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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · OCTOBER 1990

Impact Factor: 5.33 · DOI: 10.1021/es00080a003

ES&T RESEARCH

Determination of Picomolar Concentrations of Carbonyl Compounds in Natural Waters, Including Seawater, by Liquid Chromatography

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■ Low molecular weight carbonyl compounds in natural waters were determined at picomolar to nanomolar levels by derivatization with 2,4-dinitrophenylhydrazine followed by liquid chromatography. The uniqueness of the method is attributed to the extremely low blanks obtained and the minimal sample preparation involved. The detection limit for direct injection of derivatized natural water samples is 0.5 nM for aldehydes and 5 nM for ketones with a precision of ~7% RSD at the 30 nM level for aldehydes. The detection limit can be further lowered by using off-line cartridge enrichment in which derivatized natural water is passed through a C18 extraction cartridge. Recoveries for the enrichment method were 95–105% for a sample volume of 20 mL and for concentrations of carbonyl compounds in the 1–30 nM range. A field procedure for storage of derivatized sample extracts for extended periods is also presented. Applications of enrichment and sample storage techniques to marine and estuarine waters are presented.

Low molecular weight (LMW) carbonyl compounds are involved in several important biotic and abiotic processes in natural waters, including microbial transformations, air/sea exchange, and photo- and thermochemical reactions (*1*, *2*). LMW carbonyl compounds are produced during the photodegradation of dissolved organic matter in natural waters, and their photochemical production is closely correlated with their biological uptake in those waters (*3*). These compounds are major organic constituents of aqueous phases in the atmosphere (*4–6*), where they play important roles in cloud chemistry and in the speciation of sulfur compounds (*7–9*). Low molecular weight carbonyl compounds are also released into natural waters as a result of man's activities, such as ozonation of wastewaters (*10*), and are major byproducts of industrial processes, e.g., production of industrial surfactants (*11*). Because of their high chemical reactivity and potential toxicity, these compounds are of environmental concern.

A variety of analytical techniques are available for determination of carbonyl compounds in aqueous atmospheric samples (*12–15*), treated natural waters (*10*, *16*), food and beverages (*17*, *18*), and biological fluids (*19*). However, there has been no reliable method reported for the determination of subnanomolar concentrations of carbonyl compounds in open ocean seawater and coastal water where analyses are hindered because of the complexity of the sample matrix and low concentrations. Solvent extraction (*10*, *16*) and cartridge enrichment (*20*, *21*) techniques have been used in previous studies in attempts to lower detection limits for aqueous samples. Although these techniques work well for certain applications, the reported blank levels are much too high for use in analysis of most natural waters. Furthermore, the published cartridge techniques are not particularly convenient since they require hand packing of the cartridges and they use nonstandard packing materials, e.g., custom-synthesized resins and zeolites (*20*, *21*).

In this paper we present methods for the analysis, preconcentration, and storage of LMW carbonyl samples in seawater and other natural waters. The analysis is based on derivatization with 2,4-dinitrophenylhydrazine (DNPH). One of the distinguishing features of this method is the extremely low blanks obtained, resulting in the low detection limits required for natural waters, especially seawater. In addition, very little sample preparation is required, so contamination problems are avoided.

A simple enrichment method using commercial C18 extraction cartridges for preconcentration and storage of samples for carbonyl analysis is also described. The ability to store analytes for extended periods allows for collection of large numbers of samples over a relatively short period, which greatly facilitates field studies. In addition, if concentrations of carbonyl compounds are low, e.g., picomolar to nanomolar, a large sample volume (e.g., 20 mL) can be preconcentrated onto the extraction cartridge, thereby significantly lowering the detection limit. Applications of the cartridge enrichment and sample storage procedures to coastal and open ocean seawater are given.

Experimental Section

Reagents and Standards. Acetonitrile used for sample preparation and HPLC analyses was HPLC grade (Burdick and Jackson, Muskegon, MI). Deionized water was obtained from a Millipore Q-water system with an Organex attachment (Millipore, Milford, MA). 2,4-Dinitrophenylhydrazine (DNPH) (Sigma, St. Louis, MO) was recrystallized twice from acetonitrile and stored in the dark in air-tight Teflon vials. Carbon tetrachloride, used for purification of the DNPH reagent solution, was Burdick

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0013-936X/90/0924-1477$02.50/0

and Jackson high-purity solvent. Carbonyl compounds were obtained from Aldrich (Milwaukee, WI) or Sigma.

