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## Flow Injection Analysis of Organic and Inorganic Carbon in the Low-ppb Range

Stefan A. Huber and Fritz H. Frimmel\*

*Engler-Bunte-Institut der Universität Karlsruhe, FB Wasserchemie, 7500 Karlsruhe, Germany*

A cylindrical thin-film reactor with an actively rotating inner cylinder and a central low-pressure mercury lamp can be used for the continuous determination of organic carbon (OC) and inorganic carbon (IC) in the low  $\mu\text{g/L}$  concentration range. The separation of inorganic carbon is performed in the upper UV-shielded part of the reactor by continuous acidification. In the lower part the sample is exposed to UV irradiation and organic carbon is converted into carbon dioxide. The carbon dioxide released in both processes is quantified by high-sensitivity infrared spectrometry. The linear range is about 3 orders of magnitude. Owing to the low dead volume, the reactor can be used as an organic carbon detector for liquid chromatography (LC, HPLC). Furthermore, the oxidized reactor outflow can be used for further analyses. The first prototype of the reactor was developed by a private company in 1980. Since then it has constantly been improved. This is the first publication on the reactor since 1983.

Some 20 years ago, two different reactor principles for oxidation of organic compounds were developed. The analyzer described by Axt (1) was based on thermal oxidation and was

operated in a continuous working mode. Although the instrument was later used for liquid chromatography detection (2), it has never been adopted for routine analysis because of practical problems with accumulating salts. Another analyzer developed by Woelfel (3) used a low-pressure ultraviolet (UV) lamp in a batch reactor for wet combustion. This method proved to be inconvenient for continuous measuring because the irradiation exposure times for quantitative oxidation were far too long.

The manufacturer of both prototypes recognized the pitfalls of these principles and began to develop a new reactor type which used UV thin-film technology for the separation and oxidation of inorganic carbon (IC) and organic carbon (OC). To improve the speed and completeness of both reactions, a novel active stirring mechanism was introduced. The first commercially available instruments appeared in 1981 and two papers (4, 5) assessed the potentials of the new instrument, which is the subject of a patent (6). Since then several studies and master theses devoted to the apparatus have remained unpublished. In cooperation with our institute the manufacturer has further improved the reactor in recent years. The constancy of all gaseous and liquid reactor inflows and outflows was improved, and optimal working conditions were

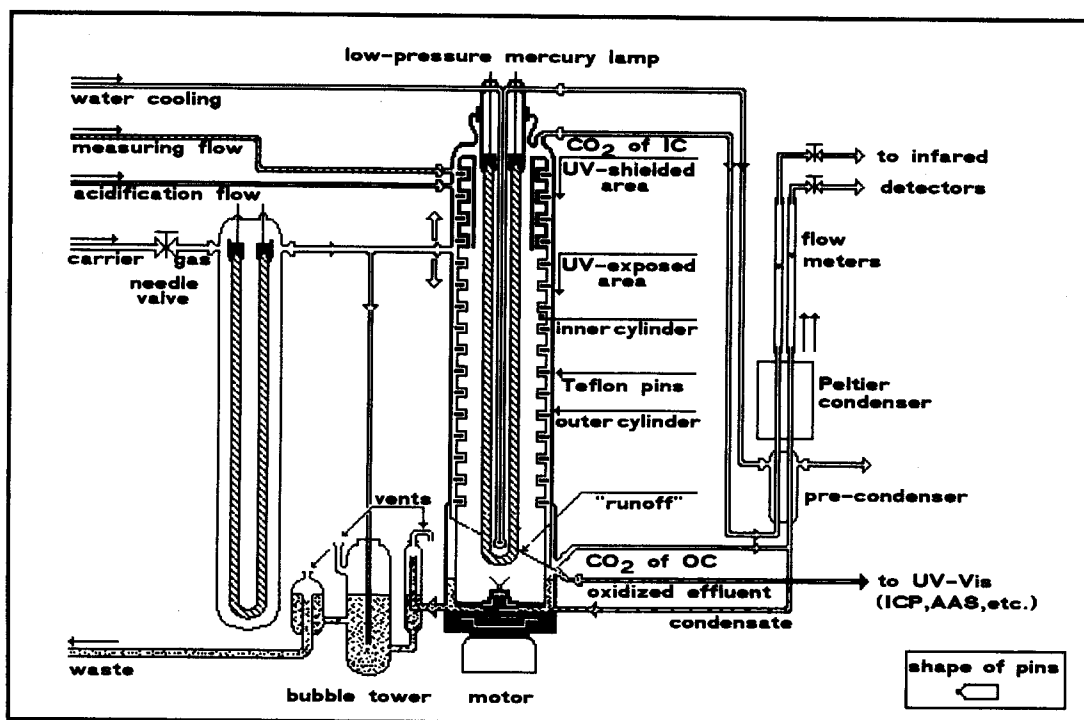


Figure 1. General outline of the thin-film reactor for high-sensitivity OC detection.

Table I. General Features of the Thin-Film Reactor

total length	47 cm
total diameter	8 cm
rotor speed	350–750 rpm
liquid volume	2–3 mL
sample residence time	1–3 min
exposed area UV	600 cm <sup>2</sup>
exposed area stripping	250 cm <sup>2</sup>
thickness of aqueous film	0.1–0.2 mm
length of UV lamp (U-shape)	1 m
energy input	300 mA, 450 V
wavelengths	254 nm (82%), 185 nm (18%)

systematically determined. A cooling device for the UV lamp was installed to increase the energy output. The improved reactor can now be used for OC determination in routine analysis or in combination with liquid chromatography as an OC detector in the low  $\mu\text{g/L}$  range. To our knowledge, this is the first report on a nonselective and high-sensitivity detector for liquid chromatography.

The objective of this work is (a) to describe the recent status of the system, (b) to show some results gained under typical working conditions, and (c) to give an application for LC.

**Description of the Reactor.** The working principle of the reactor is a gravity-flow falling film (Figure 1).

The sample to be measured is fed into a continuous flow of extremely low OC water. This flow ("measuring flow") enters the upright reactor at its upper end and flows downward by gravity. At the lower end the flow leaves the reactor either by reason of hydrostatic pressure differences inside and outside the reactor and/or by means of pumping through a separate outlet. Some data on the reactor are given in Table I.

