

A MEASUREMENT TECHNIQUE FOR HYDROXYACETONE

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Introduction

Hydroxyacetone (HA) is mainly produced in the atmosphere from oxidation of hydrocarbons of the type, $\text{CH}_3(\text{R})\text{C}=\text{CH}_2$. Tuazon and Atkinson (1990) reported HA yield of 41% from the OH-initiated oxidation of methacrolein in the presence of NO_x . Since methacrolein is a major product of isoprene oxidation (Carter and Atkinson, 1996), isoprene, a key biogenic hydrocarbon, is therefore expected to be an important source for HA. Consequently, knowledge of ambient concentration of HA would provide information needed to examine the applicability of isoprene reaction mechanisms developed in laboratory and to assess the contribution of isoprene to photooxidant production.

The commonly used GC-FID technique involving cryo-focusing is unsuitable for HA owing to HA's thermal instability. When subjected to a temperature of 100 C for only a few seconds, HA was found to disappear completely. Since HA is highly soluble in water (it's Henry's law constant being $\sim 2 \times 10^4 \text{ M atm}^{-1}$ at 20 °C, Zhou and Lee, unpublished data), we developed a wet chemical technique similar in principle to the one we reported earlier (Lee and Zhou, 1993), namely, based on derivatization following liquid scrubbing. To increase the sensitivity, we adopted a fluorescence detection scheme based on *o*-phthalaldehyde (OPA) chemistry. The technique was deployed in the field during two measurement periods at a NARSTO site located on Long Island (LI), New York. We report the principle and the operation of this technique and the results obtained from these field studies.

Experimental Section

HA and other soluble carbonyls (e.g., formaldehyde) are incorporated into an aqueous solution using a 28-turn glass coil scrubber; typical conditions used a sample air flow rate of 2.0 L min^{-1} and a liquid flow rate of 0.30 mL min^{-1} . The collected samples containing the soluble carbonyls are first derivatized using NaHSO_3 to form the respective sulfonic acid complexes which are then analyzed using ion chromatography (DuVal et al., 1985). The eluted sulfonic acids are detected on-line by way of a post column derivatization technique which decomposes the acids to the respective carbonyl compounds and S(IV), and detects the released S(IV) fluorometrically following derivatizing using OPA in the presence of NH_3 . This analysis scheme is a variation of that used for NH_3 detection (e.g., Zhang et al., 1989). A schematic diagram showing the technique in an automated configuration is given in Fig. 1. A chromatogram showing the detection of the carbonyl compounds is shown in Fig. 2.

This technique was tested during the summers of 1997 and 1998. The measurement site, which is located at Brookhaven National Laboratory (BNL), is exposed to a fair amount of vehicular emissions from traffic within the laboratory. In addition, the site is within 3 miles of two major highways, subjecting it to pollution when winds are from the south and the west. However, since LI is covered with dense vegetation, biogenic emissions are also important.

HA was determined along with formaldehyde (FA) using a variation of the technique, namely, the pre-column S(IV) derivatization was carried out in a batchwise fashion rather than continuously on-line. The detailed procedure follows. Liquid samples collected in glass vials representing an integration of ca. 15 min period were added with a pre-determined amount of 0.50 M S(IV) solution (pH 7.0) to result in a final [S(IV)] of 10 mM. The sample was then manually injected into the IC for analysis. The IC system consisted of an HPLC pump (Hitachi, model 6200A), a 6-port injection valve (Rheodyne, model 7161)

