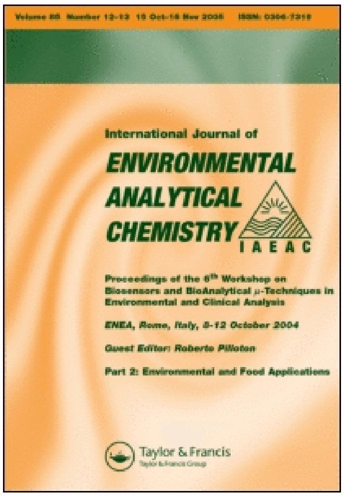

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The Determination of Low Molecular Weight Aldehydes in Rain, Fog and Mist by Reversed Phase Liquid Chromatography of the 2, 4-Dinitrophenylhydrazone Derivatives

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The Determination of Low Molecular Weight Aldehydes in Rain, Fog and Mist by Reversed Phase Liquid Chromatography of the 2,4-Dinitrophenylhydrazone Derivatives

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An improved analytical procedure has been developed for the detection and identification of volatile carbonyl compounds in wet deposition. The procedure is based on the reversed phase liquid chromatographic separation of 2,4-dinitrophenylhydrazone derivatives. Both the reproducibility and the precision of the procedure are better than ±10%. Four aldehydes have been identified in rainwater samples from Los Angeles. The identities of the compounds were verified by mass spectrometry.

KEY WORDS: Aldehydes, dinitrophenylhydrazone, reversed phase liquid chromatography, wet deposition.

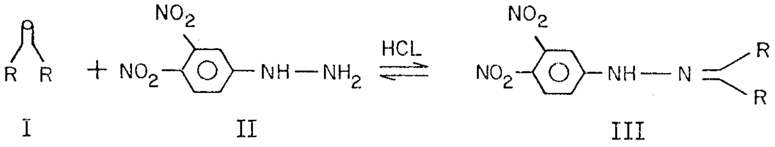
INTRODUCTION

The environmental consequences of acid wet deposition has generated intensive public and scientific concern due to the possible deleterious effects on plant and animal life.[1,2,3] The inorganic chemical properties of acidic wet deposition has been extensively characterized and the anthropogenic influences on sulfate and nitrate concentrations documented.[4,5] In contrast, the organic chemical properties of acid rainwater has scarcely been investigated.[6] Indeed, the presence of reactive organic compounds in wet deposition, as well as in aerosols, may have profound ecological implications.

The importance of carbonyl compounds in the formation of urban smog and haze is well established.[7] Washout may represent an important removal mechanism for the low molecular weight carbonyl compounds. Therefore, it is important to develop a methodology for the routine monitoring of these compounds in wet deposition.

A simple and sensitive single step procedure based on the reversed-phase liquid chromatographic separation of the 2,4-dinitrophenylhydrazone (DNPH) derivative has been developed for the rapid analysis of volatile aldehydes and ketones in rain, mist and fog water.

Carbonyl compounds (I) condense with 2,4-dinitrophenylhydrazine (II) to form the DNPH (III). The reaction is given below in (1). This reaction is catalyzed by a moderate quantity of HCl and proceeds rapidly at room temperature and in aqueous media.



(1)

Once formed, the DNPH derivatives are easily separated by HPLC technique, where they can be detected due to their intense absorption at 360 nm.[8,9,10,11,12,13] In addition, the DNPH derivatives are normally sufficiently volatile for separation and quantification by GC. These properties make the DNPH derivatives highly suitable for the identification and quantitation of carbonyl compounds in wet deposition.

Our studies have identified the following four aldehydes in rain, fog and mist: formaldehyde, acetyldehyde, glyoxal and methylglyoxal. The preliminary identification of these compounds by HPLC was subsequently verified by mass spectrometry. The analytical protocol introduced here differs from previous work[8,9] in that the reaction mixture is analyzed directly without prior separation of the DNPH derivatives.

