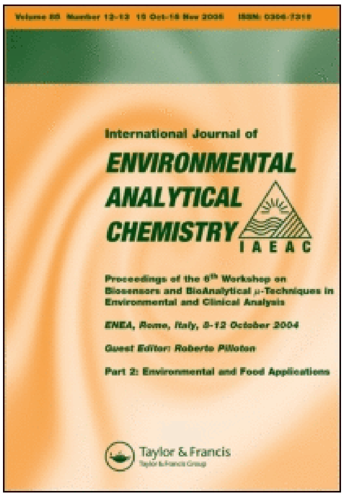
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Comparison of Gas Chromatography and Liquid Chromatography Methods for Measuring Low Levels of Cyclohexanone in Air

E. Grosjean[a]; D. Grosjean[a]
[a] DGA, Inc., Ventura, CA, USA

To cite this Article Grosjean, E. and Grosjean, D.(1996) 'Comparison of Gas Chromatography and Liquid Chromatography Methods for Measuring Low Levels of Cyclohexanone in Air', International Journal of Environmental Analytical Chemistry, 62: 4, 311 — 321

To link to this Article: DOI: 10.1080/03067319608026251

URL: http://dx.doi.org/10.1080/03067319608026251

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem., Vol. 62, pp. 311–321
Reprints available directly from the publisher
Photocopying permitted by license only

© 1996 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

COMPARISON OF GAS CHROMATOGRAPHY AND LIQUID CHROMATOGRAPHY METHODS FOR MEASURING LOW LEVELS OF CYCLOHEXANONE IN AIR

E. GROSJEAN and D. GROSJEAN

DGA, Inc., 4526 Telephone Road, Suite 205, Ventura, CA 93003, USA

(Received, 23 May 1995; in final form, 30 August 1995)

Downloaded At: 20:49 17 January 2011

Parts per billion (ppb, μL/L) levels of cyclohexanone in air have been measured using two methods, gas chromatography with flame ionization detection following collection on Tenax cartridges (GC-FID) and liquid chromatography with uv-visible detection following collection on DNPH-coated C_{18} cartridges (DNPH-LC). The comparison involved measurements of cyclohexanone in laboratory experiments carried out with ozone-alkene-cyclohexane mixtures in dry air (RH = 3–7%). Data for experiments with thirteen alkenes yielded the following relation:

$$\text{CYH (DNPH-LC)} = (0.504 \pm 0.031)\ \text{CYH (GC-FID)} + (7.44 \pm 3.60),\ n = 99,\ R = 0.857$$

where CYH is the cyclohexanone concentration in μL/L. Deleting data for three alkenes for reasons discussed in the text resulted in a better correlation (R = 0.954, n= 75) with a slightly higher slope of 0.534 ± 0.020. These results indicate that the two methods agree within ca. ± 25 percent of their mean value and that the average (GC-FID/DNPH-LC) concentration ratio is ca. a factor of two. Three possible causes for the observed difference between the two methods were examined using the DNPH-LC method. Co-located samples collected using two sampling lines (line A vs. line B for each pair) were well correlated (slope = 1.01 ± 0.05, R = 0.974, n= 24). Co-located samples (high value vs. low value for each pair) were also well correlated (slope = 1.03 ± 0.03, R = 0.989, n = 24). Measured (DNPH-LC method) and nominal concentrations in control experiments with cyclohexanone in dry air (no ozone or cyclohexane present) were in good agreement (slope = 0.987 ± 0.021, R = 0.999, n = 8). These results show that sampling line-specific effects, overall method precision and air humidity effect on DNPH-coated C_{18} cartridge collection efficiency did not account for the observed difference between GC-FID and DNPH-LC measurements.

KEY WORD: Cyclohexanone, air, GC, HPLC.

INTRODUCTION

As part of recent studies of the gas phase reaction of ozone with alkenes, two series of experiments have been carried out at the Statewide Air Pollution Research Center (SAPRC), U. C. Riverside[1-3]. These experiments, carried out in dry air (RH = 3–7%), involved mixtures of alkene and ozone, with sufficient cyclohexane added to scavenge the hydroxyl radical which forms as a product of the alkene-ozone reaction[1,2]. The reaction of OH with cyclohexane yields cyclohexanone, cyclohexanol and other products[1,2]. In these alkene-ozone-cyclohexane experiments, cyclohexanone was measured using two methods, gas chromatogaphy with flame ionization detection following sample collection on Tenax cartridges (SAPRC group, hereafter GC-FID method) and liquid chromatography with ultraviolet detection following sample collection on DNPH-coated C_{18} cartridges (our group, hereafter DNPH-LC method). The method comparison was carried out in an "after the fact" mode, with the two groups exchanging data at the completion of the first and second series of experiments, respectively. The two series of experiments, carried out some two years apart and with different alkenes, involved essentially identical experimental protocols.

