Quantitation, Detection and Measurement Precision of Organic Molecular Markers in Urban Particulate Matter

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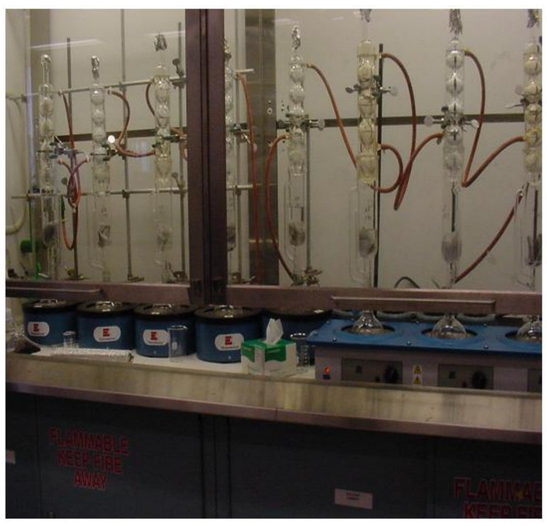
Abstract

This work focuses on improving the widely used analytical approach for qualifying organic molecular markers in airborne particulate matter (PM) by Gas Chromatography/Mass Spectrometry (GC/MS). The protocol employs detailed compound identification by ion trap mass spectrometry (GC/IT MS), five-point mass calibration for compound quantitation and estimates of measurement uncertainty for marker compounds in ambient particulate samples. This systematic procedure produces measurement precision for individual organic marker compounds. The precision is critical input to current source apportionment models. Particulate samples used in the method development were collected as PM10 in metropolitan Philadelphia area during 2000.

Sample Extraction and Preparation



4 hrs Soxhlet extraction

500 ml (1:1) acetone:CH_2Cl_2

Extract concentration

Kuderna-Danish appar. (5ml) N_2 gas (1ml)

Extract Split (1:1)

Neutral organics Acid+Neutral organics

Diazomethane synthesis

Conversion Acid+Neutral to methyl esters, dimethyl esters

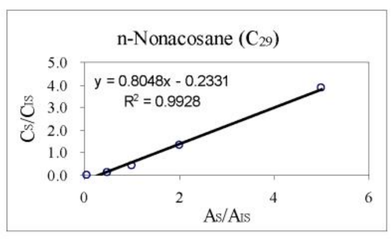
Ambient particulate matter sample

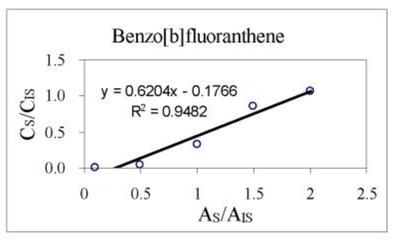
PM10 was collected for 24 hours from 1/20/00 – 2/6/00, 3/28/00 – 4/20/00, 7/31/00 – 8/12/00, and 10/16/00 – 11/2/00 at the City of Philadelphia's Air Management Service's North Broad Street site.

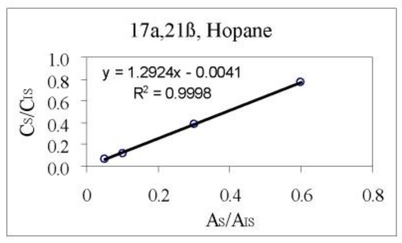
Five-Point Mass Calibration as a Quantitation Tool

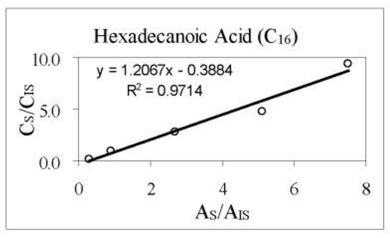
$$RRF = \frac{A_S}{A_{IS}} \times \frac{C_{IS}}{C_S}$$

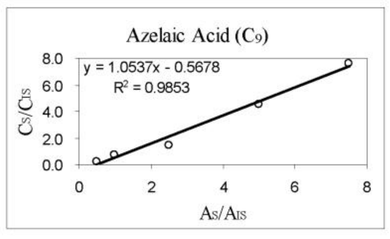
RRF is the relative response factor; A is integrated area expressed as area counts; C is concentration (μg/ml); subscript S is standard, IS is internal standard, X is the unknown compound.