Stock solutions of formaldehyde, acetaldehyde, and propanal (10 mM) were prepared in 50% acetonitrile/water (v/v). All other stocks (10 mM) were prepared in pure acetonitrile. Stock solutions were kept at 4 °C and were stable several months. The 10 mM standards were serially diluted to concentrations typically found in natural waters (10–300 nM). A mixed standard was prepared containing all naturally occurring carbonyl compounds except formaldehyde, which was made up separately. The dilute, mixed standard was prepared fresh just prior to use.

Derivatization Reaction. The reagent is prepared in a 20-mL Teflon vial by dissolving 20 mg of recrystallized DNPH in 15 mL of a solution containing concentrated HCl (~12 M), water, and acetonitrile in the ratio 2:5:1 (v/v/v). Carbonyl contamination contained in the DNPH reagent solution is removed by successive extractions with CCl_4 just prior to use. Carbon tetrachloride (2 mL) is added to the 15-mL reagent solution and shaken on a wrist-action shaker for at least 5 min. The mixture is then placed in a tabletop centrifuge (ca. 2000 rpm) for ~5 min in order to separate the phases. The organic layer is removed and the reagent solution is reextracted as above. The second extraction of the reagent solution is essential for low-level work. The purified reagent solution is stable for at least 1 week, but should be reextracted with fresh carbon tetrachloride on a daily basis if the lowest detection limit is required.

Samples are generally not filtered prior to derivatization because filtration often results in an increase in concentrations of carbonyl compounds, which is in agreement with past studies (*1*, *2*). Natural water samples are derivatized by adding 50 μL of purified reagent solution to a 5-mL sample in a 7-mL Teflon vial (prerinsed at least two times with sample). An Eppendorf repeater pipet with a polypropylene 2.5-mL tip is used for adding reagent solution. The solution can be stored at least 4 h in the pipet tip with no detectable increase in the blank. Prior to adding reagent to the sample, one or two "shots" from the pipet are discarded to waste. The vial is capped and shaken briefly, and the reaction is allowed to proceed for 1 hour at ambient temperature (~25 °C). The reaction conditions employed in this study (e.g., reagent concentration, reaction pH, time, and temperature) are within optimal ranges reported in previous studies (*2*, within *16*, *22*). A 2-mL aliquot is removed and directly injected into the HPLC system. Injection volumes larger than 2 mL result in an unacceptably large reagent peak, as well as peak broadening. A reagent blank is obtained in an analogous fashion except the 2-mL aliquot is injected immediately after addition of reagent (Figure 1a). For cartridge enrichments, 200 μL of DNPH solution is added to a 20-mL water sample in a 30-mL Teflon vial and the reaction is allowed to proceed for 60 min before extraction.

Sample Collection. Sampling gear and sampling procedures were similar to those used previously (*1*, *2*). Great care must be exercised when samples are obtained for analysis of carbonyl compounds because of the potential for contamination. Sampling should be performed upwind of sources of contamination (e.g., smoke stacks, cigarette smoke, engine room fumes, etc.). The operator should wear polyethylene gloves and should stand downwind of the samples while withdrawing them.

Cartridge Extractions. Samples can be extracted and stored for later analysis with the aid of C18 Sep-Pak cartridges (Waters Assoc., Milford, MA). Prior to use, the cartridge is cleaned by passing through it 20 mL of acetonitrile and 10 mL of underivatized water sample sequentially. By use of an all glass syringe, 20 mL of derivatized natural water is pushed through the conditioned extraction cartridge at a flow rate of ~10–15 mL/min. Excess reagent is washed off the cartridge with 25 mL of 17% acetonitrile in water followed by 5 mL of water. The remaining liquid is blown out of the cartridge with air, and the carbonyl hydrazones are eluted with 1 mL of acetonitrile into Teflon vials. The extracts are stable at least 2 months if stored refrigerated in the dark. Prior to HPLC analysis, the extracts are reduced to dryness with a stream of carbonyl-free N_2 at room temperature and then redissolved in 2 mL of 10% acetonitrile in water, resulting in a 10-fold enrichment. The 2-mL, enriched sample is then injected directly into the HPLC system.