The objective of this report is to compare the results obtained using the two methods, GC-FID[1,2] and DNPH-LC[3–5], when sampling parts per billion (ppb, µL/L) levels of cyclohexanone in dry air. Comparisons of this type are important in the field of environmental analytical chemistry for two reasons. First, in spite of the importance of carbonyls in atmospheric chemistry and as indoor and outdoor air pollutants, few comparisons have been made of the several methods that can be employed to measure parts per billion levels of carbonyls in air. Comparisons carried out to date have focused on only one carbonyl, formaldehyde[6,7]. To our knowledge, no comparison of methods has been made for higher molecular weight carbonyls such as cyclohexanone. Second, cyclohexanone is of special interest since cyclohexane has been employed to scavenge OH in a number of recent studies of the ozone-alkene reaction[1–3]. In these studies, it is important to obtain accurate measurements of cyclohexanone in order to calculate the formation yield of OH[1,2] and to develop a better understanding of the ozone-alkene reaction mechanism[1–3].

Downloaded At: 20:49 17 January 2011

EXPERIMENTAL

The experimental protocol for the alkene-ozone-cyclohexane experiments has been described in detail elsewhere[1,2]. The GC-FID method, described in detail elsewhere[1,2], involved sampling of the reaction mixture using Tenax cartridges followed by thermal desorption of the cartridge and gas chromatography analysis with flame ionization detection. The DNPH-LC method, also described in detail elsewhere[3–5], involved sampling of the reaction mixture on C_{18} cartridges coated with 2,4-dinitrophenylhydrazine (DNPH). The sampling duration was 30–60 min. During the second series of experiments, co-located cartridge samples were collected for each alkene studied. This was done by connecting two sampling lines to a 3-way adaptor whose third outlet was connected to the reaction chamber. Cyclohexanone was measured as its DNPH derivative by liquid chromatography with uv-visible detection. Calibration involved the use of external standards, i.e. acetonitrile solutions of cyclohexanone-DNPH synthesized in the laboratory. An example of calibration curve is given in Figure 1. Linear least squares regression analysis of the data shown in Figure 1 yielded a slope, i.e. response factor, which was used to calculate the concentration of cyclohexanone in the samples collected in the alkene-ozone-cyclohexane experiments. The relative standard deviation on the response factor for cyclohexanone-DNPH, i.e. the regression line shown in Figure 1, was 0.98%, consistent with results for earlier calibrations[3–5]. Cyclohexanone-DNPH calibration standards were injected along with each batch of samples. Calibration audits, all indicating agreement within a few percent, have been previously carried out using commercially available carbonyl-DNPH standards[4]. The detection limit for cyclohexanone, calculated from the analytical detection limit[4] and the volume of air sampled, was 0.54 µL/L in 30 min. samples and was 0.27 µL/L in 60 min. samples.