EXPERIMENTAL SECTION

Sample collection for analytical procedures

Rainwater was collected from a single station located on the roof of the Geology Building at UCLA. All rain samples were collected using the procedure outlined in Kawamura and Kaplan,[6] preserved with $HgCl_2$ and stored at 4°C until analyzed. Repetitive analysis conducted over a period of several months indicated that the aldehydes are stable under these conditions.

Fog and mist samples, from stations located near Topanga Canyon, Los Angeles and at Heninger Flats, at the foot of the San Gabriel Mountains, were provided by Global Geochemistry Corporation, Canonga Park, California. Fog was collected by pumping the water particles through a tube and impaction on polypropylene mesh.[14] Mist was collected by settling onto a polyethylene sheet.[14] Fog and mist samples were immediately frozen after sampling and then stored at $-10°C$ until analysis.

Materials

2,4-dinitrophenyldrazine can be purchased from Sigma Chemical Company, Saint Louis, MO. The 2,4-dinitrophenylhydrazine is recrystallized before use from glass-distilled methanol. A 1.66 gm/l solution of 2,4-dinitrophenylhydrazine, in acetonitrile, is freshly prepared each day. HPLC grade acetonitrile can be obtained from Fisher Scientific Company, Fairlawn, N.J. The water that is used for liquid chromatography is deionized and distilled in an all-glass still, and then filtered through a 0.45 μ millipore filter. All other water is nanno-pure in which any dissolved organic matter has been oxidized for five hours in alkaline $KMnO_4$ and then distilled in an all-glass still.

The following aldehyde and ketone standards are used. Formaldehyde solutions are prepared by the hydrolysis of solid paraformaldehyde (from Sigma Chemical Company, Saint Louis, MO; 15). Similarly, glyoxal was prepared by the hydrolysis of glyoxal-trimeric dihydrate (from Sigma Chemical Company, St. Louis, MO). Methylgloxal was purchased as a 40% solution from Aldrich Chemical Company, Milwaukee, WS. Acetaldehyde was analytical grade from

Mallinkrodt, St. Louis, MO. All other standard compounds were obtained from Polyscience, Niles, IL.

Rain, mist and fog, as well as standard mixtures of aldehydes and ketones in water, are derivatized as follows. A 1 ml aliquot of sample is acidified with 10 μl of 6 M HCl. Then, 50 μl of the 2,4-dinitrophenylhydrazine solution in acetonitrile is added and the reaction is allowed to proceed at room temperature, for exactly 10 minutes, at which time 10–50 μl is injected directly into the HPLC with no other treatment. In this manner, highly reproducible ($\sigma \leqq \pm 5\%$) responses and blanks are achieved.

Larger volumes can be derivatized using the following modifications. Using the same proportions of the 2,4-dinitrophenylhydrazine solutions as above, the reactions are allowed to proceed for 10 minutes and are then terminated by rapidly extracting the sample with CH_2Cl_2. The organic layer is separated and back extracted one time with an equal volume of 2NHCl and twice with an equal volume of water.

Liquid chromatography

All liquid chromatography is performed using a system composed of two Waters model 6000A solvent delivery pumps, a Waters model U6K sample injector and a Waters model 660 solvent programmer. The column effluent is monitored with an Altex model 155-01 uv/vis detector adjusted to 360 nm set at a sensitivity of 0.02 absorption units full scale. The data is recorded and integrated with a Waters data module.

In the procedure developed, an Alltech C_{18} silica column (5μ, 0.46 × 25 cm) was used for all separations. In order to prolong column life, the solvent is pre-saturated with silica using a column (0.46 × 25 cm) containing Whatman precolumn silica gel which is placed in-line between the solvent pumps and the injector. The analytical reversed phases column is protected from irreversible contamination with a Vydac guard column kit.