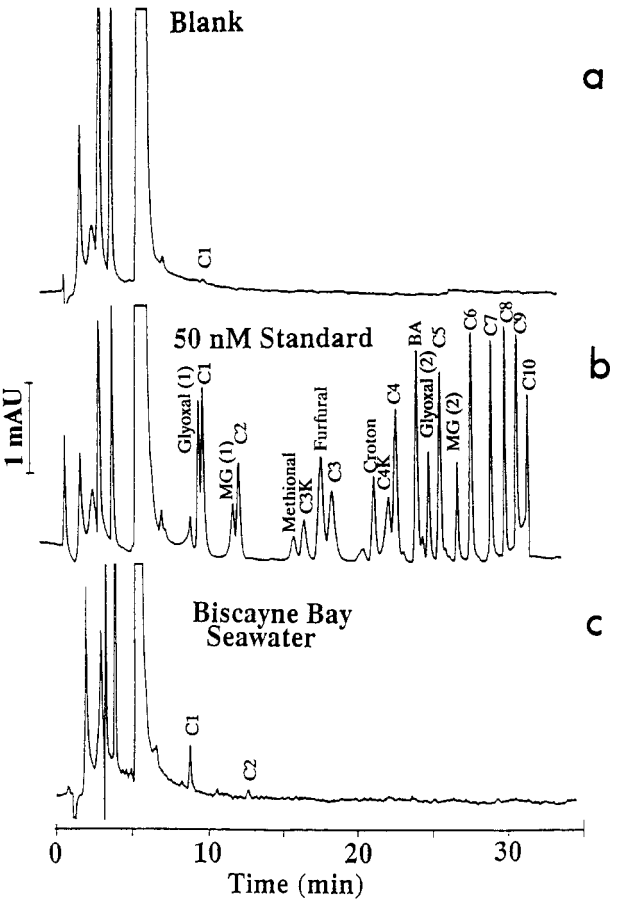

Figure 1. HPLC chromatograms. (a) Reagent blank after two successive extractions with CCl_4. A 50-μL sample of purified DNPH solution was added to 5 mL of seawater and 2 mL of the resultant mixture was injected immediately into the HPLC system. (b) Carbonyl standards added to seawater: Cl–C10, straight-chained aliphatic aldehydes; glyoxal(1, 2), glyoxal mono- and disubstituted derivatives; MG(1,2), methylglyoxal mono- and disubstituted derivatives; C3K, acetone; croton, crotonaldehyde; C4K, butanone; BA, benzaldehyde. (c) Direct injection of 2 mL of derivatized coastal seawater.

Apparatus. The HPLC system consisted of an E-Lab Model 2020 gradient programmer and data acquisition system (OMS Tech, Miami, FL) installed in an IBM compatible PC, and Eldex Model AA pump (Eldex Laboratories, Menlo Park, CA) and a Valco six-port injector (Valco Instruments, Houston, TX) with a 2000-μL sample loop. The mobile-phase gradient was generated by an inert solenoid valve placed on the low-pressure side of the pump and controlled by the E-Lab system. Derivatized hydrazones were separated on a Radial compression separation system with an 8 mm i.d. C18 reversed-phase Radial-Pak cartridge (type 8NVC184) (Waters) and detected by an Isco Model V4 variable-wavelength absorbance detector

Table I. Recoveries[a] of DNPH-Derivatized Carbonyl Compounds in Seawater (20 mL) Extracted on C-18 Cartridges

% acetonitrile in wash	% reagent removed	formaldehyde		acetaldehyde		glyoxal	
		nM	% rec[b]	nM	% rec	nM	% rec
0	0	33	96	4.5	95	1.2	103
10	63	34	100	4.8	101	1.1	95
15	75	36	105	4.7	99	1.2	103
17	99	34	100	5.0	105	1.2	103
20	99	28	82	4.3	91	1.1	95

[a] Recoveries are expressed as a function of acetonitrile strength (second column) of the 25-mL solution used to rinse off excess, unreacted reagent from the cartridges prior to elution of carbonyl hydrazones. [b] The percent recovery was calculated relative to the unextracted seawater sample (n = 5).