The reactor has two distinct features, one is the on-line stripping of  $\text{CO}_2$  derived from IC, the other is the mechanism by which the measuring flow is spread out as a thin film to improve the efficiency of stripping and oxidation.

**Separation of Inorganic Carbon.** One of the biggest problems in high-sensitivity OC measurements is the quantitative removal of primary  $\text{CO}_2$  and carbonaceous salts in the sample. Some analyzers require a carbonate stripping step

before sample injection, while others conduct automated stripping in a chamber separate from the oxidation reactor. The reactor described here consists of only one cylindrical chamber in which both elimination of carbonate and oxidation of OC are performed on-line.

A carrier gas flow (purified nitrogen) enters the reactor and is forced after splitting to flow in two opposite directions. In the upstream direction, the gas passes a UV-shielded upper part of the reactor and purges the  $\text{CO}_2$  from the acidified measuring flow. The gas leaves the reactor via a small opening at the top of the outer cylinder and carries all the  $\text{CO}_2$  equivalent to the carbon of inorganic origin. Volatile organic compounds (VOC) will also leave the reactor through this opening. This may lead to lower yields when the total organic carbon (TOC) content of the sample has to be determined. However, this loss is negligible in most cases. For the control and quantification of VOCs, flame ionization detection (FID) may be suitable.

The continuous acidification of the measuring liquid is accomplished inside the reactor by means of acidified low OC water. This "acidification flow" is brought into the reactor by gravity flow through glass capillaries.

In the downstream direction, the carrier gas passes the UV-irradiated part of the reactor and purges the  $\text{CO}_2$  that has been produced by UV oxidation of nonvolatile organic carbon. This  $\text{CO}_2$  leaves the reactor via a small opening at the bottom end.

The reactor outflows for IC and OC are connected to high-sensitivity infrared detectors for the quantification of  $\text{CO}_2$ . Infrared spectrometry is probably the most sensitive and most reliable detection method for  $\text{CO}_2$  in current use (7). The spectrometers employed for this purpose were equipped with large flow cells and a series of filters to reduce cross sensitivity.

**Oxidation of Organic Carbon.** The effectiveness of oxidation of organic compounds is greatly enhanced when a low-pressure mercury lamp is used as a source for short wavelength UV irradiation (8). The details of the photochemical processes in the reactor have not yet been investigated, but it is assumed that organic molecules are attacked in two ways. The long-wavelength UV irradiation (254 nm)

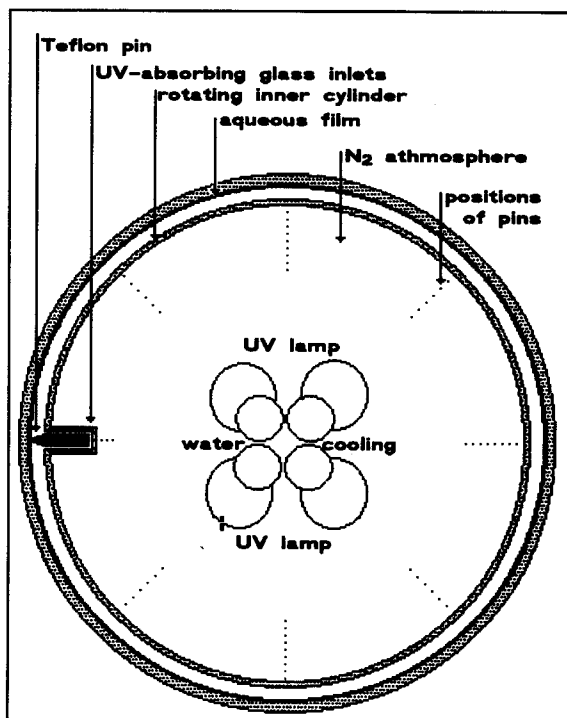


Figure 2. Cross section through the UV-irradiated part of the thin-film reactor showing the cooling device, the positions for the UV lamp, the Teflon pins, and the liquid film.

attacks mainly UV-active areas in the molecule and the short-wavelength UV irradiation (185 nm) produces OH radicals that react nonspecifically with organic compounds. No oxygen-carrying agents were introduced. Radiolysis of water is therefore assumed to be the source for oxygen since oxygen-free conditions prevail in the reactor. Hydrogen should be the resulting byproduct.

The temperature of the lamp can be controlled through a recently patented water-cooling device (9, Figure 2). By this means, the emission spectrum and energy distribution can be influenced.

**Active Stirring of the Thin Film.** One property of low-pressure UV irradiation is its low-penetration depth in water. Spreading of the liquid as a thin film will greatly improve oxidation efficiency and reaction speed. To achieve this, some problems have to be solved. Firstly, cohesion processes that disrupt the thin film and form "water channels" toward the lower end of the reactor have to be avoided. Secondly, the kinetics for the oxidation of OC has to be fast enough to guarantee a quantitative yield for the given reactor residence time. The required oxidation speed can be obtained when active stirring moves the molecules close to the liquid film surface for optimal UV exposition. Finally, for the CO<sub>2</sub> removal from the solution, a highly effective phase transfer has to be achieved.

To meet these objectives, an active stirring mechanism is mandatory. An inner cylinder, rotating at high speed, was fitted into the reactor. The cylinder is equipped with about 200 minute Teflon pins that are placed perpendicularly in small glass sockets into the inner cylinder surface (Figure 2). Rotation of the cylinder at 350 up to 750 rpm forces the pins to penetrate the liquid film. Thus they act as minute stirring, cleaning, and grinding bars.