The solvent system consists of a gradient mixture of 0.02 M NaH_2PO_4 (A) and acetonitrile (B). The column is initially equilibrated with a 50:50 mixture of A and B. Upon injecting the sample, a 15-minute linear gradient to 80% B is initiated. A flow rate of 1 ml/min is maintained throughout. This system affords baseline resolution of n-C_1 to C_9 aldehydes. In addition, acetone benzaldehyde, glyoxal, and methylglyoxal were well resolved fron n-C_1 to C_9 aldehydes. However, 2-ketones are normally incompletely resolved from aldehydes with the same number of carbons. The α-keto acids, glyoxalic acid and pyruvic acid are also well resolved and eluted before excess derivatizing agent. However, because the peaks are highly assymmetric, reliable quantitation of the α-ketoacids by this technique is presently unobtainable.

Gas chromatography/mass spectrometry (GC-MS)

To verify the identities of the carbonyl compounds GC-MS measurements, in this study, were performed on a Finnigan 4000 quadrupole instrument, which is interfaced with a Finnigan 9610 GC. Separations were performed on a DB-5 fused silica capillary column (30 m × 0.25 mm, J&W Scientific), under the following conditions: injector temperature, 275°C; column, 30–310°C at 12°C/minute: linear (He) velocity, 30 cm/sec. Samples were injected in the splitless mode, with CH_2Cl_2 as solvent. The mass spectrometer conditions were: ion source, 240°C; electron beam 70 eV. Mass spectral data were stored and processed with a Finnigan INCOS 2300 data system.

Direct insertion probe/mass spectrometry (DIP-MS)

For DIP-MS measurements, the samples (in CH_2Cl_2) were loaded into a borosilicate capillary at the end of the probe. The solvent was allowed to evaporate at room temperature. The probe was then inserted and heated ballistically to 120°C and then at 10°C/min to 310°C. The ion current was monitored continuously.

RESULTS AND DISCUSSION

The reversed phase separation of a standard mixture of aldehydes is given in Figure 1. In Figure 2, a chromatogram resulting from a rainwater analysis is shown. The various peaks are identified in the figure captions. The α-dicarbonyl compounds, glyoxal and methylgloxal, produce two and three peaks respectively in the chromatogram. These multiple peaks result from the formation of both a mono- and a bis-DNPH. With a prolonged reaction time the peaks

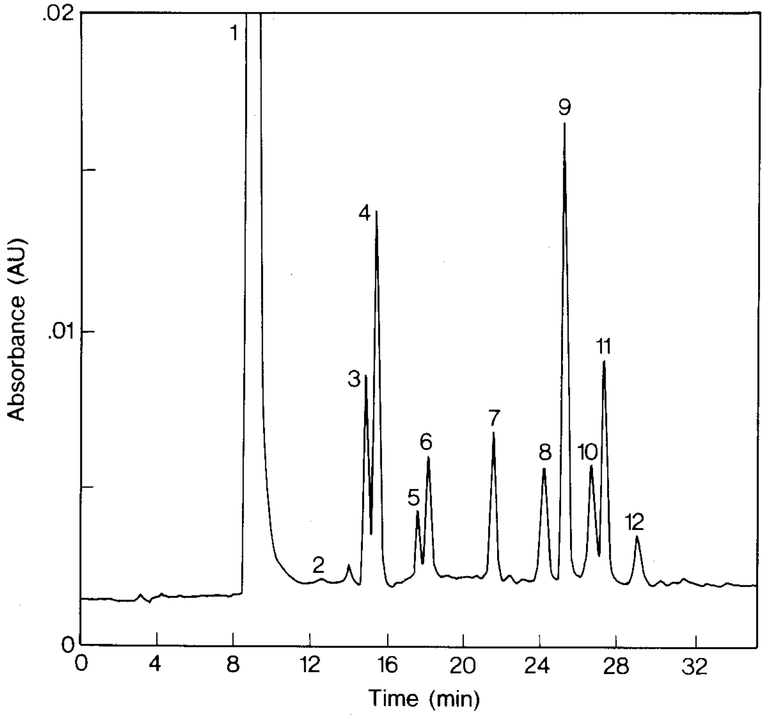


FIGURE 1 DNPH-aldehyde standard mixture separated by reversed-phase HPLC. The peak identities are as follows: (1) 2,4-dinitrophenzyl hydrazine, (2) glyoxal-mono-DNPH; (3) methyl glyoxal-mono-DNPH; (4) formaldehyde-DNPH; (5) methylglyoxal-mono-DNPH; (6) aceteal-DNPH; (7) propanal-DNPH; (8) butanal-DNPH; (9) glyoxal-bis-DNPH; (10) pentanal DNPH; (11) methylglyoxal-bis-DNPH; (12) hexanal-DNPH.