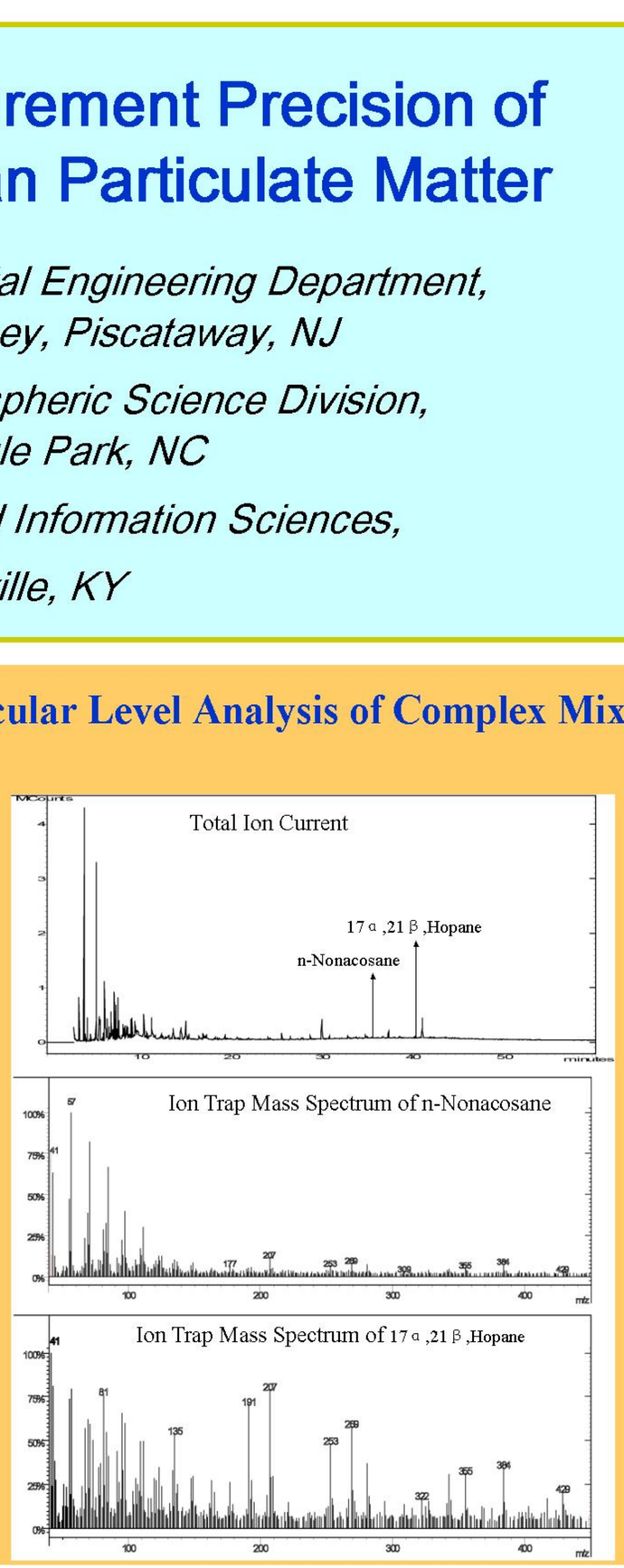


Calibration curves for most of the molecular markers are highly linear.
(R^2) > 0.97 for the *n*-alkanes (C25-C32)
(R^2) >0.9998 for the hopane (C27-C32)
(R^2) >0.95 for *n*-alkanoic acids (C10-C30)
(R^2) >0.97 for the dicarboxylic acids.
(R^2)>0.86 for PAH compounds (MW>252)