The positions of the pins describe the shape of a spiral. Depending on the direction of rotation of the inner cylinder, this will either "drag" the film downward or upward, which then will yield a thicker film. By this means the pins can influence the residence time of the liquid in the reactor. The inner cylinder is made of ultrapure silica glass ("Suprasil"),

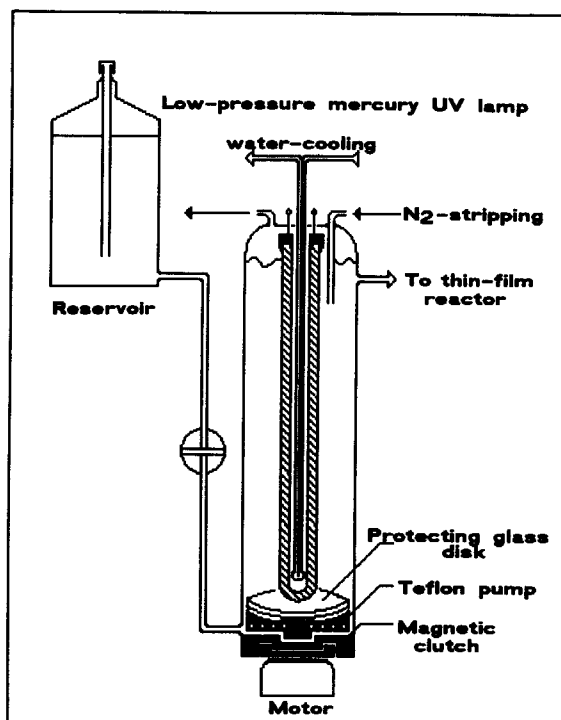


Figure 3. General outline of the UV batch reactor for the production of low organic carbon water.

which allows penetration of low-wavelength UV irradiation. The small inlets for the pins are made of UV-absorbing glass in order to prevent long-term destruction of the pins. The UV lamp itself is placed in the center of the inner cylinder. The space between the UV lamp and the inner cylinder is continuously purged with carrier gas (N<sub>2</sub>) to prevent the production of ozone and to minimize UV absorption.

**Production of Low Organic Carbon Water.** The reactor operates with two constant water flows, transporting (a) the measuring liquid and (b) the acidification liquid. Both liquids bring a certain OC contamination into the reactor. When low concentrations of carbon are measured, the background OC level for both liquid flows must be minimal. For this, two external "zero water" batch reactors were added which use UV for photochemical oxidation (Figure 3).

Both reactors are filled with double-distilled water (DDW) and are operated in a continuous working mode. The reactors are made of silica glass and are equipped with Teflon centrifugal pumps (10) for intensive stirring. All Teflon parts are protected against UV irradiation by UV-absorbing glass disks. The average residence time of a solution in the reactor is more than 30 h at flow rates of 1 mL/min. A nominal OC background concentration of 4 µg/L was found by addition. The original DDW has OC concentrations between 40 and 120 µg/L.

## EXPERIMENTAL SECTION

**Experimental Setup.** For all measurements, an analytical combined system (Figure 4) with two infrared detectors and two UV detectors was used.

The UV detectors were connected to the reactor measuring liquid inflow and liquid outflow. By this means, the UV absorbance of the calibration solution before and after oxidation was controlled. Figure 5 shows the signals of the four detectors according to Figure 4 obtained for seven measurements of nicotinic acid.

The final two measurements were made with the reactor UV lamp shut off in order to assess peak broadening. Due to the change in pH by acidification in the reactor a direct comparison of the two UV signals is not possible. Nicotinic acid, which showed no signal response in the outflow when the lamp was on, gave a

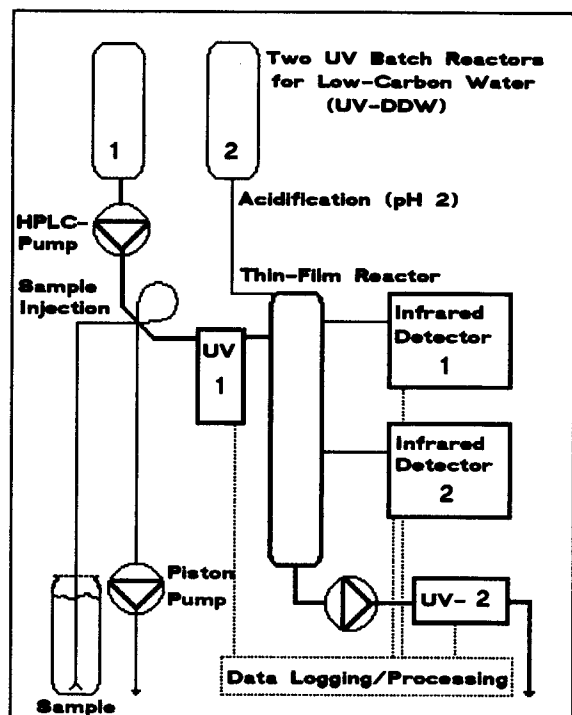


Figure 4. Flow diagram of the analytical system for the characterization and determination of organic matter in aqueous samples: UV<sub>1</sub>, 2 (UV-vis detectors); UV DDW<sub>1,2</sub> (UV batch reactors for low-carbon water).

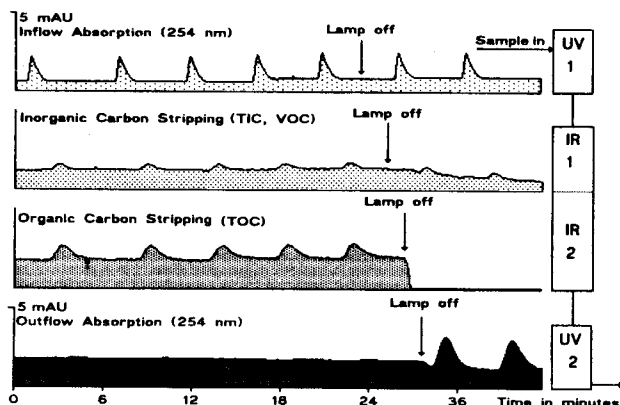


Figure 5. Multidimensional detection of seven injections of 38 ng of nicotinic acid: UV<sub>1</sub> (254 nm, 5 mAUFS reactor inflow side); IR<sub>1</sub> (IC); IR<sub>2</sub> (OC) and UV<sub>2</sub> (254 nm, 5 mAUFS at reactor outflow side). Impact of switching off the reactor lamp is shown (injections 6 and 7).

clear response when the lamp was shut off. The signal time shifts reflect the dead volumes of the tube connections of the combined analytical system.

The sample injector was a four-way manual valve with Teflon loops. The liquid sample is brought into the loops through capillaries (PEEK) by means of reduced pressure to minimize the risk of contamination.