corresponding to the mono-DNPH derivatives disappear with a concomitant increase in the bis-DNPH peak. The linear responses achieved by this derivatization technique is illustrated in Figure 3. Spiking rainwater with aldehydes verified that the responses are linear and that the response factors are identical for both standard mixtures and samples. This result is illustrated in Figure 4 for formaldehyde and propanaldehyde additions to a rain sample. Similar results were obtained for other compounds. High precision is achieved by frequent calibration of the HPLC by analysis of standard mixtures of aldehydes. The instrument calibration is

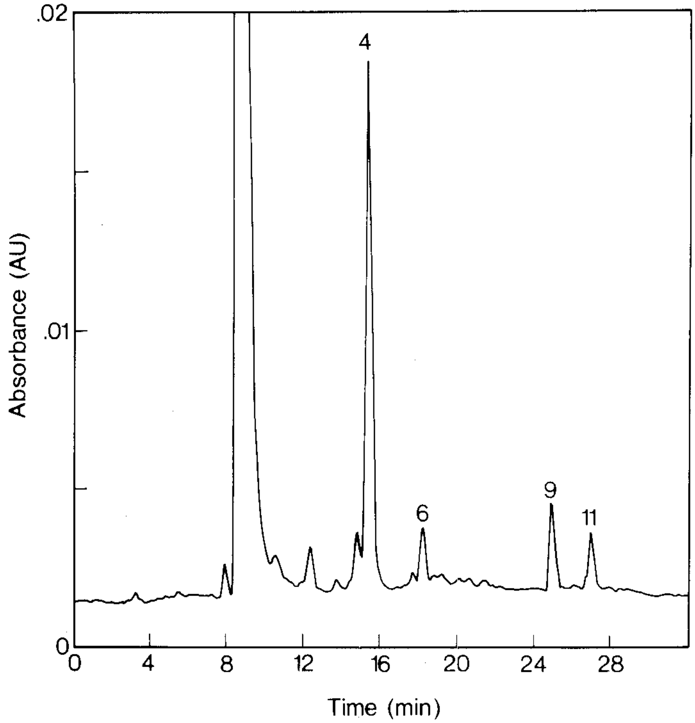
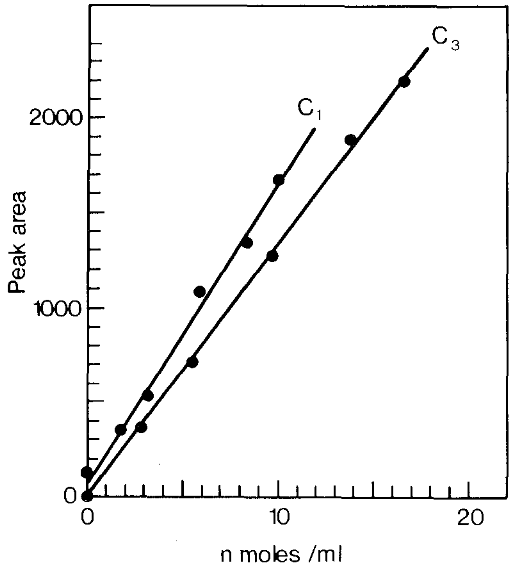


FIGURE 2 A chromatogram resulting from a rainwater analysis. Peak identifications are as in FIGURE 1.

checked each day to ascertain the consistency of response factors. Both samples and standards are reproducible within ±2% when rerun on the same day. We estimate a maximum error of ±10% in concentration using this technique.