Downloaded At: 20:49 17 January 2011

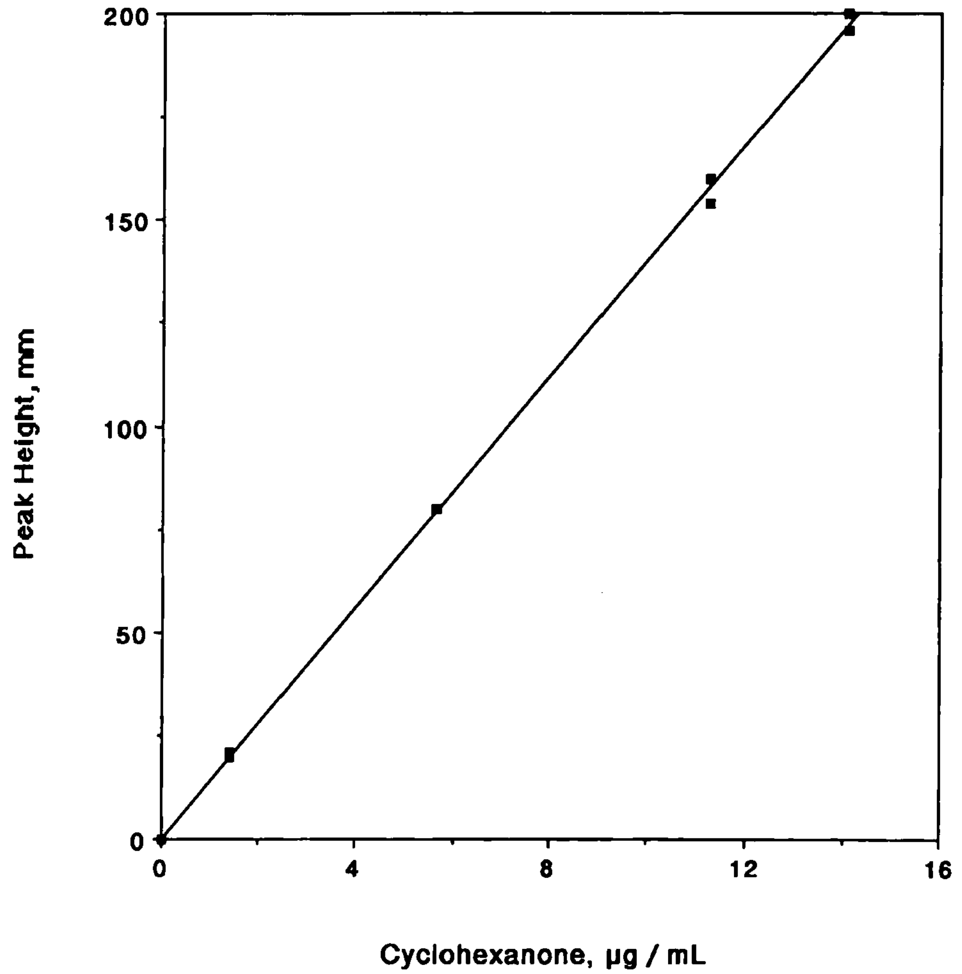


Figure 1 Calibration curve for cyclohexanone-DNPH. Linear least squares regression analysis of the data (peak height, mm, attenuation setting 7 vs. cyclohexanone-DNPH concentration, µg/mL as cyclohexanone) yielded a slope of (716 ± 7) × 10^{-4} (relative standard deviation = 0.98%) and a near-zero intercept of—(0.042 ± 0.085), R = 0.9997, n = 9.

RESULTS AND DISCUSSION

Statistical analysis of GC-FID vs. DNPH-LC cyclohexanone data

The first series of experiments involved seven alkenes: trans-2-butene, 1-butene, methyl propene (isobutene), 2-methyl-2-butene, 2-methyl-1-butene, 2,3-dimethyl-2-butene and 1,3-butadiene. The ranges of cyclohexanone concentrations measured were 5–214 µL/L (GC-FID method) and 3–125 µL/L (DNPH-LC method). A scatter plot of the data is shown in Figure 2. Least squares linear regression of the data (unit-weighted, not forced