The UV<sub>1</sub> detector was used to correct for systematic errors caused by badly calibrated sample loops. The UV<sub>2</sub> detector was used to control the oxidation efficiency and to detect a possible formation of UV-active inorganic reaction products.

**Instruments. Reactors.** The UV thin-film reactor and both UV batch reactors for the production of water with low organic carbon are of the design by Graentzel, Karlsruhe (Germany). For all measurements the instrument was operated as follows: carrier gas (nitrogen) for both "organic" purge and "inorganic" purge 20 L/h; acidification liquid 2 mL of H<sub>3</sub>PO<sub>4</sub> concentrated, diluted in 2 L of UV-DDW (pH 2.07); acidification flow rate 0.37 mL/min (capillary with 0.4 mm diameter); measuring flow rate (UV-DDW) 1 mL/min; rotor speed of inner cylinder 450 rpm in the downward direction. The thin-film reactor UV lamp was set at 300 mA. The UV lamp cooling device was set at 9 °C. At the time of this study,

this lamp had passed about 8.500 h of operation in 5 years. The nitrogen carrier gas was purified ("continuous flow") in a 2-L batch reactor with a low-pressure UV lamp, placed at the thin-film reactor gas inflow side.

**Infrared Detectors.** Ultramat 3 detectors, Siemens, Karlsruhe (Germany) with 18-cm flow cells and a flow cell volume of 88.5 mL were used. The nominal sensitivities were set at 5 IAUFs (infrared absorption units full scale) for the organic flow (IR<sub>1</sub>) and 20 IAUFs for the inorganic flow (IR<sub>2</sub>).

**Both UV-vis Detectors.** Model 200 detectors, Linear Instruments (USA) with variable wavelength were used. The flow cells had a volume of 15 µL. Wide capillary metal tubings were used in order to have minimum flow resistance. The inflow detector (UV<sub>1</sub>, 254 nm) run with a sensitivity of 5 mAUFS for 100 µg/L OC solutions and 25 mAUFS for 1 mg/L OC solutions. The outflow detector (UV<sub>2</sub>) was set at 210 nm with a sensitivity of 2 mAUFS.

**Pumps.** An HPLC pump was used at the reactor inflow side ("Solvent Delivery Module 112", Beckman, Fullerton) and at the reactor outflow side ("420" (double-piston pump with 25-µL head volume)), Kontron, Eching (Germany). The sample injection pump was a "P-500" (low-pressure piston pump), Pharmacia, Uppsala (Sweden).

**Sample Injection Valve and Connections.** A four-way manual valve with Teflon tubing, Rheodyne (USA) was used. The UV-vis detectors were connected with PEEK tubing of 0.5 mm inner diameter (i.d.). The infrared detectors were connected with Teflon tubing of 5 mm i.d. with a length of about 1.5 m.

Masses were determined with a microbalance 4503 micro, Sartorius, Goettingen (Germany). Data logging, data processing, and data presentation were by Rhrothron, Homburg-Saar (Germany), on ATARI-compatible computers.

**Chemicals.** The chemicals used were potassium hydrogen phthalate (PHP, Merck 4874) for all calibrations, nicotinic acid (NIC, Fluka, 72309), pentachlorophenol (PCP, ICN 18397), dried fulvic acid (FA), and UV-irradiated seawater. The FA dry material was prepared according to ref 11 in the following way: Brown water from Lake Hohloh (Black Forest, 1000 m above sea level) with a DOC of 17 mg/L was filtered through filter paper (black ribbon, Schleicher & Schuell No. 595), acidified to pH 2 with concentrated HCl. The FAs were adsorbed onto a column filled with purified XAD-2 resin. The adsorbate was cleaned with DDW and eluted with 0.2 M NaOH. The eluate was transformed into the H<sup>+</sup> form by passage through a protonated cation-exchange column (Dowex, Serva 41551). The eluate was freeze-dried immediately.

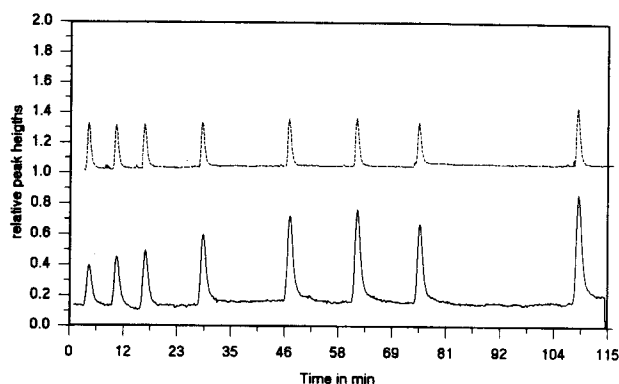
The seawater was sampled from an offshore oligotrophic area of the western Mediterranean (kind donation of Dr. Spitzi, Max-Planck-Institute of Meteorology, Hamburg, Germany).

The calibration solutions with a concentration of 100 µg/L OC were prepared after the following procedure: A stock solution "A" was prepared by dissolving 2125 mg of KHP in 1 L of DDW. A 10-mL aliquot of "A" was added to 1 L of DDW (stock solution "B" with 10 mg/L OC). This solution is stable for several weeks. For most calibrations a solution of 0.1 mg/L was prepared by pipetting 10 mL of solution "B" into 1 L of UV DDW. This solution was freshly prepared every 5 h. The solutions for NIC, PCP, and FA were prepared by dissolving weighed amounts of the substances (0.396 mg for NIC, 0.291 mg for PCP, and 0.630 mg for FA). These were quickly transferred into a 1-L calibration flask and were dissolved in 1 L of UV DDW about 2 h before measurements. For PCP, a drop of 0.1 M NaOH (purified under UV irradiation for 4 h) was added to improve dissolution.

**Chromatographic Conditions.** Column TSK HW 40 (S) (distributed by Merck) 90 × 1.6 cm; sample volume 1.5 mL; elution rate 1 mL/min with UV DDW and phosphate buffer pH 6.37 (2.5 g/L KH<sub>2</sub>PO<sub>4</sub> and 1.5 g/L Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O). The buffer solution was irradiated in one of the UV batch reactors for 30 h to eliminate organic impurities. UV<sub>1</sub> setting was 254 nm and 5 mAUFS; IR<sub>1</sub> was set at 5 IAUFs and IR<sub>2</sub> was set at 20 IAUFs.