(Isco, Lincoln, NE) at 370 nm. The detector signal was stored and processed by the E-Lab data system. "On-the-fly" UV–visible spectra of different compounds were obtained by an HP 1040A diode-array detector controlled by an HP 9000 data system (Hewlett-Packard, Avondale, PA).

HPLC Conditions. A two-solvent gradient elution was used: (A) 10% acetonitrile in water adjusted to pH 2.6 with 10 N sulfuric acid, and (B) 100% acetonitrile. The gradient program was as follows: isocratic at 36% B for 2 min, 36% B to 53% B in 4 min, isocratic at 45% B for 8 min, 45% B to 80% B in 10 min, and then isocratic at 100% B for 20 min. The flow rate was 1.5 mL/min. The column was at ambient temperature, ~25 °C. A typical chromatogram for carbonyl standards (50 nM) is presented in Figure 1b and for Biscayne Bay seawater in Figure 1c.

Results and Discussion

Optimization of Cartridge Extraction Procedure. The trapping efficiency for carbonyl compounds was evaluated by pumping different volumes of derivatized seawater through two cartridges in series. We found that all carbonyl-DNPH derivatives and unreacted DNPH reagent were trapped on the first cartridge for sample volumes up to 250 mL. Unfortunately, this large amount of unreacted reagent when eluted with the hydrazones seriously interferes with subsequent HPLC analyses. Therefore, experiments were performed to determine if the unreacted reagent could be preferentially rinsed off the cartridges prior to eluting the carbonyl hydrazones. One liter of Biscayne Bay seawater was derivatized and 20-mL aliquots were loaded onto C18 extraction cartridges. The percentage of acetonitrile used to rinse off excess reagent from the Sep-Paks was varied between 10 and 20% (in water); the rinse volume was always 25 mL. The percentage of reagent removed as a function of percent acetonitrile in the wash is presented in Table I. The optimal percent acetonitrile is achieved when the maximum amount of reagent is removed while the concentration of derivatized carbonyl compounds remains constant. Table I shows that 17% acetonitrile is appropriate for 20-mL water samples, since 99% of the reagent was removed with 100% recovery of the analytes. As mentioned above, larger samples volumes (up to 250 mL) can be quantitatively extracted by the cartridges; however, this procedure has not yet been optimized.

With no pH control in the rinse solution there is a significant loss of α-keto acid derivatives (pyruvate and glyoxylate) during the reagent removal step. The pH of the wash mixture was therefore varied between 2.1 and 4.1 to see if protonation of the carboxy group could improve recovery of these compounds. The results are presented in Table II. Above pH 2.6 there was a significant loss of α-keto acids during the reagent removal step. At pH 2.6 and below there was no significant loss in these compounds. As expected, recoveries of other carbonyl compounds were not affected by the pH of cartridge rinse solution.

Table II. Effect of pH of the Cartridge Rinse Solution on Recoveries of α-Keto Acids Added to Seawater (n = 1)[a]

pH of rinse	glyoxylate		pyruvate	
	nM	% rec	nM	% rec
2.1	118	115	94	100
2.6	106	104	101	107
3.0	67	65	101	107
3.8	0	0	93	99
4.1	0	0	70	74
neutral[b]	0	0	76	80

[a] α-Keto acids were added to a Biscayne Bay seawater sample to final concentrations of 102 (glyoxylate) and 94 nM (pyruvate) and 20-mL aliquot samples were extracted on Sep-Paks followed by 25 mL of 17% acetonitrile reagent rinse adjusted to various pH values with H_2SO_4. [b] No pH control.

