNMHC" (AIRS Parameter 43102), which actually stands for total non-methane hydrocarbons, a subset of TNMOC. This has caused some confusion in what should be reported. In addition, some sites are reporting the sum of PAMS target compounds only, a subset of TNMHC. To provide more comparable and useful numbers, specific changes to AIRS and recommendations to agencies are provided below. A more in-depth discussion follows of the fundamental differences between TNMOC, TNMHC, and PAMS hydrocarbons and the associated analysis and reporting methods.

### **Changes to AIRS:**

- 1) The abbreviation for the parameter code of 43102 has been changed from TNMHC to TNMOC.
- 2) Three sets of method codes have been assigned to the new parameter 43102.
  - Method Code 200 - Describes the sum of all C2 through C12 data following analysis by gas chromatography with flame ionization detection (GC/FID).
  - Method Code 012 - Describes the sum of data gathered by preconcentration direct flame ionization detection (PDFID). This is the TO-12 EPA-approved method which includes not only the sum of C2 through C12 data, but also any compounds larger than C12 that make it through to the detector.
  - Method Code 300 - Describes data collected by methods other than those involving separation by gas chromatography.
- 3) A new parameter, PAMHC (AIRS Parameter 43000) has been created to describe the sum of the PAMS target compounds only.

These changes were presented to the PAMS Data Management Group, were approved, and have been implemented in the Geo-Common Subsystem. The TAD will be revised to include both parameters 43000 and 43102 on the PAMS Target Compound List.

### **Recommendations:**

1. Agencies should begin reporting **both** of the new parameter codes (43000 and 43102) and using the new method codes (200, 012, and 300) no later than June 1, 1997, the official start of the PAMS monitoring season in most areas.
2. Agencies should attempt to revise PAMS data previously entered to ensure comparability of data year-to-year.

### **Discussion:**

● **TNMOC** is defined in the TAD as the unspiciated total concentration of VOC (C2 through C12) in ambient air as determined by “summation of peaks” from GC/FID analysis, expressed in ppbC (**AIRS method code 200**). The value of TNMOC is determined in three steps:

Step (1) - Sum the area counts for all peaks ( $\Sigma$ ), both target compound peaks and all other peaks, with GC retention times inclusive of ethylene (or acetylene if it elutes first) through dodecane.

Step (2) - Divide the result of Step (1) by the area counts resulting from analysis of 1 ppbv of propane ( $\epsilon$ ), to obtain  $\Sigma/\epsilon$ . When compounds are separated on two columns leading to two FIDs, both propane and benzene standards (propane for the column intended to separate light VOC and benzene for the column intended to separate the higher molecular weight compounds) must be used.

Step (3) - Multiply by the factor 3 (number of carbon atoms in propane) or by the factor 6 (number of carbon atoms in benzene) as appropriate.

Step (4) - Obtain and record the TNMOC in ppbC, e.g.,  $\text{ppbC} = 3 (\Sigma/\epsilon)$ .

The actual meaning of the term TNMOC implies the inclusion of compounds beyond C12. The restriction to C2 through C12 compounds appears to have originated in the data handling protocol during the 1990 Atlanta Study. Hence, **the definition of TNMOC is an operational one, specific to PAMS.**

● **AIRS method code 012.** The TAD also states that the PDFID method (TO-12) can be used. In this method, the carbon-containing compounds from an atmospheric sample are concentrated by condensation/adsorption and then thermally desorbed directly into a flame ionization detector. This results in an overall detector response expressed in area counts. The detector response is calibrated using a single compound of accurately known concentration, e.g. a NIST propane standard, to give a per-carbon response in area counts per ppbC. The PDFID signal is divided by this number to give a TNMOC response in ppbC.

Because of the inherent differences between the “sum of peaks” and PDFID approaches, they will not provide equivalent TNMOC results and should not be expected to be directly comparable. The flame chemistry is not generally known to be the same for the two approaches, i.e. one compound at a time vs. a batch of organic compounds. Also as noted above, the sum of peaks stops at C12; the PDFID does not. However, since the vapor pressure of carbon containing compounds decreases with increasing molecular weight, compounds above C12 are not expected to contribute significantly (more than a few percent) to the TNMOC.

Although the FID response factor (response per carbon atom), for each of the “sum of peaks” and PDFID approaches, is known to be approximately the same for many hydrocarbons including those on the PAMS target list, the FID will respond to all carbon-containing compounds. The FID response for the oxygenated organic compounds, and the nitrated organic compounds, etc. will have a lower per-carbon response than will hydrocarbons. As a result, TNMOC values will be the sum of responses from compounds having variable per carbon response factors. Hence mixtures of organic compounds having the same carbon count but different composition can give very different responses. As a result TNMOC is not a precisely defined parameter.

