

Standardizing GC-FID Measurement of Nonmethane Hydrocarbons in Air for International Intercomparison Using Retention Index and Effective Carbon Number Concept

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Abstract : Accurate measurements of ozone precursors are required to understand the process and extent of ozone formation in rural and urban areas. Nonmethane hydrocarbons (NMHCs) have been identified as important ozone precursors. Identification and quantification of NMHCs are difficult because of the large number present and the wide molecular weight range encountered in typical air samples. A major plan of the research team of the Climate and Air Quality Taiwan Station (CATs) was the measurement of atmospheric nonmethane hydrocarbons. An analytical method has been developed for the analysis of the individual nonmethane hydrocarbons in ambient air at ppb (v) and subppb(v) levels. The whole ambient air samples were collected in canisters and analyzed by GC-FID with Al₂O₃/KCl PLOT column. Our targeted for quantitative analysis 43 compounds that may be substantial contributors to ozone formation. The retention indices and molar response factors of some commercially available C₂ ~ C₁₀ hydrocarbons were determined and used to identify and quantify air samples. A quality assurance program was instituted to ensure that good measurements were made by participating in the International Nonmethane Hydrocarbon Intercomparison Experiments (NOMHICE).

Keywords : Nonmethane hydrocarbons, International intercomparison, Flame ionization detection, Al₂O₃/KCl PLOT column, Retention index, Molar response factor, Effective carbon number concept.

1. Introduction

The measurement of atmosphere nonmethane hydrocarbons (NMHCs) involves the analysis of extremely complicated components. Since the capacity for forming ozone of each component of NMHCs covers several orders of magnificence [1,2], quantitative data are important for the determination of ozone-forming in troposphere of nonmethane hydrocarbons. For simultaneous quantification of complex mixtures of nonmethane hydrocarbons, gas chromatography with flame ionization detection (GC-FID) is a powerful tool.

In survey the literature, there are two capillary columns which are usually used for separation complicated components of NMHCs. One is a J&W DB-1 capillary column and the other is a Chrompack Al₂O₃/KCl PLOT column [3-7]. The latter has a good resolved ability for light hydrocarbons when the GC oven temperature was started from only room temperature [7].

Relationships between the chromatographic retention and flame ionization detection relative response factors of C₂~C₁₀ nonmethane hydrocarbons (NMHCs) in Al₂O₃/KCl PLOT column and their structural and physico-chemical properties have been studied. The influence of volatility and carbon content of NMHCs on their relative response factors is also discussed. The effective carbon number of each component of NMHCs has been calculated. A series of retention indices and molar response factors of C₂ ~ C₁₀ NMHCs are established and applied to real air samples. This paper will further discuss the results we participated in the International Nonmethane Hydrocarbon Intercomparison Experiments (NOMHICE). These programs are sponsored by the National Center for Atmospheric Research (NCAR) of U.S.A..

2. Experimental

The apparatus included a sampling device (canister) and an analysis device, which were combined with a

preconcentration unit, a cryofocusing unit and a gas chromatograph (GC) unit (detailed in [7]). Samples were preconcentrated in a U-tube (20 cm length, 1/4" o.d.) filled with 40-60 mesh glass beads and immersed in liquid nitrogen. Trapped samples were desorbed for 3 min at approximately 100°C. The total amount of sample was determined by measuring the pressure difference in a previously evacuated known fixed reservoir using a baratron pressure gauge (MKS model 122A, U.S.A.). The Chromatographic study was carried out using a Hewlett-Packard (Palo Alto, CA, U.S.A.) model 5890 Series II Gas Chromatograph with flame ionization detection (FID). All of the signal-acquisition, storage, plotting and peak-area calculations were managed by a HP 3365 Chemstation software package installed in a PC AT microcomputer. A PLOT fused-silica capillary column coated with Al₂O₃/KCl passivated with KCl (Chrompack, Holland) was used. The operating conditions and column characteristics are given in Table I. The standard compounds used are listed in Table II and obtained from Scott Specialty gases (San Bernardino, CA, U.S.A.) as CRM standards. Chosen these compounds were also based on their effectiveness in question in forming ozone.