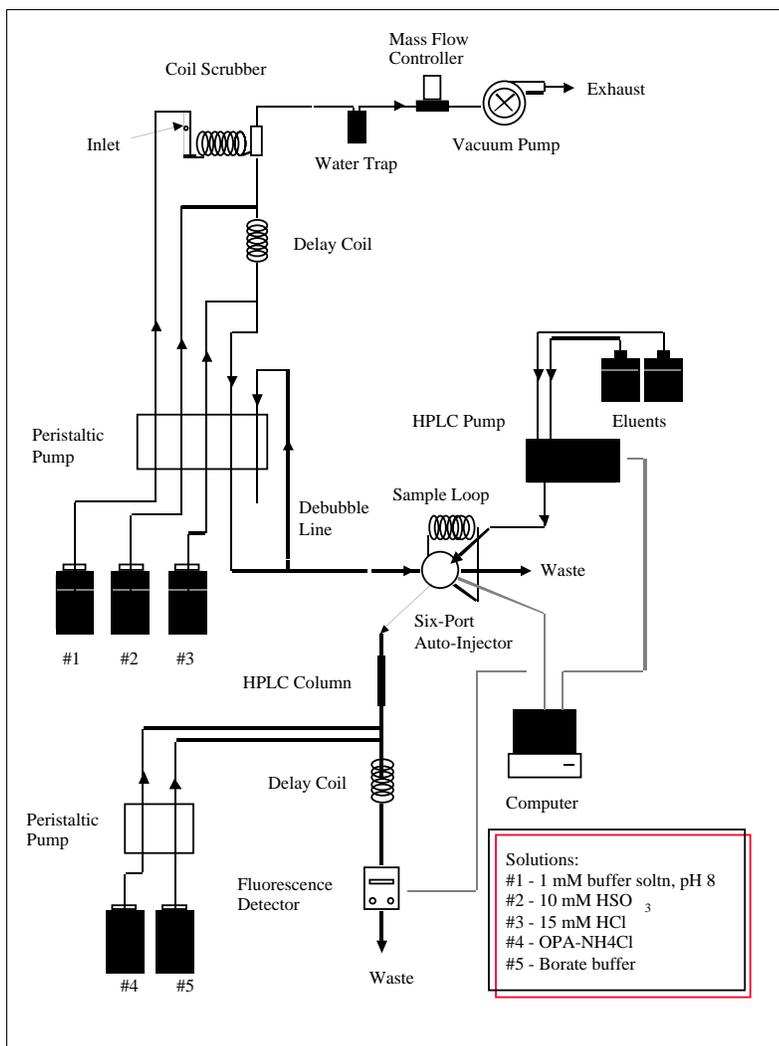


Figure 1. Schematic diagram of the hydroxyacetone measurement system in an automated configuration.

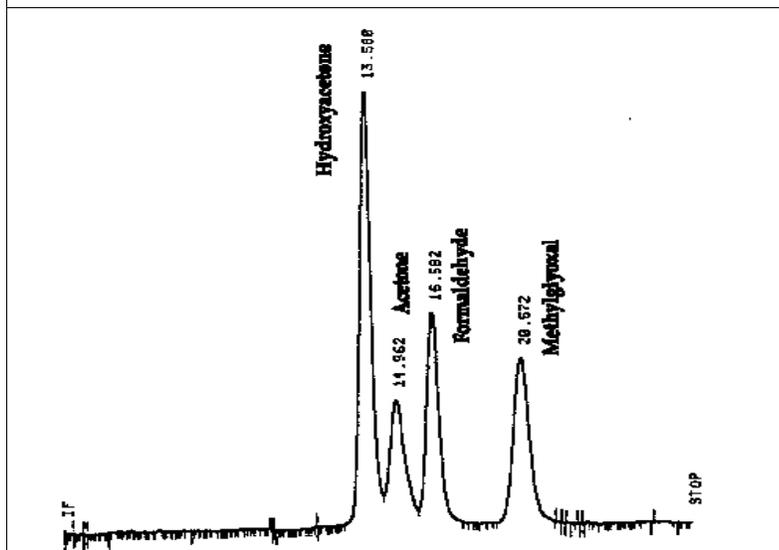


Figure 2. A chromatogram showing the detection of a mixture of aqueous standards of the indicated carbonyl compounds. HA and acetone were 5.0 μM and FA and methylglyoxal were 1.0 μM .

equipped with a 50 μL sample loop, an IC column (Vydec, cat. No. 300 IC405), and a fluorescence detector (Shimadzu, model RF-551) with the excitation and emission wavelengths set at 330 nm and 380 nm, respectively. The eluant whose flow rate was 0.60 mL min^{-1} contained a 2.0 mM potassium hydrogen phthalate buffer maintained at pH 2.73 with the presence of formic acid (40 mM). The effluent exiting the IC column was mixed with (1) a 0.10 M borate buffer containing 4.0 mM NH_4Cl maintained at pH 10.5 and

(2) a 3.0 mM OPA solution containing 30% methanol. The two reagents were each mixed in at 0.31 mL min^{-1} using a peristaltic pump.

Because of the substantial amount of S(IV) contained in the sample, the efficiency of the column was found to have deteriorated after 5 or 6 injections when the column was saturated with S(IV). To remedy this shortcoming, we limited the samples to 4 per day. At the end of the day, the column was regenerated by flushing the column using a solution containing 20 mM H_2O_2 and 3 mM HCl followed by a 50 mM HNO_3 solution.