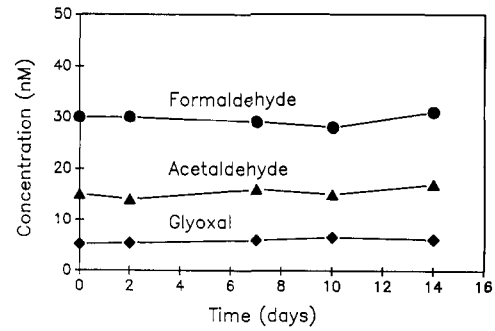

Figure 2. Test of storage procedure. Five 20-mL aliquots of a derivatized coastal seawater sample were extracted on Sep-Paks; each time point represents the analysis of a different sample aliquot.

Storage of Derivatized Carbonyl Compounds. In order to test for stability of extraction cartridge eluates, a 300-mL Biscayne Bay seawater sample was derivatized with DNPH, and 20-mL aliquots were loaded onto cartridges. Unreacted reagent was washed off and the carbonyl derivatives were eluted with acetonitrile into Teflon vials. The samples were stored in the dark at 4 °C. A different vial was analyzed over a 2-week period. The results are presented in Figure 2, which shows that for the three main carbonyl compounds found in the sample, formaldehyde, acetaldehyde, and glyoxal, there was no change (within the precision of the method 5–10%, 1σ) in concentrations over 14 days.

Methanol cannot be used in place of acetonitrile in the Sep-Pak procedure because the extracts were unstable in methanol. Significant decomposition of the DNPH derivatives was observed after 3–4 days of storage.

Blank and Detection Limit. The only detectable carbonyl contamination in the procedural blank is formaldehyde, at concentrations typically less than 3 nM for a 2-mL injection (Figure 1a). This blank is several times to orders of magnitude lower than those reported in the literature for similar techniques (*10, 12–16, 18–21*). We attribute this low blank to two factors: (1) our purification procedure for the DNPH reagent solution, and (2) direct injection of a large volume (2000 μL) of the derivatized sample. The latter results in a large sensitivity increase (relative to methods using smaller injection volumes, e.g., 10–100 μL) without the need for solvent extraction/preconcentration of carbonyl hydrazones, as used by other

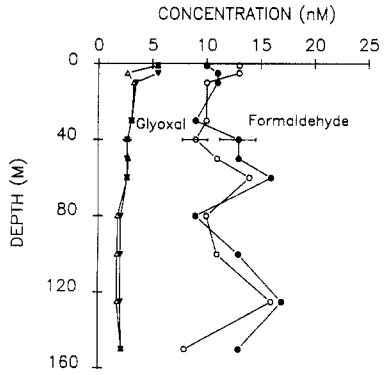

Figure 3. Formaldehyde and glyoxal concentrations (n = 2) from different depths at an oligotrophic station in the Caribbean Sea. Open symbols: direct injection of 2-mL derivatized samples on the day of collection. Closed symbols: cartridge extracts of 20 mL of the same samples stored 2 weeks in acetonitrile prior to analysis. The error bars represent typical standard deviations at the ambient levels of these analytes.

Table III. Regression Parameters for Linearity Test[a]

carbonyl compound	regressn coeff, r^2	no. of data points, n	SE y axis, mm	slope, mm/nM	y - intercept, mm
formaldehyde	0.988	7	0.06	0.12	0.42
acetaldehyde	0.995	7	0.75	0.17	1.20
propanal	0.988	10	0.86	0.31	−0.07
butanal	0.995	10	1.31	0.29	1.33

[a] Peak height (mm) versus concentration of carbonyl compounds added to coastal seawater (20–250 nM) and analyzed by direct injection.

investigators (*10*, *16*). We found that, even with the use of "carbonyl-free" solvents, solvent extraction steps introduce serious contamination at concentration levels present in seawater. In contrast, our cartridge enrichment/storage procedure apparently does not introduce any additional contamination, since there are no significant differences ($\pm 1\sigma$) between concentrations obtained by this procedure versus the direct injection method (Table I; Figure 3).

The detection limit of the direct injection method (signal-to-noise ratio of 3) is approximately 0.5 nM for most aldehydes and α-keto acids and ~5 nM for ketones. The detection limit can be easily lowered by about an order of magnitude by preconcentration of samples onto C18 extraction cartridges prior to analysis (Figure 4), but this results in a slightly higher error in the determination of formaldehyde.