Downloaded At: 20:49 17 January 2011

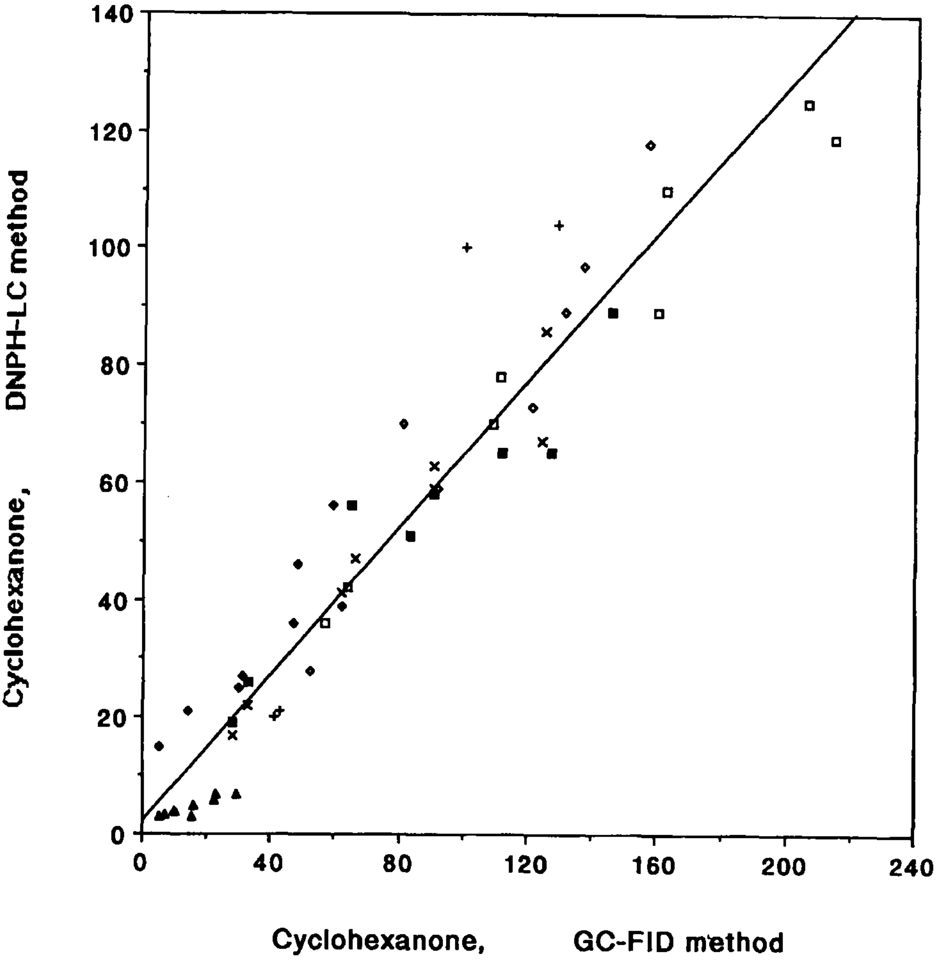


Figure 2 Scatter plot of cyclohexanone concentrations (in µL/L) measured by GC-FID and by DNPH-LC in ozone-alkene-cyclohexane experiments in dry air. The regression line shown is that given by equation 1. Also see equation 2 for regression parameters with data for 1,3-butadiene omitted. Symbols are + for trans-2-butene, ◆ for 1-butene, x for isobutene, ◇ for 2-methyl-2-butene, ■ for 2-methyl-1-butene, □ for 2,3-dimethyl-2-butene and ▲ for 1,3-butadiene.

through the origin) yielded the following relation, where CYH is the cyclohexanone concentration in units of ppbv:

$$\text{CYH (DNPH-LC)} = (0.627 \pm 0.024)\ \text{CYH (GC-FID)} + (2.27 \pm 2.27),$$
$$n = 51,\ R = 0.965 \qquad (1)$$

As can be seen in Figure 2, DNPH-LC data for the 1,3-butadiene experiments fall below the regression line, possibly due to the fact that ozone, which may react with carbonyl-DNPH derivatives[8], was still present at the time of sample collection. Excluding data from the 1,3-butadiene experiments yielded the following relation:

$$\text{CYH (DNPH-LC)} = (0.589 \pm 0.027)\ \text{CYH (GC-FID)} + (7.07 \pm 2.79),\quad n = 43,\ R = 0.958 \tag{2}$$

The second series of experiments involved six alkenes: 1-pentene, 1-hexene, 1-heptene, 2,3-dimethyl-1-butene, cyclopentene and 1-methylcyclohexene. In the 2,3-dimethyl-1-butene experiments, the DNPH derivative of cyclohexanone co-eluted with the DNPH derivative of another reaction product, 3-methyl-2-butanone. Cyclohexanone concentrations were calculated using two methods, (a) from the relative abundance of the cyclohexanone and 3-methyl-2-butanone MH peaks in the samples' chemical ionization mass spectra[4], and (b) by liquid chromatography analysis using a weaker eluent that resolved the two carbonyl-DNPH derivatives[4]. The cyclohexanone/(cyclohexanone + 3-methyl-2-butanone) concentration ratios obtained using the two methods were in good agreement, i.e. 0.245 from liquid chromatography analysis and 0.237 from mass spectrometry analysis. Thus, a ratio of 0.24 was employed to calculate the cyclohexanone concentrations in the 2,3-dimethyl-1-butene experiments.

The range of cyclohexanone concentrations measured in the second series of experiments was 19–313 μL/L (GC-FID method) and 13–167 μL/L (DNPH-LC method). A scatter plot of the data is shown in Figure 3. Linear least squares regression of the data (unit-weighted, not forced through the origin) yielded the following relation:

$$\text{CYH (DNPH-LC)} = (0.465 \pm 0.054)\ \text{CYH (GC-FID)} + (7.47 \pm 7.39),\quad n = 48,\ R = 0.788 \tag{3}$$

As can be seen in Figure 3, DNPH-LC data for cyclopentene fall below the regression line and DNPH-LC data for 2,3-dimethyl-1-butene fall above the regression line. For cyclopentene, this observation will require further investigation. For 2,3-dimethyl-1-butene, the estimation method described above may result in a systematic positive bias for the data obtained using DNPH-LC method. Excluding data for cyclopentene and for 2,3-dimethyl-1-butene, the relation becomes:

$$\text{CYH (DNPH-LC)} = (0.529 \pm 0.021)\ \text{CYH (GC-FID)} + (1.03 \pm 2.82),\quad n = 32,\ R = 0.977 \tag{4}$$