Table I Chromatographic operating conditions

Stationary phase	Al ₂ O ₃ /KCl
Film thickness (μm)	10
Column length (m)	50
Column inside diameter (mm)	0.53
Preconcentration conditional	Liq. N ₂ Cold Trap
Cryofocusing temperature (°C)	-175 to -180
Desorption temperature (°C)	150
Detector : FID, temperature (°C)	250
Burning gas flow rate	
Air (mL/min)	300
Hydrogen (mL/min)	30
Carrier gas (N ₂) flow-rate (mL min ⁻¹)	6
Initial time (min)	5
Temperature programming rate	
from 33 to 200 °C (°C min ⁻¹)	5

Table II Target compounds that can be analyzed by an Al₂O₃/KCl PLOT column .

ethane	2,2-dimethylbutane
ethene	methylcyclopentane
propane	1-butyne
propene	cyclohexane
isobutane	2-methylpentane
acetylene	3-methylpentane
n-butane	n-hexane
trans-2-butene	4-methyl-1-pentene
1-butene	2-methyl-1-pentene
isobutene	1-hexene
cis-2-butene	methylcyclohexane
2,2-dimethylpropane	n-heptane
cyclopentane	benzene
2-methylbutane	n-octane
propyne	toluene
n-pentane	n-nonane
1,3-butadiene	ethylbenzene
3-methyl-1-butene	m-xylene
1-pentene	p-xylene
2-methyl-1-butene	o-xylene
2-butyne	n-decane

The samples of NOMHICE were first analyzed by NCAR to ensure integrity and then shipped to participating laboratories. The participant laboratories were asked to perform canister analyses as quickly as possible using their existing techniques and then to return the canister with a sufficient amount of sample to permit reanalysis at NCAR. The reanalysis was done to determined sample integrity over the time of the experiment.

3. Results and Discussion

3.1 Gas-chromatographic qualitative analysis using retention index

An Al₂O₃/KCl PLOT column was found to have good resolution for light hydrocarbons when GC oven temperature was started from only room temperature. Since different laboratories used various conditions of

the temperature-programmed range, the rate of the oven temperature increase as well as the rate of carried gas, it is expected that they would obtain different retention times for each eluent. However, the retention index of each eluent between the various laboratories was remarkably close and consistent [7]. Retention index was calculated by using follow formula:

$$R.I. = \left(\frac{\log(t_R)_x - \log(t_R)_n}{\log(t_R)_{n+1} - \log(t_R)_n} + n \right) \times 100 \quad \text{Eq. 1}$$

Where (t_R)_x is the retention time of unknown, (t_R)_n and (t_R)_{n+1} are the retention time of normal alkane of n and n+1 carbon number. Figure 1 and Figure 2 show the retention indices versus carbon number of various groups of NMHCs. Comparison n-alkanes with other hydrocarbons of the same carbon number finds that the branch alkanes have lower retention indices. However unsaturated hydrocarbons such as alkenes, alkynes and aromatic hydrocarbons have higher retention indices than n-alkanes. It is worth noting that the retention indices of aromatic hydrocarbons are extraordinary higher than n-alkanes. This situation is due to the strong interaction between the aromatic hydrocarbons and stationary phase of Al₂O₃/KCl PLOT column.