Linearity and Precision. The response is linear for all compounds tested over the concentration range of 20–250 nM (typical for lake, river, and seawater) for both the cartridge enrichment procedure (20-mL sample volume) and direct injection (Table III). The precision of the direct injection method at levels typically found in natural waters was determined. The relative standard deviation at the 30 nM level for formaldehyde, acetaldehyde, propanal, hexanal, glyoxal, and glyoxylate was ~7% (n = 8). The additional error introduced by the cartridge extraction and storage procedure was usually negligible for most compounds tested, except for formaldehyde, where the relative standard deviation rose to ~15% at the 30 nM level (Figure 2). At lower concentrations, e.g., 10 nM formaldehyde, the precision of the cartridge technique remained at ~15%, as shown in Figure 3.

On-the-Fly Spectra and Peak Identification. A Hewlett-Packard photodiode array detector was used in

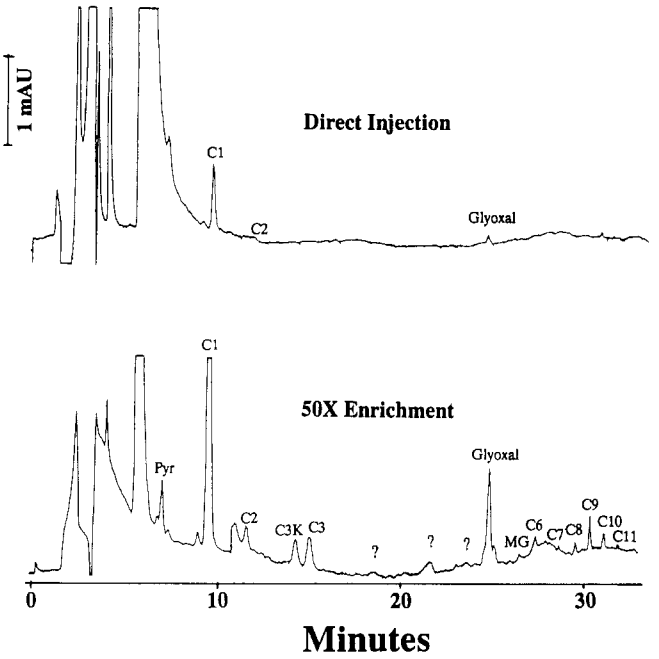

Figure 4. Comparison of direct injection with a cartridge enrichment (~50-fold) of an oligotrophic open ocean sample (Tongue of the Ocean, Bahamas; sampling depth, 200 m). Notation and concentrations (nM): Pyr, pyruvate (0.3); C1, formaldehyde (10); C2, acetaldehyde (0.3); C3K, acetone (6); C3, propanal (0.7); glyoxal (1.2); MG, methylglyoxal (<0.1); C6, hexanal (0.1); C7, heptanal (<0.1); C8, octanal (0.1); C9, nonanal (0.2); C10, decanal (0.1).

Table IV. Absorption Maxima of Carbonyl Hydrazones

carbonyl compound	λ_{max}, nm	carbonyl compound	λ_{max}, nm
DNPH	355	methional	360
glyoxal	435	glyceral	356
syringaldehyde	397	α-ketoglutarate	369
vanillin	392	hydroxybenzaldehyde	393
acetophenone	380	p-hydroxyacetophenone	390
acrolein	367	dihydroxyacetone	367
formaldehyde	350	acetoacetic acid	375
hexanal	350	ketoisovalerate	365
acetone	366	glyoxylate	351
butanone	366	pyruvate	351
hydroxyacetone	360		

conjunction with HPLC to obtain information concerning structure and purity of carbonyl compounds eluting from the chromatograph. Absorption spectra of standards in Figure 1b, as well as less common carbonyl compounds, were taken. The absorption maxima of these compounds in the HPLC eluate, ~60% acetonitrile/water (pH 2.6), are presented in Table IV and are in general agreement with past work (*17*, *23*).