The derivitization kinetics for various aldehydes is illustrated in Figure 5. These results imply that for a 10-minute reaction time, the formation of DNPH derivatives is essentially complete for formaldehyde and other mono-aldehydes, whereas for the α-dicarbonyls the formation of the bis-DNPH is about 60% complete. However, the response factors which are determined with standard aldehyde mixtures can be used to correct the results to 100%. In spite of the non-quantitative reaction for the α-dicarbonyls, the sensitivity of the procedure was generally adequate for this application. In addition,



Correlation Coefficient	
C_1	0.995
C_2	0.995
C_3	0.999
C_4	1.000
C_5	1.000
C_6	1.000
C_7	0.999

FIGURE 3 Linear correlation of aldehyde peak areas with standard concentration. Only data for two aldehydes are illustrated. The correlation coefficient show that similar linearity has been achieved for other compounds.

the appearance of multiple peaks can be useful verification of compound identity. Higher sensitivity can be obtained for the α-dicarbonyls by allowing a longer reaction time so that the formation of the bis-DNPH is quantitative (at 3.5 hours peaks corresponding to mono-DNPH derivatives of the α-dicarbonyls were not apparent on the chromatograms).

Four aldehydes were identified by their HPLC retention times. Mass spectrometry was used to confirm these assignments. A 5 ml fog sample which was provided by Global Geochemistry Corporation, was processed using the procedure outlined in the Experimental Section in order to obtain enough DNPH derivative for mass spectral identification.

Two aldehydes (formaldehyde and acetaldehyde) could be identified by their GC retention times, as well as by comparison of their mass spectra with standard compounds. A compound that elutes just after acetaldehyde-DNPH was also believed to be a carbonyl-DNPH. The molecular ion of this compound has an assigned

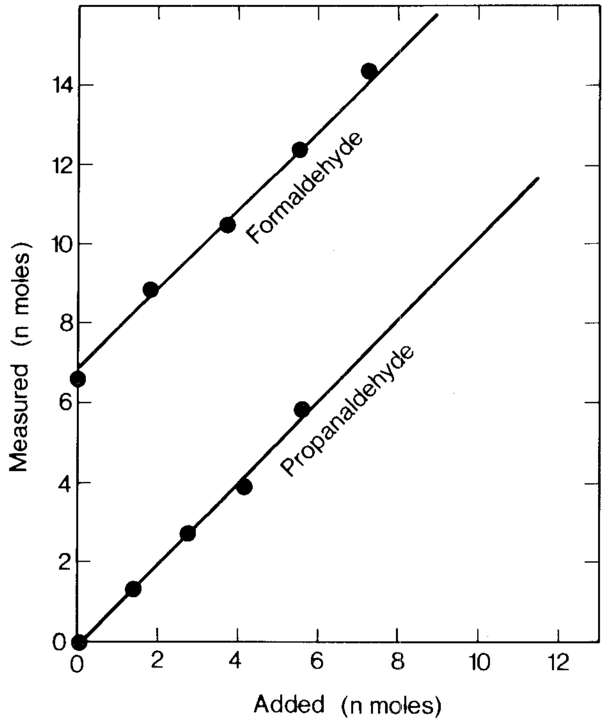


FIGURE 4 Recovery of formaldehyde and propanaldehyde added to rainwater sample. The slopes are 1.04 and 1.03 for formaldehyde and propanaldehyde, respectively.

fragment at 252 m/e. Fragmentation of the DNPH derivatives yield dominant ions at 153±2, 164±2, and 181±2, as well as clusters centered at ~51, ~63, ~75 and ~91, in addition to the molecular ion peak. The most probable assignment for this spectrum is a mono-DNPH derivative of methylgloxal.

No evidence for the bis-DNPH derivatives of glyoxal or methylglyoxal could be observed by GC/MS. It was found that the standard reference compounds failed to elute under the GC conditions used. Therefore, to confirm the presence of these compounds in the fog samples, the two derivatives were isolated by HPLC. Mass spectra values were then obtained using DIP-MS.