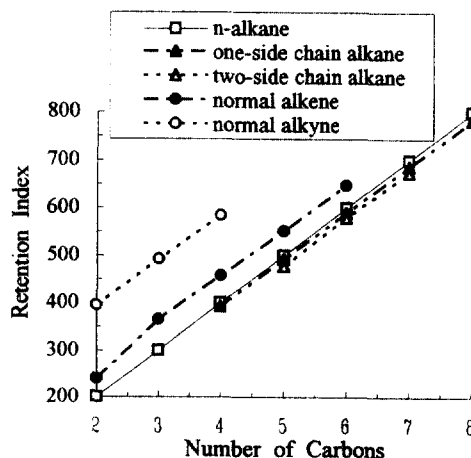


Fig. 1 R.I. versus carbon number for various groups of hydrocarbons

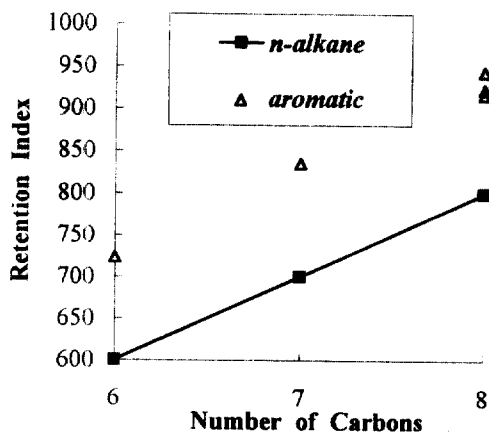


Fig. 2 R.I. versus carbon number for n-alkane and aromatic hydrocarbons

3.2 Quantitative analysis using relative response factors and effective carbon numbers

Obviously the response factors determined here will be affected not only by the detector and injection technique used, but also by the human factor, technique, operating conditions and characteristics of the gas chromatograph and column used. The FID relative response factors (RRF) obtained here for various compounds, using as reference compound normal pentane. The relative response factor of a compound *i* in relative to a reference compound *r* will be defined by:

$$RRF_i = \frac{A_r M_i}{M_r A_i} \quad \text{Eq. 2}$$

Where *A* and *M* are peak-area counts and weight of the compounds, respectively. This equation is based on a response factor of 1.0 for the reference component. From this definition, it is clear that compounds with a response lower (higher) than that of the reference compound show their RRF greater (less) than 1. The reciprocal of the relative response factor is the relative sensitivity of the FID to equal weights of the component and standard. As defined by Equation 2, a response

factor greater than 1.0 means that the detector is less sensitive to the component than to the reference material and thus the observed area must be multiplied by a number greater than 1.0 to give the same corrected area per unit weight for the component and the reference compound.

The molar Response Factor (Molar R.F.) of a compound *i* in relative to a reference compound *r* was calculated by using follow formula:

$$\text{Molar R.F.} = \frac{MW_i \times 500}{MW_r \times RRF_i} \quad \text{Eq. 3}$$

Where MW_i and MW_r are the molecular weight of the compound *i* and reference *r*, respectively. The effective number (ECN) of a compound *i* in relative to a reference compound *r* (n-pentane) was calculated by relative response factor and molecular weight as follow formula.

$$ECN_i = \frac{MW_i \times ECN_r}{MW_r \times RRF_i} \quad \text{Eq. 4}$$

Since ECN_r is simply the carbon number of hydrocarbon, the ECN_r is 5 in this study. Base on the above definition, it is clear that the ECN also can be calculated by the Molar R.F. dividing 100.

The small values of the relative standard deviation R.S.D. (< 3%), obtained in the determination of the RRF values are notable except nonane and decane. These show the high reproducibility of the chromatographic run obtained under the conditions applied for $C_2 \sim C_8$ non-methane hydrocarbons. Figure 3 presents the relative response factors versus carbon numbers in graph form for six of hydrocarbon classes studied. Figure 4 is the plot of effective carbon numbers versus the actual number of carbons. In generally accepted that, if entire amount of solute injected reaches the flame ionization detector, the

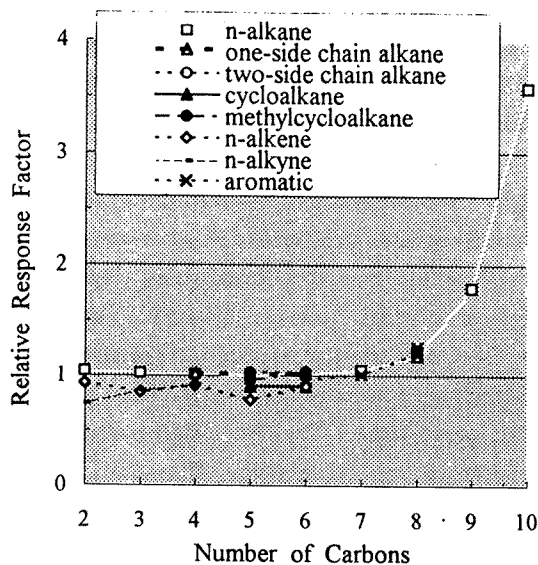


Fig. 3 Relative Response Factor versus carbon number for various groups of hydrocarbons