The purity of an eluting compound was determined by comparison of absorption spectra at the leading edge, apex, and trailing edge of its peak. If these three spectra were identical, then the eluted peak was considered pure. Structural information was obtained by overlaying, scaling, and ratioing the absorption spectrum of an unknown peak to an authentic standard. This technique is useful for distinguishing between two compounds with similar retention times but different absorption characteristics, such as benzaldehyde and glyoxal. Cartridge enrichment was advantageous with respect to obtaining spectra of unknown compounds in natural samples, where ambient concentrations are usually too low to obtain good spectra.

Natural Samples. Concentrations of formaldehyde and glyoxal were determined as a function of depth at an oligotrophic site in the Caribbean Sea (Figure 3). Con-

Table V. Test of Sample Storage Procedure for Samples of Different Salinities in the Orinoco Estuary[a]

salinity, ppt	formaldehyde, nM		acetaldehyde, nM		glyoxal, nM	
	A	B	A	B	A	B
13.4	27.8	36.6	20.0	20.0	3.3	2.3
9.6	26.4	33.3	16.7	17.0	4.4	2.7
7.5	38.7	32.3	5.3	5.5	4.4	3.3
4.9	28.1	27.7	8.2	8.4	3.3	3.0
3.4	61.1	55.5	24.6	24.0	7.7	4.4
2.0	53.3	60.0	32.5	33.0	18.2	14.5
0.9	25.3	32.2	13.8	13.3	5.5	4.4
SD	±15%		±3%		±24%	

[a] Column A represents concentrations of carbonyl compounds obtained on day of collection by direct injection and column B after storage for 2 weeks in Sep-Pak acetonitrile eluate. Only one sample was analyzed at each site because the salinity was rapidly changing at that point in the estuary.

centrations were in the low nanomolar to midnanomolar range, which is similar to what was reported earlier for seawater (*1*, *2*), but significantly lower than observed for aqueous atmospheric samples (*4–6*, *12–15*). The good agreement between samples stored for 2 weeks and samples run by direct injection on the day of collection supports that the cartridge extraction/storage procedure is effective even when concentrations are in the low nanomolar range (average mean deviation for formaldehyde and glyoxal are 12 and 4%, respectively). In Figure 3, formaldehyde and glyoxal display several maxima in the water column as a result of natural processes, including photochemical production (*1–3*), atmospheric input (*12–15*), and biological processes (*24*).

A comparison of direct injection and sample storage techniques was also done for coastal water samples. Table V shows the results of analyses of carbonyl compounds through a salinity gradient in the Orinoco Estuary. Samples were analyzed on the day of collection by direct injection (column A) and after a 2-week storage period in the acetonitrile cartridge eluate (column B). Concentrations of carbonyl compounds in stored samples were in good agreement (within the precision of the cartridge method) with those determined on the day of storage, indicating that salinity had little effect on the enrichment procedure. The error for glyoxal is somewhat greater than that observed for the open ocean samples (Figure 3); however, considering that most concentrations were <5 nM, this error is still acceptable.

One of the major advantages of the cartridge enrichment method is that it can be used to greatly lower the detection limit when concentrations in samples are below 1 nM. An enrichment of an oligotrophic open ocean sample is shown in Figure 4. To our knowledge, this represents the most complete analysis of LMW carbonyl compounds in a natural water sample reported in the literature. Detailed open ocean (Sargasso Sea) profiles of carbonyl compounds using this approach will be presented elsewhere.

Acknowledgments

We thank R. J. Sikorski, X. Zhou, and D. J. Kieber for technical assistance and for valuable discussions during the development of this method.

Registry No. Formaldehyde, 50-00-0; acetaldehyde, 75-07-0; propanal, 123-38-6; butanal, 123-72-8; glyoxylate, 298-12-4; pyruvate, 127-17-3; glyoxal, 107-22-2; methional, 3268-49-3; furfural, 98-01-1; heptanal, 111-71-7; octanal, 124-13-0; nonanal, 124-19-6; decanal, 112-31-2; methylglyoxal, 78-98-8; acetone, 67-64-1; water, 7732-18-5; 2,4-dinitrophenylhydrazine, 119-26-6.

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Received for review January 12, 1990. Accepted May 1, 1990. This work was supported by grants from the Chemical Oceanography Program of the U.S. National Science Foundation (OCE-8613940 and OCE-8917709).