Although the two series of experiments were carried out ca. two years apart, the experimental protocols were essentially identical and it seems reasonable to pool the two sets of data together. Regression analysis of the entire data set yielded the following relation:

$$\text{CYH (DNPH-LC)} = (0.504 \pm 0.031)\ \text{CYH (GC-FID)} + (7.44 \pm 3.60),\quad n = 99,\ R = 0.857 \tag{5}$$

and, with 1,3-butadiene, cyclopentene and 2,3-dimethyl-1-butene excluded for the reasons discussed above:

$$\text{CYH (DNPH-LC)} = (0.534 \pm 0.020)\ \text{CYH (GC-FID)} + (7.01 \pm 2.30),\quad n = 75,\ R = 0.954 \tag{6}$$

Equations 1–6 include small positive intercepts ranging from 1 ± 3 to 7 ± 7 μL/L. This observation is consistent with data for samples collected in all alkene-ozone-cyclohexane

Downloaded At: 20:49 17 January 2011

Downloaded At: 20:49 17 January 2011

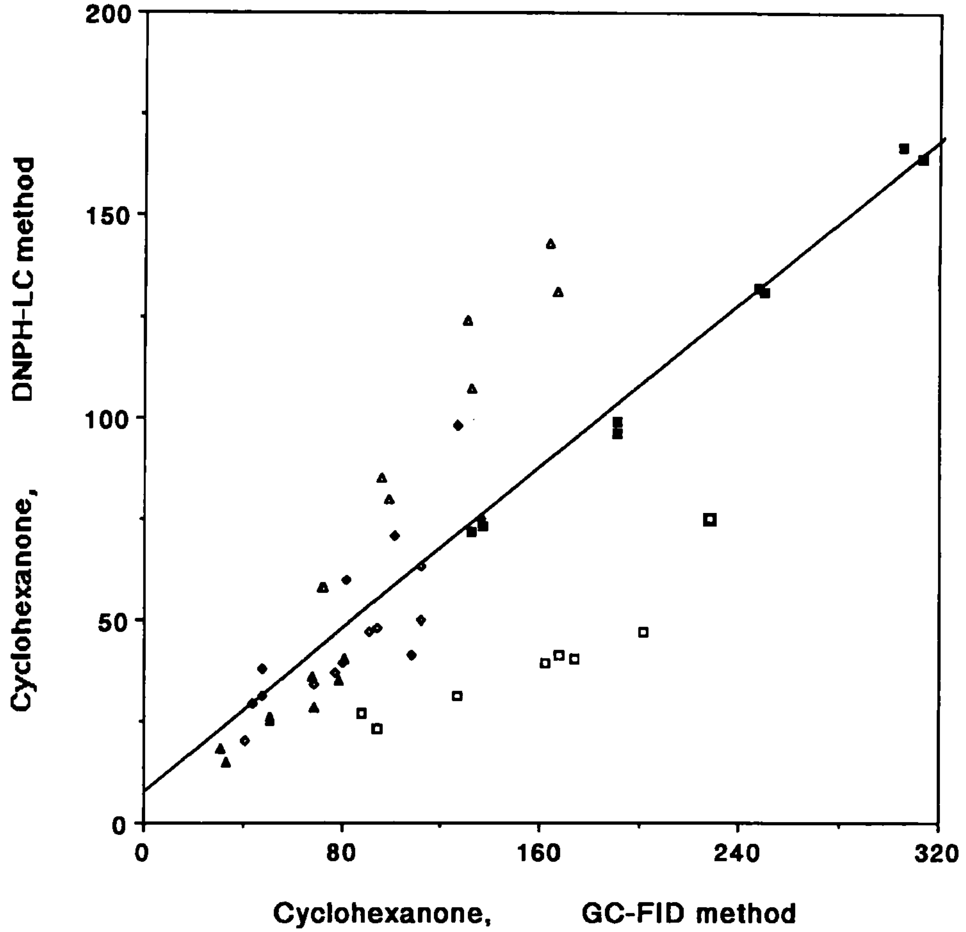


Figure 3 Scatter plot of cyclohexanone concentrations (in μL/L) measured by GC-FID and by DNPH-LC in ozone-alkene-cyclohexane experiments in dry air. The regression line shown is that given by equation 3. Also see equation 4 for regression parameters with data for cyclopentene and for 2,3-dimethyl-1-butene omitted. Symbols are ◆ for 1-pentene, ◇ for 1-hexene, ▲ for 1-heptene, □ for cyclopentene, ■ for 1-methylcyclopentene, and △ for 2,3-dimethyl-1-butene.

experiments prior to the addition of ozone (i.e., when only cyclohexane and the alkene were present). For these control samples, GC-FID measurements yielded cyclohexanone concentrations of 2–12 μL/L (average 4.8 μL/L). In contrast, no cyclohexanone was detected using the DNPH-LC method (detection limit = 0.54 μL/L). The cause of this apparent discrepancy is not known at the present time.