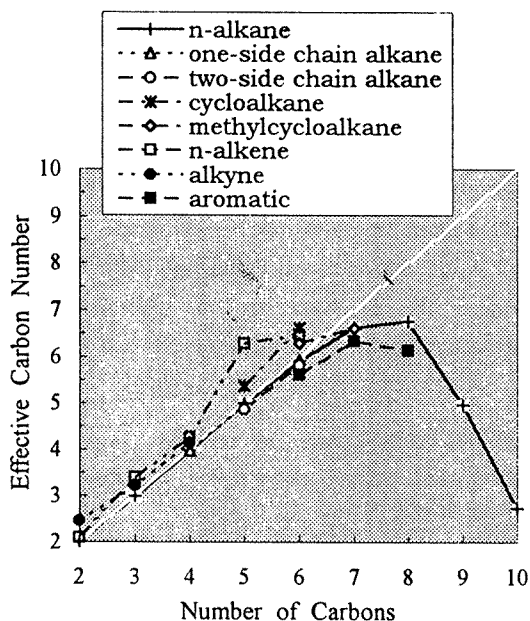


Fig. 4 ECN versus carbon number for various groups of hydrocarbons.

response factor will theoretically only be a function of the carbon content of each compound [8]. However, the normal alkanes (> C7) regardless of their carbon

content, show a decreasing response (and for that reason the RRF increase) as the boiling point increase. This situation is quite obvious for high molecular weight of hydrocarbons such as nonane and decane (Figure 3). It can be clear observed from Figure 4 that the experimental measured molar response factors of normal alkanes (< C7) are close to their expected values of effective carbon number (adoption of 100 responses units for carbon).

The response is not exactly the same for alkane isomers with the same carbon content. The branch alkanes show an FID response lower (and higher RRF) than their straight chain alkanes. The ECN for all methyl-substituted alkanes are less than the actual carbon numbers of molecules. Comparison response factors between side chain alkanes shows that two side chain has a smaller response (and a higher RRF) than one side chain. It is worth noting that the peaks due to 2-methylpentane and 3-methylpentane were partial overlap under the running conditions of this GC analysis system. The resolution of 2-methylpentane and 3-methylpentane is 1.0 and the overlap is 4%. Comparing the typical differences between the same alkanes of the corresponding straight- and branched-chain alkanes of the characteristic role of isopropyl radical is obvious. Since free radicals are more stable if they are more highly substituted, the order of stability of free radical is tertiary, secondary and primary. The strong electron stability property of $(CH_3)_2CH$ radical could lead to its preferential formation and its resistance against scission into single carbon atoms in the flame [9]. Above reason causes the higher relative response factors and the lower effective carbon numbers of branched-chain alkanes than their straight-chain alkanes.

The four cycloalkanes have near the same carbon content and higher than their relative n-alkanes. The cycloalkanes show higher responses and boiling points than relative n-alkanes. Moreover, the ECN of the cycloalkanes show higher than their expected values except methylcyclohexane.

All alkenes (the same as cycloalkane) have near the same carbon contents and higher than their relative normal alkanes. Moreover, comparison response factors of alkenes with their relative normal alkanes shows that all alkenes have a higher response than their relative normal alkanes. In the isomers of alkenes, we can find that the normal alkene has the highest response. The branch hydrocarbons have more stability than normal hydrocarbons cause their lower responses of flame ionization detection. All olefinic compounds have higher ECN than the carbon number of the molecular except 1,3-butadiene and methyl-substituted pentenes. The normal olefines have more extra contribution to ECN than other isomers. For example, n-pentene has an ECN of 6.28 about 1.28 carbon extra contribution to ECN. From these experimental results, it is clear that the olefinic compound has a positive contribution to ECN and the methyl-substituted compound has a negative contribution to ECN. The balance of these two effects decides whether the experimental ECN is higher or lower than the carbon number of the molecule.