## RESULTS AND DISCUSSION

To assess the performance of the reactor for OC and IC measurements in combination with infrared detection, the following studies were carried out to determine and to optimize the (a) reactor residence times for liquids, (b) detection limit



**Figure 6.** Influence of airborne material in the laboratory on OC concentration and UV absorption: A series of eight measurements of UV-irradiated double-distilled water in an open glass beaker shows almost constancy for UV (254 nm, 5 mAUFS, stippled line above), while the OC concentration rose from 31  $\mu\text{g/L}$  up to 110  $\mu\text{g/L}$  (solid line below).

and determination limit for OC, (c) linear range, (d) universality (oxidation power), (e) elimination efficiency of IC, (f) matrix effects, (g) measurable size range, and (h) application to liquid chromatography.

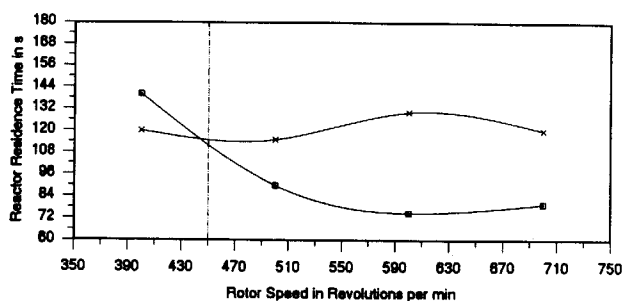
As a prerequisite to all experiments, the stability of the calibration solutions and potential contamination problems had to be investigated. The OC concentration values obtained in these experiments were determined post festum following eq 4.

**Stability of Solutions.** The stability of low OC solutions was qualitatively checked. A solution of 100  $\mu\text{g/L}$  OC (as potassium hydrogen phthalate, PHP) had a half-life of about 40 h and a solution of 50  $\mu\text{g/L}$  OC had a half-life of about 4 h at ambient temperatures only. This showed that for practical purposes the minimum concentration for calibration should not be below 100  $\mu\text{g/L}$  OC for longer measuring sequences. For single measurements, 50  $\mu\text{g/L}$  OC concentrations seemed to be acceptable.

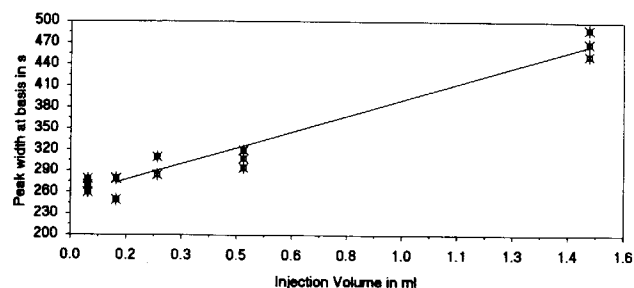
**Contamination via Air.** To assess the influence of airborne OC in the laboratory, a simple experiment was carried out. A 100-mL aliquot of UV DDW with a nondetectable OC background concentration was poured in an open glass beaker of 300-mL volume with a magnetic stirring device (beaker and stirring bar cleaned with 0.01 M NaOH and UV DDW three times, 20 min each time). The OC concentrations were determined over a period of 2 h. The initial OC concentration right after pouring the water into the beaker was 31  $\mu\text{g/L}$  OC. Within the following 1.5 h the OC first rose continuously and seemed to level off at a concentration of about 110  $\mu\text{g/L}$  OC (Figure 6). The UV absorbance (254 nm, 5 mAUFS) was checked parallel to the measurements and did not show any significant increase.

We assume that the instantaneous OC increase could be attributed to airborne organic material which was trapped while the beaker was filled. The following increase may reflect a homogenization of particulate matter distribution by the stirring mechanism, rather than dissolution of particulate matter in the water. This would explain the constancy of UV absorption, since UV absorption is little influenced by particulate matter at low concentrations. Additionally, glass wall contamination and adsorption/desorption processes may have contributed to the results.

As a consequence, great care must be taken when preparing calibration solutions with low OC concentrations. Transfer of low OC water should be kept to a minimum, and unnecessary contact with the surrounding atmosphere should be avoided. The glass surface to liquid ratio should be similar for all calibration solutions. The flasks should be opened only once and then should be sealed quickly with aluminum foil during measurements. Only with these precautions repro-



**Figure 7.** Influence of rotor speed and rotor sense of direction on the reactor residence time ( $\square$  = downflow direction,  $\times$  = upflow direction).



**Figure 8.** Determination of the influence of injection volumes on peak width.

ducible measurements can be expected.

Due to these findings we decided to carry out all further experiments with solutions of similar OC concentrations and to change the loop volumes instead. Systematic errors would then be reduced to the variances in the loop volumes, which can be corrected (if necessary) by means of the UV absorption signals that were obtained at the same time. For UV absorption, linearity can be assumed according to Lambert-Beer's law. In a second step the determined OC masses obtained in this way were converted into concentrations since, in practice, concentration values are far more valuable than absolute masses.

**Reactor Residence Times for Liquids.** A solution of potassium permanganate as a stable mineral dye was used to determine the reactor residence times for the liquid phase dependent on the inner cylinder direction of rotation and revolutions per minute. The residence times were determined by eye with a stopwatch. The results are shown in Figure 7.

All further measurements were carried out at 450 rpm in the downflow direction with an average reactor residence time of about 110 s.

**Conversion of Masses OC into Concentrations OC.** This conversion step was necessary since calibrations were carried out by changing both loop volumes and sample concentrations (see last paragraph in the Introduction). Absolute quantities of OC can be converted into concentrations when no significant peak broadening is observed within a given quantity range of injected liquid. In other words, if the peak widths are similar for the smallest loop used (0.132 mL; see below) and for the largest loop used (1.5 mL), then it can be assumed that the amount of organic carbon detected in the 0.132-mL loop can also be found in the 1.5-mL loop. Figure 8 shows the influence of the sample volume on the peak width. The measurements were carried out with a 50  $\mu\text{g/L}$  OC solution.