Possible causes for differences between methods

Equations 5 and 6 indicate that the two methods agreed within ± 24.8 percent (all data) or ± 23.3 percent (three alkenes excluded) of their mean, a reasonable result when measuring ppb levels of cyclohexanone in complex mixtures including hydrocarbons (alkene, cyclohexane) as well as a number of carbonyls and other reaction products. Equation 6 also indicates that, on the average, the radio (GC-FID/DNPH-LC) of the results is ca. a factor of two, i.e. 1.98 (all data) or 1.87 (with 3 alkenes excluded). Possible causes for differences between the two methods include (a) systematic errors associated with sampling lines, (b) poor precision of one or both of the measurement methods, and (c) poor performance of the DNPH-LC method in dry air, as suggested by results obtained for formaldehyde in dry and humid air[9]. These three possible causes for discrepancy are examined below for the DNPH-LC method. The results given in the following three sections show that these possible causes can be ruled out as major contributors to the difference between the two methods, leaving the difference of ca. a factor of two between the DNPH-LC and GC-FID methods unresolved at this time.

Effect of sampling line

Since Tenax cartridge and DNPH cartridge samples were collected on different sampling lines, it is pertinent to examine the data for possible differences caused by, among others, sampling line-specific losses of cyclohexanone. For this purpose, co-located DNPH-coated C_{18} cartridges were collected using two sampling lines, hereafter "line A" and "line B".

Linear regression of the results yielded the following relation:

$$\text{CYH (line B)} = (1.01 \pm 0.05)\ \text{CYH (line A)} - (1.3 \pm 3.5),\ n = 24,\ R = 0.974 \qquad (7)$$

where CTH is the cyclohexanone concentration, in units of μL/L, measured in co-located cartridges using sampling lines A and B, respectively. Results for other carbonyls, not shown, were entirely consistent with those for cyclohexanone. The results summarized in equation 7 show good agreement for co-located samples collected using sampling lines A and B (Figure 4). The results also indicate that sampling line-specific effects are not likely to account for the observed difference between the DNPH-LC and GC-FID methods when measuring cyclohexanone in dry air.

Overall method precision

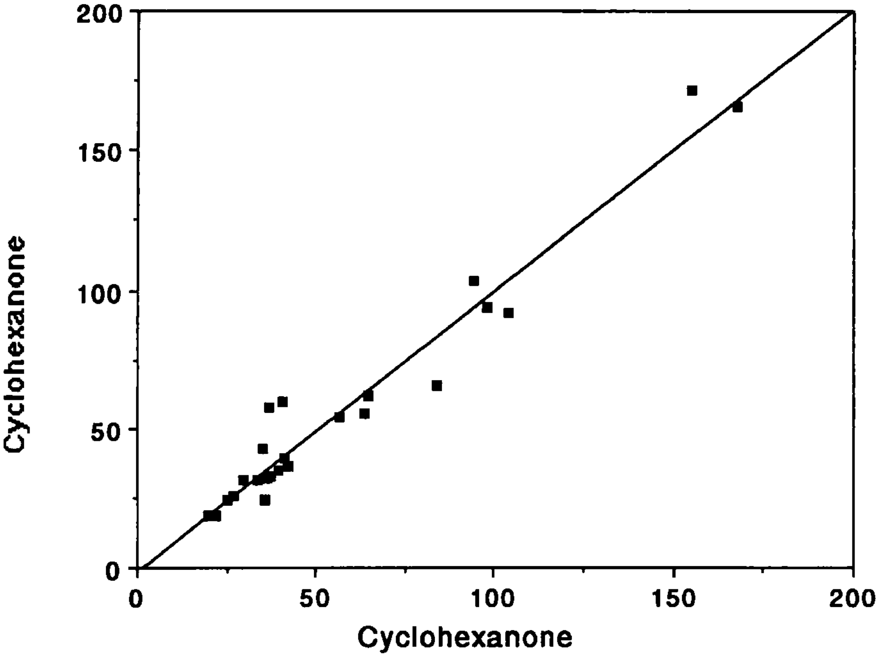
A measure of overall (sampling + analytical) method precision for the DNPH-LC method is given by results for co-located C_{18} cartridges. For all alkenes studied in the second series of experiments, co-located cartridges were collected and analyzed for cyclohexanone and other carbonyls. The results, i.e. comparison of high vs. low values for each pair of co-located samples irrespective of the sampling line employed, are shown in Figure 4. Linear least squares regression analysis of the results yielded the following relation:

$$\text{CYH ("high", ppb)} = (1.03 \pm 0.03)\ \text{CYH ("low", ppb)} + (5.1 \pm 2.2),\\ n = 24,\ R = 0.989 \qquad (8)$$

where "high" and "low" denote the two cyclohexanone concentrations for all pairs of co-located samples. The results summarized in equation 8 compare well to those given by equation 7 and indicate good agreement for co-located DNPH-coated C_{18} cartridges.