The alkynes have a higher carbon content than alkenes and alkanes and decreasing as molecular weight increase. The relative response factors of alkynes are close to their relative alkenes, of course higher than their relative alkanes. However the acetylene has a higher response than ethene and has the highest response of all hydrocarbons in this study. The acetylenic hydrocarbons have a higher ECN than the carbon number of the molecule. The simplest acetylenic hydrocarbon (acetylene) has 0.5 carbon extra contribution to ECN. However other acetylenic compounds have about 0.2 carbon extra contribution to ECN.

Aromatic hydrocarbons show higher carbon contents and boiling points than their relative n-alkanes and their carbon contents decrease as molecular weight increase. Benzene and toluene have a lower relative response factor than hexane and heptane respectively. However ethylbenzene and xylene have higher relative response factors than their relative normal alkane (normal octane).

The ECN for all aromatic compounds in this study is less than the carbon number of the molecule and the difference in ECN increases as the molecular weight and boiling point of these aromatic compounds increase.

3.3 The International Nonmethane Hydrocarbon Intercomparison Experiments

The International Nonmethane Hydrocarbon Intercomparison Experiments (NOMHICE) are run by the National Center for Atmospheric Research (NCAR, Atmospheric Chemistry Division, U.S.A.). There are four stages from 1991 to 1994. The purposes of these comparison tests are reliability of standard, ability to separated, identify and quantify the amounts of individual components, analysis real whole-air sample and analysis clear air from aircraft.

Test 1

The first phase of NOMHICE program was held in December of 1991. The objective of this comparison test was that evaluated the quantitative accuracy of the participant laboratories through analysis of a simple two-component standard of known composition (n-butane and benzene) and unknown concentration. NCAR ordered and obtained standard mixtures from the National Institutes of Standards and Technology (NIST). NIST prepared the standards via the microgravimetric technique followed by dilution to obtained the final

Table III The results of the first international hydrocarbon intercomparison experiment in December of 1991.

Canister Number	21427 A	21467 C
n-butane (ppbv)		
NIST ^a	7.92	8.99
Our Lab.	7.1 ± 0.5	7.8 ± 0.5
benzene (ppbv)		
Our Lab.	8.0 ± 0.6	8.3 ± 1.1

^a: NIST - National Institutes of Standards and Technology

concentrations (ppb mole/mole) [10]. Table III shows the results of this test. Comparison our results of n-butane with NIST by using Student's t test finds that there is no significant difference in statistics. There was a slight adsorption of benzene onto the canister walls under the canister conditioning protocol employed. We can be assured that this will not be a problem in phase 2 (19 components mix) under the new canister conditioning protocol.

Test 2

The second phase of NOMHICE program was held in October of 1992. Each sample had a 16 component standard mixture. It was distributed as an unknown (composition and concentration). The participating laboratories must report the major peaks found in their chromatograms and identify and quantify them. Thirteen compounds were precisely identified by using the retention index (R.I.) values and retention time (R.T.) values of alkanes as the internal standards [7]; that is, ethane, ethene, propane, propene, isobutane, acetylene, 1-butene, isopentane, n-pentane, n-hexane, isoprene, benzene and toluene. However oxylene, α -piene and 1,2,4-trimethyl benzene were missed in this comparison test. Figure 5 is a plot of relative response factor

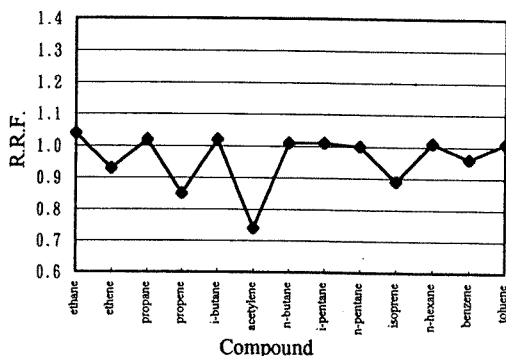


Fig. 5 Relative response factor (RRF) of the FID detector versus compound for the second NOMHICE sample. An HP 5890 Series II GC was used with an Al₂O₃/KCl 50 m, 10-micron film thickness column installed.