The peak width was measured manually at the peak basis between the integration limits after signal enlargement. It was found that a peak volume ratio of 1:10 yielded a peak width ratio of 1:1.7 only. The reason for this only slight increase is the relatively large reactor dead volume (2 mL) and the large IR detector flow cells (88.5 mL). Thus the injection volumes did not influence strongly the width of the signal peaks.

Table II. Calibration Data Set for the Determination of the Linear Range

	calc loop vol, mL (see text)	effective conc, $\mu\text{g/L}$ OC	calc conc, in $\mu\text{g/L}$ OC (see text)	mean ( $n = 4$ )	st dev	var coeff, %
UV	1.13	1000		3.90	0.0071	1.8
	0.63	1000		2.50	0.0034	1.3
	1.63	100		0.566	0.0129	4.4
	0.63	100		0.215	0.0112	1.8
	0.38	100		0.143	0.003	2.0
	0.18	100		0.074	0.0036	4.9
	0.13	100		0.049	0.0035	7.1
	0.13	50		0.028	0.0038	14
OC			770	7.24	0.031	0.43
			504	4.82	0.034	0.85
			134	1.485	0.031	2.1
			44.6	0.51	0.029	5.7
			26.0	0.362	0.022	6.1
			12.3	0.21	0.028	13.3
			9.0	0.104	0.021	19.7
			4.5	0.054	0.0063	11.7

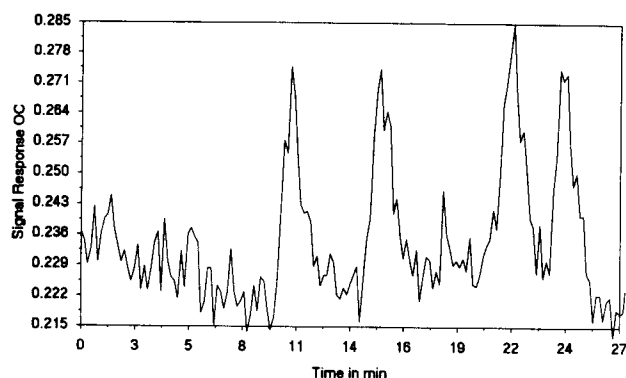


Figure 9. Signal responses for 6.6 ng of organic carbon (four injections) for the assessment of the detection limit and the determination limit (counting rate 5 s).

On the basis of these findings it can be postulated with good confidence that the detected minimum mass of OC in the smallest loop (0.132 mL; see below) could also be detected without difficulty in the largest loop used (1.5 mL). Therefore all quantities of OC were normalized for 1.5 mL:

$$\text{calc sample conc } (\mu\text{g/L}) = \frac{\text{quantity of OC (ng)} \times 1/\text{reference volume (1.5 mL)}}{(1)}$$

**Detection Limit and Determination Limit.** According to IUPAC guidelines, the detection limit is given as 3 times the standard deviation, and the determination limit is given as 10 times the standard deviation. A 132- $\mu\text{L}$  aliquot (see below) of 50  $\mu\text{g/L}$  OC was injected. The total mass of OC was 6.6 ng. Figure 9 shows four measurements at this level.

According to eq 1, the injected mass was converted into a concentration (4.5  $\mu\text{g/L}$  OC, see also Table II below). For the detection limit a concentration of 1.5  $\mu\text{g/L}$  OC was obtained; the resulting determination limit is 4.9  $\mu\text{g/L}$ .

**Linear Range.** The linear range was studied with sample volumes of 1.5, 0.5, 0.25, 0.05, and 0.132 mL (injector dead volume; see below). The carbon concentration used was 100  $\mu\text{g/L}$  OC as PHP. For higher OC amounts, a concentration of 1 mg/L OC with the 0.5- and 1-mL loops was used. A correction for the 0.5-mL loop was necessary because the experimental data were about 10% above the regression line. Without this loop, the correlation coefficient rose from 0.989 to 0.999. On the basis of assumed linearity for UV absorbance values, a "bad loop" was presumably the reason. The correction was carried out by putting the mean of this level on the linear regression line. The correction factor was then

applied to the corresponding OC values.

The linear regression function for the UV calibration is  $f(x) = 0.00504x + 0.0133$ ,  $r = 0.9995$ ; the linear regression function for OC is  $f(x) = 0.00939x + 0.0762$ ,  $r = 0.9996$ . The poor correlation between the variation coefficients at different concentration levels (Table II) was attributed to technical problems with the manual injection valve. We found that the reproducibility of the UV signals was strongly influenced by the speed with which the valve was switched. The switching may have caused turbulences and/or may have released UV-active substances. However, this had no impact on the general linearity of the graph.

An adjustment was made to correct for the dead volume of the sample injection valve to all injected volumes. This was done by directly connecting the loop fittings of the injection valve. The dead volume of the valve was determined by extrapolating the regression line for the 0.25-mL loop, the 0.05-mL loop, and the dead volume loop (nominally 0.0 mL). A volume of 0.132 mL ( $\pm 10\%$ ) was found. All processed data for UV and OC calibration are shown in Table II.

A simple linearity test for the entire range of the OC signals was carried out. The variances of the residuals of the linear regression function  $f(x) = bx + a$  were compared with the variances of the residuals obtained by the parabolic function  $f(x) = a + bx + cx^2$ .  $S_{1xy}$  are the residuals of the linear regression with  $n = 32$  and  $f = n - 2$

$$\frac{S_{1xy}^2}{S_{2xy}^2} < F_{95} ? (3.44, \text{ for } n = 4) \quad (2)$$

$S_{2xy}$  are the residuals of the parabolic function with  $n = 32$  and  $f = n - 3$ .