Results

The technique was found to perform reasonably well, although it is labor intensive in the manual mode. The column performance deterioration arising from excess amount of S(IV) which limited the number of measurements to 4 per day can be eliminated by back flushing the column in an automated configuration. The limit of detection for HA was only marginal, i.e., $\sim 0.4 \text{ ppbv}$, and was due mainly to the post-column derivatization which resulted in dilution from the added reagents and axial mixing associated with the increased tubing length which broadened the peaks, lowering the sensitivity. The measurement uncertainty is estimated to be $\pm 15\text{-}20\%$.

The concentrations of FA and HA measured during the summers of 1997 and 1998 are shown in Fig. 3; the available O_3 concentrations are also included. With the limited number of measurements, FA and O_3 appear to be correlated. HA exhibits a slightly stronger diurnal dependence than FA, albeit both are weak (Fig. 4). The median concentrations of FA and HA for the two measurement periods were 2.4 ppbv and 0.9 ppbv, respectively (Fig. 4).

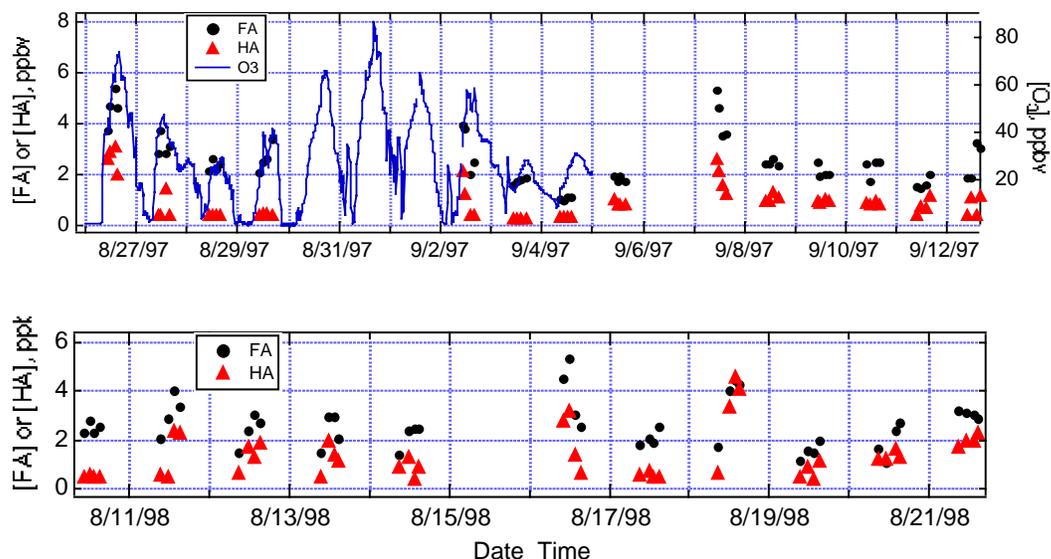


Figure 3. Concentrations of formaldehyde and hydroxyacetone determined during summers of 1997 (upper panel) and 1998 (lower panel) at a NARSTO site located at BNL, LI, NY. Available data on O_3 are also shown.

A correlation plot of HA and FA (Fig. 5) showed that the $[\text{HA}]/[\text{FA}]$ ratios were confined within a region below a line with a slope of ~ 1.2 and an x-axis intercept of $\sim 0.7 \text{ ppbv}$. One may interpret this maximum $[\text{HA}]$ to $[\text{FA}]$ ratio to have resulted from a common precursor which dominates the production of these two species when present in sufficient concentration. The data points having ratios less than 1.2 reflect the presence of other precursors of FA which do not concomitantly produce HA. A plausible candidate of such a precursor is isoprene, which has also been shown to be an important precursor for formaldehyde (Lee et al., 1998). Since a molar yield ratio of 1 to 6 for HA/FA is estimated from the isoprene-OH reaction