(RRF), with respect to n-pentane, for the 13 compounds in this comparison test. The RRF for most hydrocarbons are near one except acetylene, propene and isoprene. Acetylene has an anomalously high response and this situation is the same as reports in the literature [10]. Figure 6 illustrates the results for this comparison test. Lower values were obtained compared to the NIST values for all of the analytes. They were 18% lower except ethane.

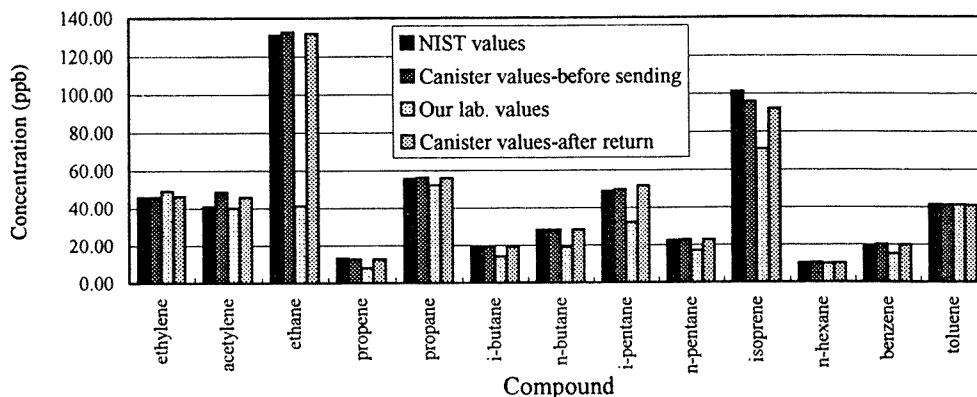


Fig. 6 The report information supplied to our laboratory for the second phase of the NOMHICE. Our lab. values can be compared to NIST values, as well as to NCAR values obtained before sending out canister and after canister return.

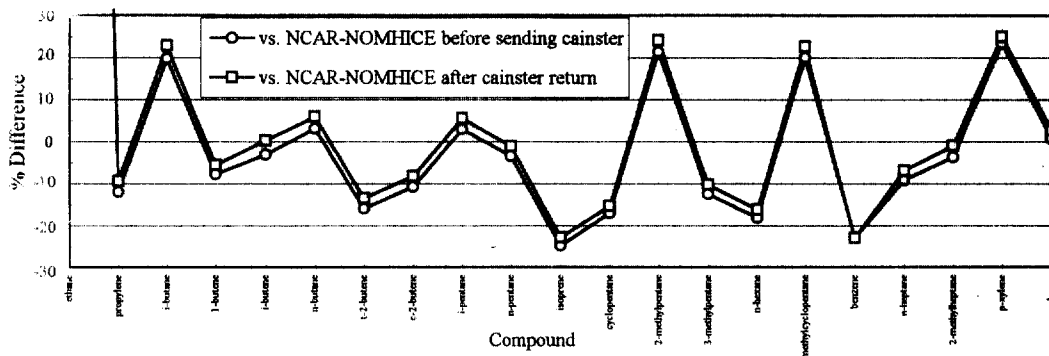


Fig. 7 Percentage deviation vs. NCAR before sending canister and after canister return for the third of the NOMHICE.

Test 3

The third phase of NOMHICE was held in November of 1994. The sample was prepared by Scott Marrin Laboratory and contained 60 hydrocarbons ranging from C₂ to C₁₁. Since this mixture was not a gravimetric standard (unlike first two experiments) the reference values for the intercomparison are determined from intercalibrations among three independent laboratories; EPA (Bill Lonneman), NCAR-NOMHICE (Eric Apel) and a third lab. A total of 55 peaks appeared in our chromatogram. We identified and quantified correctly 49 components C₂ to C₁₀ hydrocarbon for this test. For most compounds, the difference was satisfactory. However, for ethane, the difference was larger. The larger uncertainty of ethane was found to inappropriately control the temperature of the cryotrap. The cryotrap temperature (e.g. 77 K) must be assured by an appropriate constant trapping time during each analytical run.

Conclusions

Finally, as a result of our systematic study, we completed the knowledge and validity of the R.I. and ECN concept for NMHC. We apply them successfully in the NOMHICE and real ambient air samples. By participating in NOMHICE can enhance the reliability of measured data in ambient air.

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