Due to an additional free parameter, the parabolic function will give a better fit. By means of the  $F$  test it was checked whether this improvement of fit was significant (95% confidence limit) or not. A value of 3.44 was found, which by coincidence is just the  $F$  test significance value. This shows that the linearity test did not conflict with the postulated linear relationship between concentration and signal response. The linear range extends from 4.5  $\mu\text{g/L}$  OC up to 770  $\mu\text{g/L}$  OC. This is more than 2 orders of magnitude. The calibration function is given as

$$f(x) = 0.00939x + 0.0762 \quad (3)$$

The analytical function is given as

$$(\text{conc})x (\mu\text{g/L}) = \frac{\text{area units} - 0.0762}{0.00939 \times \text{sample vol (mL)}} \quad (4)$$

In this study only the dynamic range that could be used

**Table III. Calibration Data Set for Assessing the Oxidation Rate for NIC, PCP, and FA**

	calc loop vol, mL (see text)	mass, ng as OC	mean (n = 4)	st dev	var coeff, %
nicotinic acid (NIC)	1.63	351	2.22	0.059	2.6
(0.369 mg/L)	0.63	136	0.806	0.036	4.5
	0.38	82	0.57	0.048	8.4
	0.18	38	0.228	0.027	11.8
pentachlorophenol (PCP)	1.63	128	0.58	0.036	3.7
(0.291 mg/L)	0.63	49	0.33	0.022	6.6
	0.38	30	0.21	0.027	12.5
	0.18	14	0.12	0.017	14.1
fulvic acid (FA)	1.63	492	2.765	0.103	3.75
(0.630 mg/L)	0.63	190	1.15	0.067	5.8
	0.38	116	0.66	0.059	8.8
	0.18	54	0.243	0.036	14.9

without changing the amplification of the detector signals was regarded. The linear range can be extended up to 3 mg/L OC and down to below 1  $\mu\text{g/L}$  OC by changing the operation conditions.

**Universality.** The universality of the detector was assessed by studying the oxidation rate of different classes of compounds that are known to be relatively stable against oxidation agents.

We chose three model compounds: nicotinic acid (NIC), pentachlorophenol (PCP), and fulvic acid (FA). NIC was chosen to see whether a stable nitrogen-containing compound can be oxidized and whether a potential formation of nitrate (or nitrite) can be detected in the reactor outflow by UV absorption. PCP is a highly chlorinated and relatively stable organic compound. Finally, FA represents one of the main organic constituents in aquatic systems.

In Table III the results of the measurements and some basic statistical data are shown. The obtained regression functions are  $f(x) = 0.009677x + 0.0257$  (NIC),  $f(x) = 0.009820x + 0.0493$  (PCP), and  $f(x) = 0.009648x + 0.0100$  (FA).

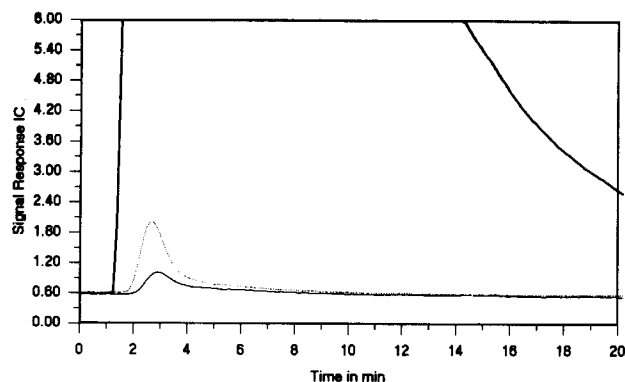
The slopes for all functions are extremely similar, which indicates that the oxidation efficiency and the sensitivity were independent of the compound used.

The ratio of the slope of one of the compounds and the reference compound (PHP, slope is 0.00939) gives the recovery rate for OC in percent. The results obtained were 103% for NIC, 104% for PCP, and 102% for FA (compared with thermal elemental analysis, 12). These data indicate a total mineralization of all three compounds.

Owing to the continuous working mode of the reactor, an independent second method for the assessment of the destruction of organic compounds is possible by analyzing potential inorganic reaction products in the reactor outflow.

For UV-active inorganic reaction products, the UV detector at the reactor outflow was set at 210 nm with the maximum sensitivity of 2 mAUFS. For PHP, no signal response was found in the outflow even at higher concentrations. This showed that the aromatic ring was destroyed completely and no UV-active products were formed. This result proves the total destruction of the aromatic ring. For PCP, weak responses were found at the highest concentration level only. FA and NIC, in contrast, gave responses that were well detectable even at the lowest concentration level.

It must be assumed that the responses obtained for PCP, NIC, and FA reflect OC-free byproducts which were formed in the oxidation process. For PCP this may have been released chloro compounds. The strong signals for NIC and FA presumably reflected secondary nitrate or nitrite. For FA, other salts such as phosphate or sulfate, which would have been formed from organically bound phosphorus and sulfur, would



**Figure 10.** Determination of 100 mg/L IC (as potassium hydrogen carbonate, thick line). At the same time a nominal OC value of 117  $\mu\text{g/L}$  was determined (stippled line). After UV treatment this OC was reduced to 46  $\mu\text{g/L}$  (thin line).

not have been sufficiently UV-sensitive to be detectable.

To assess the potential formation of nitrate, a correlation of the outflow signals for NIC and FA with nitrate was carried out. A nitrate calibration solution with a concentration of 10  $\mu\text{g/L}$  was injected, and the resulting signal was compared with the signals obtained for NIC. After conversion, a nitrogen content of 12.1% was found for NIC, which is close to the theoretically predicted value (11.3%). For FA, a nitrogen content of 1.63% was found, which correlates well with the 1.73% that was determined earlier by elemental analysis (12).

The results indicate that no UV-absorbing organic material had left the reactor. Moreover, our analytical system can also be used to quantify the organic nitrogen content or organic compounds as secondary nitrate at low concentrations.

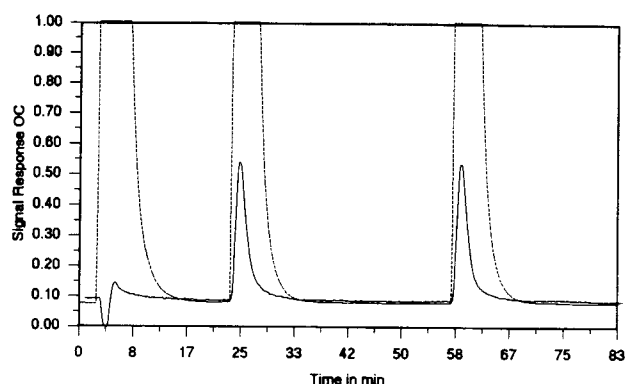
So far, all oxidizable organic substances we have measured were quantitatively mineralized. Only substances that are already in a fairly oxidized state, such as uronic acid or melamine, have shown lower yields.