Downloaded At: 20:49 17 January 2011

Downloaded At: 20:49 17 January 2011



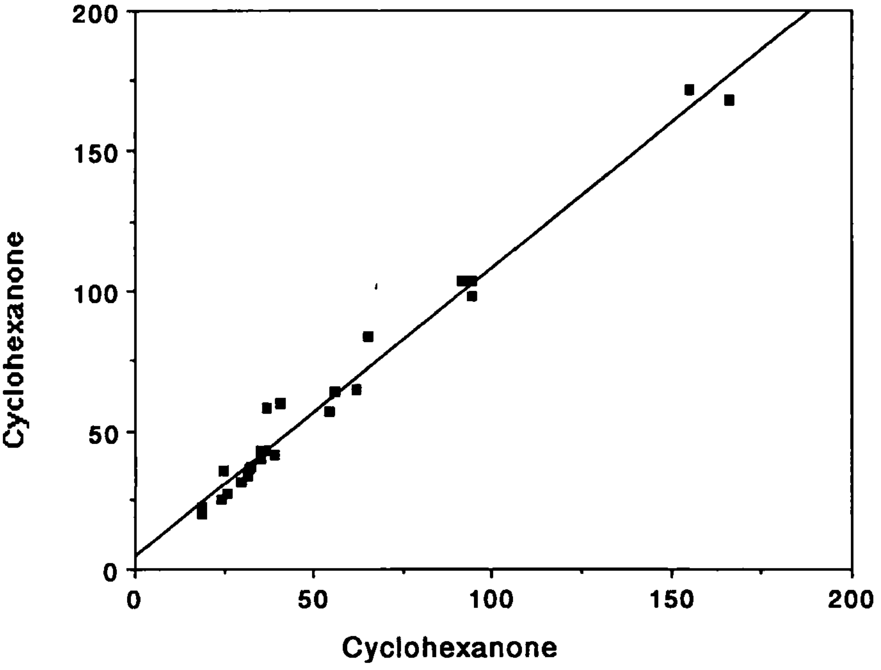


Figure 4 Scatter plots of cyclohexanone concentrations (in µL/L) (DNPH-LC method) for co-located samples in ozone-alkene-cyclohexane experiments carried out in dry air. Top: sampling line B vs. sampling line A, see equation 7. Bottom: high vs. low values, see equation 8.

Results for other carbonyls collected on co-located cartridges, not shown, were consistent with those for cyclohexanone. Overall, results for co-located samples show that the precision of the DNPH-LC method is not a major component of the observed difference between the DNPH-LC and GC-FID methods when measuring cyclohexanone in dry air.

DNPH cartridge measurements of cyclohexanone in dry air

We have recently completed a study of the performance of the DNPH-coated C_{18} cartridge when sampling carbonyls in dry air and in humid air[9]. The results of this study indicated comparable collection efficiencies for ketones in dry air and humid air but lower collection efficiency in dry air for several aldehydes, especially for formaldehyde[9]. Cyclohexanone was one of the fourteen carbonyls tested. Cyclohexanone formation yield ratios (humid air/dry air) averaged 0.85 ± 0.15 for eight alkenes and for cyclohexanone concentrations of 4–167 µL/L[9].

In addition, the collection efficiency of the DNPH-coated C_{18} cartridge for cyclohexanone in humid air was verified in two sets of experiments, one involving cyclohexanone in humid air, in which measured and nominal concentrations were in good agreement (measured/nominal concentration ratio = 1.00 ± 0.04, see Table 1), and the other involving measurements of cyclohexanone in humid air with DNPH cartridge (upstream)- DNPH impinger (downstream) sampling trains, in which no cyclohexanone could be detected in the downstream impinger[9].

Consistent with the above results are those of a third set of experiments, carried out in dry air, which indicated good agreement between measured and nominal (design) cyclohexanone concentrations (Table 1). For cyclohexanone in dry air, the ratio between measured and nominal concentrations was 0.96 ± 0.03 (n = 8). This ratio compares to that of 1.00 ± 0.04 (n = 2) obtained in humid air. Linear least squares regression analysis of the data obtained in dry air yielded the following relation:

$$\text{CYH (measured)} = (0.987 \pm 0.021)\ \text{CYH (nominal)} - (4.88 \pm 5.76), \quad n = 8,\ R = 0.999 \qquad (9)$$

Taken together, the above results show that the difference between DNPH-LC and GC-FID methods cannot be attributed to a poor sampling efficiency of the DNPH-coated C_{18} cartridge when sampling cyclohexanone in dry air.