- **AIRS Method Code 300.** In addition to the method description in TO-12, other analytical methods are being used to obtain TNMOC. The monitors include automated, cyclical operating systems designed to concentrate the sample, remove water vapor and methane by separation on a GC conditioning column, and back-flush the sample to a FID detector directly (or through a convertor to obtain conversion of all carbon to a common denominator compound, e.g., methane). Given a specific method, the detector response should be calibrated using a single response factor derived from analysis of propane or benzene (these per-carbon responses should be approximately equal) so that these responses can be compared across all stations that are using this specific method.
- **TNMHC** stands for Total Non-Methane Hydrocarbons. The actual meaning of the term implies that all organic compounds that contain only hydrogen and carbon should be counted. To do this would require that a distinction be made by identifying the content of molecules in each peak. However, this cannot be done with a nonspecific detector (FID) such as that used in the PAMS.
- **PAMHC is the sum of PAMS Compounds.** One convenient subgroup of TNMHC for the PAMS sites is the sum of the PAMS target compound responses, hence the **new parameter PAMHC** (AIRS Parameter 43000). Some PAMS operators of autoGC systems are reporting the sum of PAMS target compounds response for TNMOC. One reason for this is that the report table for speciated analysis by GC/FID may only include a summation over the target compounds. The autoGC data processing unit has to be programmed to sum all peaks to report TNMOC.
- **Both PAMHC and TNMOC are valuable data components.** Their ratio of PAMHC/TNMOC, in the absence of complicating local sources, indicates the age of the air mass, i.e. lower values indicate the conversion of ozone precursors to carbon containing products of atmospheric chemistry.
- **THC** refers to Total Hydrocarbons; this is not a PAMS parameter code and is not included on the PAMS Target Compound List.

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## NEW “UNOFFICIAL PAMS” MONITOR TYPE CREATED

Many users of the PAMS data have found it difficult to retrieve data from some PAMS monitors. The easiest way to do this in theory is to select the PAMS monitor type [Monitor Type (MT) = P selects all of the PAMS monitors types (6, 7, 8)]. However, only about 25% of the currently-operating PAMS monitors have been designated as PAMS sites in AIRS. Because they have not met the AIRS criteria (all mandatory fields filled-in) and/or received specific site approval by OAQPS, they have not been formally designated as PAMS sites in AIRS. Consequently, data from these sites are not retrieved in reports that ask for PAMS data. The reason they have not been approved as PAMS sites is due to either a lack of documentation for the validity of the proposed PAMS site, the lack of supplied information on the AIRS monitor record, and/or the process of creating the 112+ monitor records (F1 and F2 transactions). Whatever the reason, few of the operating PAMS monitors are designated as such on AIRS.

In an attempt to allow individuals to download data from “PAMS sites” that have not been formally approved as official PAMS sites, we have created a new monitor type “U” (Unofficial PAMS Monitor Type). We are also creating a special monitor type code (“R” for PAMS & PAMS Under Review) for the standard batch retrievals selection screen that would select official and unofficial PAMS monitors. [deleted last sentence - is the R in place now?]

The way this would work is if the user placed the letter “R” in the monitor type field, the standard report would select the official PAMS monitor types (6, 7, 8), as well as the monitor type “U”. If the user places a “P” in the monitor type field of the selection screen on batch retrievals, only the official PAMS monitor types would be retrieved. In order to retrieve just the unofficial monitors from AQS, the user would place a “U” in the monitor type field of the standard batch retrieval selection screen.

In order for this convention to work, the AQS monitor records need to be revised to be consistent with this new convention. As you can see from the map, many of the affected PAMS states, have been busy changing appropriate monitor records to the new monitor type “U”. Please note that not all monitors at the PAMS sites are changing to “U”. The most notable exceptions are the specific criteria pollutants that are part of either the National Ambient Monitor Station (*NAMS*) network or part of the State/Local Ambient Monitoring Station (*SLAMS*) network. These monitors remain coded as “1” (*NAMS*) or “2” (*SLAMS*) and therefore, information on these specific criteria pollutants could not be retrieved using a “U” code.

If your state is collecting PAMS type of data and you would like to have existing AQS monitors changed to the new monitor type, please notify Michael Hamlin at (919) 541-5232 or E-Mail at hamlin.michael@epamail.epa.gov. If you are designating new sites and monitors that will be collecting PAMS type of data, please designate these new monitors with the new “U” monitor type code.