The compound identified as glyoxal distilled from the probe as two broad peaks. Examination of the mass spectrum at the maxi-

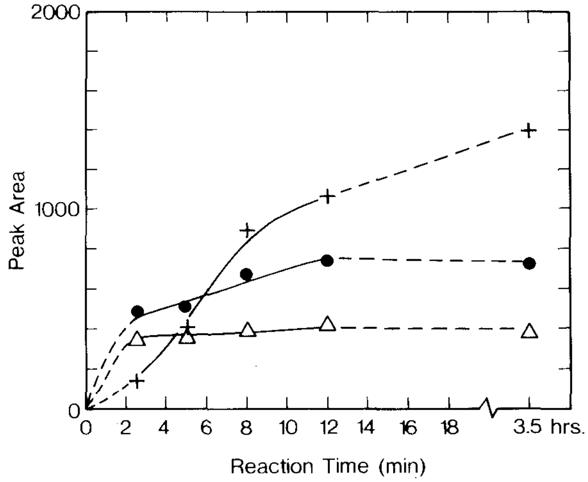


FIGURE 5 Reaction kinetics of 2,4-dinitrophenylhydrazine with aldehydes under these reaction conditions. Peak area as a function of pre-injection reaction times are shown. ●, formaldehyde; ▲, acetaldehyde, +, glyoxal.

mum of each peak indicated that both peaks corresponded to the same compound. Comparison of the mass spectrum of the compound with that of a standard glyoxal-bis-DNPH confirmed the identity of the material isolated from the fog. This identification was further verified by a library search with the INCOS data system. The material initially identified as the methylglyoxal derivative gave a mass spectrum with a parent ion at 432 (m/e), consistent with the identification of this compound as methylglyoxal.

In Table I, the concentrations of formaldehyde, acetaldehyde, glyoxal, and methylglyoxal from rain, fog and mist samples are compiled. Although over one hundred samples have been analyzed, these data are meant only to illustrate a representative sampling of our results on aldehyde concentrations in Los Angeles area wet precipitation. A more extensive compilation, including inorganic chemical data and organic acid concentrations will be published later.

At present, there are few published data regarding the wet deposition of low molecular weight aldehyde and ketones. Klippel and Warneck[16] reported formaldehyde concentrations for several sampling sites in western Europe. Their results imply a fairly

TABLE I

The concentrations of aldehydes (μM) in rain, fog and mist samples.

Date	Formaldehyde	Acetaldehyde	Glyoxal	Pyruvaldehyde	Σ
Rain					
8/18–8/19/83	6.90	0.24	0.43	0.35	7.92
8/18/83	15.30	0.80	3.98	3.42	23.50
4/28–4/29/83	12.61	1.02	0.23	0.78	0.78
2/11/82	7.34	7.1	0.78	0.36	0.36
1/20–1/21/82	2.77	0.86	0.24	n.m.[a]	3.87
1/1/82	4.54	0.86	0.61	0.71	6.72
Fog					
Topanga canyon					
5/26/83	60.70	3.50	34.10	12.50	110.80
Heninger flats					
6/11/83	51.8	1.0	14.2	20.5	87.5
Mist					
Topanga canyon					
5/26/83	55.80	4.90	20.80	15.00	96.50
Heninger flats					
6/11/83	75.2	1.2	29.6	21.3	127.3

[a] n.m. = not measurable.

uniform concentration of about 5 μM along a latitude of 50°. Thompson[17] reported comparable concentrations (2.9 ± 1.9 μM) for formaldehyde collected at Woods Hole Oceanographic Institution, Woods Hole, Massachusetts. Zafiriou *et al.*[18] reported much lower concentrations (0.263 ± 0.006 μM) for rainwater collected in the western equatorial Pacific at Enewetok Atoll. Average formaldehyde concentrations for rainwater collected at UCLA are considerably higher than these previous reports, but are lower than those recently reported by Waldman *et al.*,[19] who found values of formaldehyde concentration of up to 480 μM for Los Angeles area fogs.

The results presented in Table I also imply that the low molecular weight aldehydes represent one of the most concentrated classes of organic compounds in rainwater.[19] Formaldehyde clearly is predominant in rainwater, whereas glyoxal and methylglyoxal add a substantial contribution to the fog and mist samples.