Concluding comments

A comparison of two methods, gas chromatography with flame ionization detection following sample collection on Tenax cartridges and liquid chromatography with uv detection following sample collection on DNPH-coated C_{18} cartridges, has been carried out in experiments involving measurements of parts per billion levels of cyclohexanone as a reaction product in ozone-alkene-cyclohexane mixtures in dry air. The results indicate that the two methods yield cyclohexanone concentrations that are within ca. ± 25% of their mean and that the GC-FID method yields cyclohexanone concentrations that are a factor of ca. two higher than those measured using the DNPH-LC method. Possible causes for the difference between the two methods were examined using the DNPH-LC method. Sampling line-specific effects, variability among co-located samples

Downloaded At: 20:49 17 January 2011

Table 1 Measured and nominal cyclohexanone concentrations in control experiments involving cyclohexanone and other carbonyls in purified air, DNPH-LC method.

Cyclohexanone, µL/L		*Concentration ratio, measured/nominal*
nominal[a]	*measured*	
in dry air (RH = 3–7%)[b]:		
98.8[c]	95.2 ± 3.6[d]	0.96
198[c]	180 ± 1[d]	0.91
296[c]	298	1.01
395[c]	381 ± 2[d]	0.96
98.7[e]	94 ± 1[d]	0.95
197[e]	187	0.95
296[e]	290	0.98
395[e]	384 ± 2[d]	0.97
		average: 0.96 ± 0.03 (n = 8)
in humid air (RH = 55 ± 10%)[f]:		
605[g]	630 ± 22[d]	1.04
605[h]	582 ± 12[d]	0.96
		average: 1.00 ± 0.04 (n = 2)

[a] from amount of cyclohexanone injected and chamber volumer
[b] experiments carried out at SAPRC, U.C. Riverside
[c] mixture of cyclohexanone and butanal
[d] mean ± one std. deviation for co-located samples
[e] cyclohexanone alone (no other carbonyls present)
[f] experiments carried out in our laboratory
[g] mixture of cyclohexanone, acetone and butanal
[h] mixture of cyclohexanone, acetaldehyde, butanal and hexanal

Downloaded At: 20:49 17 January 2011

and DNPH-cartridge sampling performance in dry air have been studied and can be ruled out as major causes for the observed difference between methods. Since accurate measurements of cyclohexanone are important to, for example, calculate the yield of the hydroxyl radical formed as a reaction product of the ozone-olefin reaction[1,2], it appears prudent to recommend additional interlaboratory comparison studies and to extend these studies to measurements of cyclohexanone in humid air.

Acknowledgements

This work was supported by the Coordinating Research Council, Inc., Atlanta, GA, through contracts CRC-APRAC-AQ-1-2 and CRC-APRAC-AQ-1-2-94. We thank Sara M. Aschmann, Margaret Crowley and Roger Atkinson, Statewide Air Pollution Research Center, U. California, Riverside, for making available the results of their cyclohexanone measuremetns by GC-FID, and Roger Atkinson for useful discussions and for his comments on the draft version of the manuscript. Denise M. Velez prepared the draft and final versions of the manuscript.

References

1. R. Atkinson and S. M. Aschmann, *Environ. Sci. Technol.*, **27**, 1357–1363 (1993).
2. R. Atkinson, E. C. Tuazon and S. M. Aschmann, *Environ. Sci. Technol.*, **29**, 1860–1866 (1995).

3. D. Grosjean, E. Grosjean and E. L. Williams II, *Environ. Sci. Technol.*, **28**, 186–196 (1994).
4. E. Grosjean and D. Grosjean. *Intern. J. Environ. Anal. Chem.*, **61**, 47–64 (1995).
5. E. Grosjean and D. Grosjean. *Intern. J. Environ. Anal. Chem.*, **61**, in press (1995).
6. T. E. Kleindienst *et al.*, (12 co-authors). *Atmos. Environ.*, **22**, 1931–1939 (1988).
7. D. R. Lawson, H. W. Biermann, E. C. Tuazon, A. M. Winer, G. I. Mackey, H. I. Schiff, G. L. Kok, P. K. Dasgupta and K. Fung. *Aerosol Sci. Technol.*, **12**, 49–55 (1990).
8. A.-P. Siriu and P. B. Shepson. *Environ. Sci. Technol.*, **29**, 384–392 (1995).
9. E. Grosjean and D. Grosjean, Carbonyl collection efficiency of the DNPH-coated C_{18} cartridge in dry air and in humid air. *Environ. Sci. Technol.*, in press (1995).

Downloaded At: 20:49 17 January 2011