Reproducibility of Relative Response Factors Using Five-Point Calibration

Molecular Markers	Retention Time (minute)	RRF Nov, 2002	RRF Feb, 2003		%SD
n-Pentacosane (C25)	33.2	1.11	1.13		1.41
n-Hexacosane (C26)	35.1	1.03	0.99		2.83
n-Heptacosane (C27)	37.0	0.93	0.94		0.71
n-Octacosane (C28)	38.8	0.82	0.84		1.41
n-Nonacosane (C29)	40.6	0.81	0.81		0.00
n-Triacontane (C30)	42.3	0.80	0.86		4.24
n-Hentriacontane (C31)	44.0	0.52	0.57		3.54
n-Dotriacontane (C32)	45.9	0.22	0.28		4.24
benzo[b]fluoranthene	43.6	0.62	0.70		5.66
benzo[k]fluoranthene	43.7	0.70	0.65		3.54
benzo[e]pyrene	45.1	0.71	0.73		1.41
17α,21β,hopane	43.6	1.29	1.20		6.36
Dodecanoic acid (C12)	11.9	1.10	0.77		23.33
Palmitic acid (C16)	22.2	1.21	0.76		31.82
Tetracosanoic acid (C24)	37.6	0.61	0.32		20.51

Molecular Level Analysis of Complex Mixtures



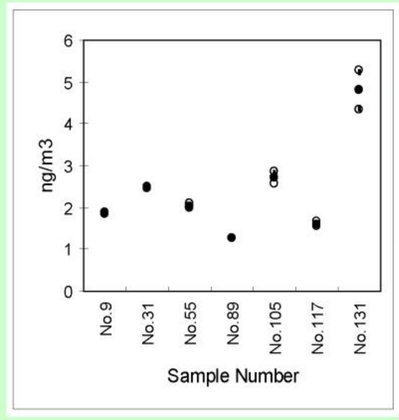
Why Precision Measurement is Needed?

Little information about the precision of these measurements has been provided specifically for the parts-per-billion determinations of single organic marker compounds in urban particular matter (PM). Such information is critical input to current source apportionment models since the uncertainty of analytical measurement itself is the primary quantifiable uncertainty in source receptor models. Measurement precision and bias can be used to evaluate analytical results of molecular marker abundance in urban PM10 samples, indicating the quality of the measurements and to what extent the measurements can be used reliably for policy and regulatory decisions.

Measurement Precision of Ambient PM Samples

17 α (H),21 β (H)-29-Norhopane (C29)

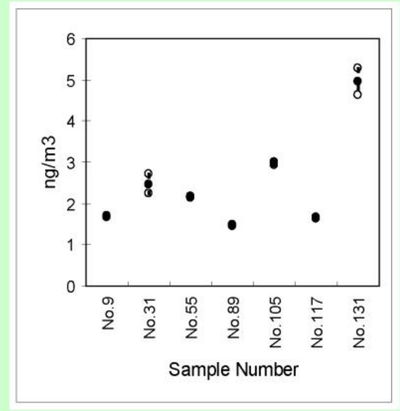
P=0.33, n=14



P ranges from 0.025 to 0.081 for all 9 hopanes and 8 alkanes

17 α (H),21 β (H)-Hopane (C30)

P=0.33, n=14



$$p = \frac{\sum_i (C_{i,ha} - C_{i,la})/C_{i,avg}}{n}$$

$C_{i,ha}$ and $C_{i,la}$ are the highest and lowest of the two duplicate analyses of concentration measurements expressed as (ng/m^3) for the same sample *i*, respectively. $C_{i,avg}$ is the average of the two duplicate measurements of sample *i*, and n is the total number of duplicate measurements taken.

Concluding Remarks

The use of five-point mass calibration allows measurement of organic marker compounds in ambient particulate matter over a wide range of concentrations. Highly reproducible relative response factors (RRFs) are determined, which are an important underlying factor for precise molecular tracer measurements. In this study the standard deviation for the five-point RRF calibrations vary less than 6.36% for the non-polar markers measured (n-alkanes, PAHs and hopanes) and 20.51% to 31.82% for polar markers (n-alkanoic acids and dicarboxylic acids). The calibrations are stable when determined 3 months apart. The precision of marker compounds analyses in urban particles from Philadelphia falls between 0.025 and 0.081based on the duplicate analyses of every tenth samples in this study.

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