Aldehydes have long been recognized as a principal component of photochemical smog. Production of aldehydes in the urban environment has been associated with motor exhaust. The internal combustion engine produces low molecular weight carbonyl species as a result of incomplete hydrocarbon combustion.[12,21] Alternatively, low molecular weight olefin compounds also produced in automobile exhaust may be oxidized by ozone in the atmosphere to produce aldehydes.[18,23] Aldehydes may undergo further reactions to contribute to the formation of the particulates associated with hazes.[24]

The aldehyde distribution pattern observed in rain, fog and mist differs from the distribution produced by gasoline engines. For example, neither glyoxal nor methylglyoxal has been reported in motor exhaust.[25] Furthermore, acetaldehyde makes an important contribution to the total concentration of aldehydes in automobile exhaust.[25] Thus, the observed aldehyde distribution of wet deposition does not directly reflect motor exhaust.

It is noteworthy that the carbonyl distribution in wet deposition differs from the distribution of carbonyl compounds observed in Los Angeles ambient air. Grosjean[26] found for Los Angeles' ambient air formaldehyde $\geqq$ acetaldehyde $\geqq$ propanal $\geqq$ butanal $>$ 2-butanone $\sim$ benzaldehyde. Grosjean[26] observed that formaldehyde normally predominates, however, its contribution is not overwhelmingly greater. Grosjean[26] did not report any α-dicarbonyls in ambient air, but he noted that there are many unknown compounds which he was unable to identify. As shown in Table I, in wet deposition, formaldehyde occurs at 10–20 times the concentration of acetaldehyde. A possible explanation is that the relative concentration of these compounds change during scavenging from the ambient atmosphere as a result of differing solubilities and because of secondary reactions such as hydration and bisulfate addition.

As discussed previously, both formaldehyde and acetaldehyde are formed directly by internal combustion engines. Thus, the concentrations of these compounds in wet deposition may be a direct reflection of traffic density. In addition, the ozonation of the volatile olefins from motor exhaust produces low molecular weight aldehydes and acids. For example, the ozonation of propylene yields formaldehyde and acetaldehyde.[22] The α-dicarbonyl compounds reported in this study have not been reported as major products of ozone olefin reactions. However, both glyoxal and methylglyoxal are important products from the reaction of ozone with aromatic hydrocarbons.[27,28,29] Thus, the reaction of aromatic compounds (produced in motor exhaust) with ozone may explain the origin of the α-dicarbonyls in wet deposition.

In general, the α-dicarbonyl compounds make a greater contribution to the aldehyde distribution of the fogs and mists than to the aldehyde distribution of rainwater. Fogs and mists are formed close to the ground, whereas, rain forms at high altitudes. Thus, the organic constituents of wet deposition may reflect the chemical processes occurring at the elevation of origin. In addition, the effects of higher surface-to-volume ratios and the lower settling velocities of smaller fog and mist droplets, in comparison to rain droplets, may explain some of the carbonyl distribution differences. Another possibility is that the ambient air concentration of the α-dicarbonyls is so low that they are efficiently washed out very early during a rain event. Thus, in a rain of moderate to long duration, these α-dicarbonyls then become very dilute.

CONCLUSIONS

The detection of carbonyl compounds in wet deposition has important implications for the mechanism of removal of such compounds from the atmosphere. These compounds are highly reactive and constitute a significant proportion of the total dissolved organic content of rainwater. These highly reactive compounds have been implicated in smog formation.

The analytical protocol described here provides a simple and accurate means of routinely monitoring wet deposition for aldehydes and ketones. Using this technique, four carbonyl compounds have been identified in rain, fog and mist. The two α-dicarbonyl compounds are believed to be reported for the first time. Presently, we are completing additional studies on the occurrence of these compounds in wet deposition along with measurements of inorganic properties. Our principal objective is to establish the relationship between the carbonyl chemistry of wet deposition and other organic and inorganic indicators of anthropogenic activity.

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