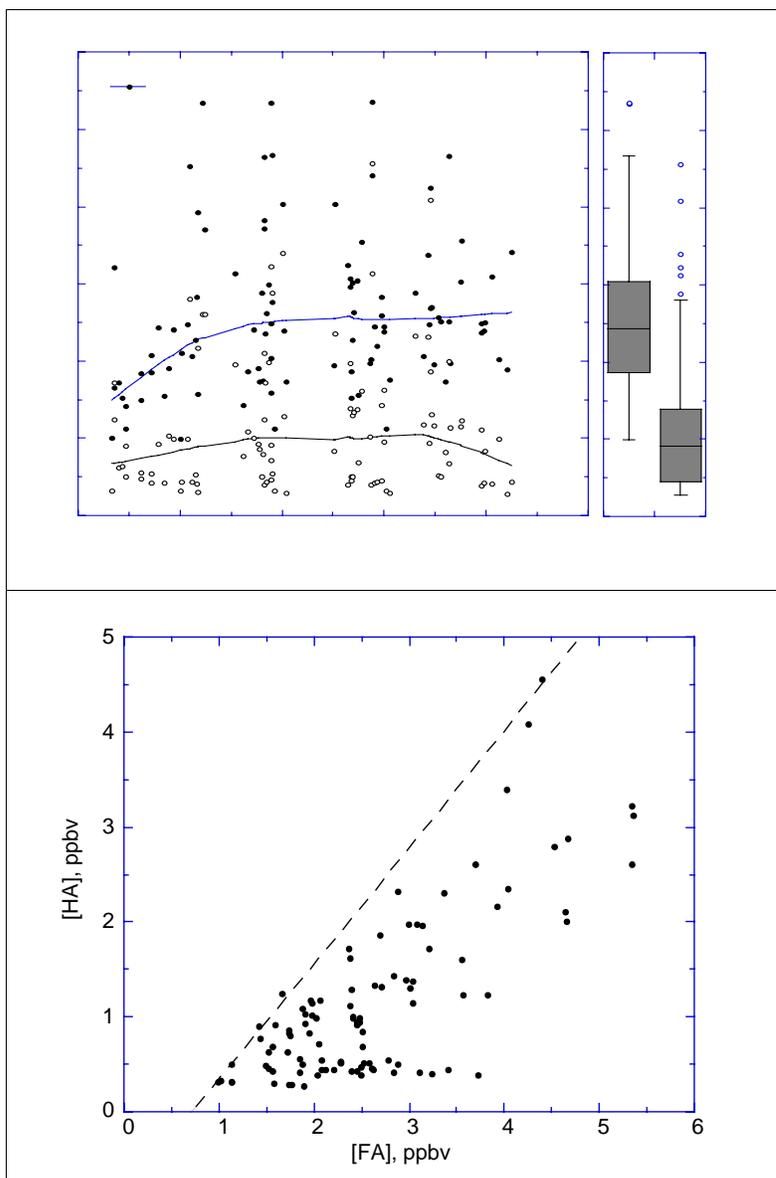


Figure 4. Composite diurnal variation of formaldehyde and hydroxyacetone (left panel). The curves represent weighted averages which are similar in magnitude to median values. The right panel shows the box plots of [FA] and [HA] where the limits of the boxes represent the mid 50 percentile. The lines in the boxes are the median values.

Figure 5. Correlation between hydroxyacetone and formaldehyde. The dash line represents an estimate of the upper limit of the ratio of [HA] to [FA], at a value of 1.2

(NRC, 1991), we need a ratio of disappearance rates of these compounds of ~ 6 to 1 favoring FA in order to maintain this steady state concentration ratio of 1.2. For a noon time $j(\text{FA})$ value of $7 \times 10^{-5} \text{ s}^{-1}$ and $[\text{OH}] \sim 1 \times 10^7 \text{ molec cm}^{-3}$, the destruction rate constant ratio of FA to HA is calculated to be ~ 5.8 (the rate constants of the OH reactions with FA and HA are 1.0×10^{-11} and $2.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, respectively), in good agreement with the suggestion of isoprene being a candidate of this precursor. It may be noted that anthropogenic hydrocarbons such as isobutene and 2-methyl-1-butene are also precursors to HA. However, since their concentrations are typically small, their contributions may be unimportant in regions where isoprene emission is significant.

Following the hypothesis given above, the observed ratio of the median concentrations of HA to FA, namely, 0.35 (Fig. 4), can be used to estimate that isoprene contributes $>1/3$ of the FA, which is a key radical precursor, at the measurement site if isoprene is the sole precursor for HA. Further, the intercept of the straight line in Fig. 5 suggests a day time background FA concentration of ~ 0.7 ppbv presumably due to long lived species such as CH_4 , in close agreement with that evaluated from the study of other isoprene products, i.e., glycolaldehyde and methylglyoxal (Lee et al., 1998).

Conclusions

A technique, which involves liquid scrubbing using a glass coil, pre-column derivatizing using S(IV), IC separation, and post-column derivatizing using OPA followed by fluorescence detection, was developed for measuring ambient hydroxyacetone. This technique was deployed in the field at a NARSTO site at BNL, LI, NY during two 2-week summer periods in 1997 and 1998. The [HA] measured showed a median concentration of 0.9 ppbv, with a maximum of ~4 ppbv, limit of detection being ~0.4 ppbv. An argument is presented that at this measurement site isoprene is the dominant source of HA and contributes >1/3 of the formaldehyde.

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