**Elimination of Inorganic Carbon.** To assess the elimination capacity of the stripping device, 100 mg of IC as potassium hydrogen carbonate was dissolved in 1 L of UV DDW and injected. The signal response for inorganic carbon was far beyond the upper limit of the detection range (Figure 10). For OC, a nominal concentration of 117  $\mu\text{g/L}$  was found. There are two attractive explanations for that: (a) the "OC" comes from an overload in IC; (b) there are organic impurities in the carbonate salt. To eliminate potential organic impurities, the carbonaceous solution was exposed to low-pressure mercury UV irradiation in a small batch reactor with a volume of 50 mL. After an exposure time of 2 h the solution was injected again, and this time a concentration of 46  $\mu\text{g/L}$  was found.

Further exposure did not change the OC concentration significantly; therefore, this concentration may reflect IC that was not stripped. The elimination rate for IC would then be about 2000:1, which should be sufficient for most purposes. For very high loads of IC in the sample, a chromatographic size-exclusion column for in-column desalting should be connected to the reactor inflow.

**Matrix Effects.** It has been shown (13) that orthophosphate, which was used as a buffer salt for liquid chromatography, did not interfere with the OC determination up to concentrations of several grams per liter. No detailed information on the effect of strongly UV absorbing nitrate is available. One unpublished study (14) shows a recovery loss of about 30% up to 1 g/L, but between 2 and 5 g/L no interference was observed. We found no influence on OC recovery at 1 g/L nitrate, but slight losses were found in the mg/L concentration range. The discrepancy may be explained by the cooling device with which our UV lamp was equipped to enhance the generation of shortwave UV irradiation. More





**Figure 11.** Determination of 250  $\mu\text{g/L}$  OC (as potassium hydrogen phthalate) in a 1:1 diluted pretreated seawater matrix. The stippled line is the UV absorption (254 nm, 5 mAUFS) at the reactor inflow side. The time offset between the two detectors was corrected. The first injection (1) is the oxidized seawater blank.

detailed studies are planned. In practice, nitrate can be separated from OC when the reactor is used in combination with size exclusion chromatography.

The same author (14) also studied the influence of metals and found no significant OC losses in the presence of the metals copper, magnesium, nickel, palladium, tin, and lead at concentrations between 10 and 1000 ppm.

For this study the influence of NaCl on OC recovery was studied by using seawater as the matrix. The seawater sample was exposed to UV light in a small batch reactor for 12 h to oxidize the natural OC content. Figure 11 shows the responses for UV and OC for the original seawater and for seawater mixed with an aliquot of 500  $\mu\text{g/L}$  OC (as PHP) solution.

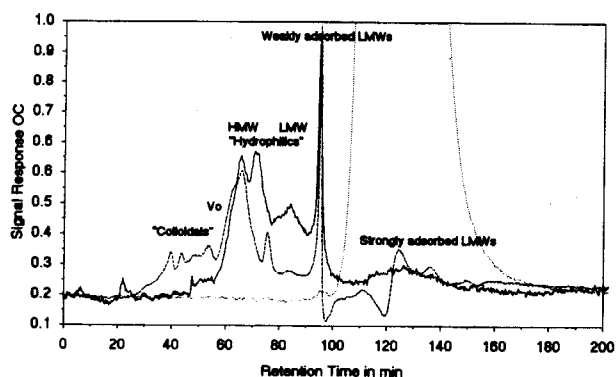
The treated seawater blank (1) showed a negative signal response for OC detection. The reason for this is not known. The OC recovery in the 1:1 diluted matrix was 83%. This value rose to 95% after correction for the negative blank value. More reliable and more informative results can be obtained when the detector is used in combination with LC. A size-exclusion mechanism would then retard the natural salt matrix.

**Measurable Size Range.** Of importance is the question as up to what size range OC can be determined with the reactor. DOC (dissolved organic carbon) is operationally defined as the fraction  $<0.45 \mu\text{m}$  and would therefore be the appropriate term for the studies presented here. However, in natural aquatic systems the DOC comprises only a fraction of TOC (total organic carbon) and is therefore only of moderate value for the analysis of natural matrices. The term TOC has no defined upper limit and would also include material in the millimeter range. Thus, TOC is, strictly speaking, not the correct term for many OC measurements.

A significant increase in the OC content of unfiltered samples compared to filtered ( $0.45 \mu\text{m}$ ) ones was found (13). Bacterial suspensions were also mineralized. This shows that at least part of the colloidal fraction,  $0.45\text{--}10 \mu\text{m}$ , can be analyzed with the reactor described.

**Application for Liquid Chromatography.** The reactor can be used in combination with liquid chromatography for the continuous determination of organic and inorganic carbon. In 1985/86 one of the early instruments was used for chromatographic separation of surface water organics with OC preconcentration (15). The high sensitivity of the new instrument now allows the direct chromatographic separation of surface water and groundwater nonvolatile organics without the necessity of a preconcentration step. Therefore, denaturing and artifact formation can be minimized.

As an example the gel chromatographic separation of tap water from Karlsruhe is shown in Figure 12 with the overlain signals for UV, OC, and IC.



**Figure 12.** Gel chromatogram of original tap water from Karlsruhe (fraction  $<10 \mu\text{m}$ ) from the 18th of Jan 1991, with UV (254 nm, 5 mAUFS, stippled line), OC (solid line), and IC (punctured line). For chromatographic conditions, see Experimental Section.

The organic fraction  $<10 \mu\text{m}$  was chromatographed and an OC concentration of 1.04 mg/L was found by integration over the whole chromatogram. With a sample loop of 1.5 mL this corresponds to a total mass OC of 1.56  $\mu\text{g}$ .

A  $<10\text{-}\mu\text{m}$  organic fraction is about the maximum that can be separated on a low-pressure column with  $40\text{-}\mu\text{m}$  spheres. Four major groups of compounds can be seen. "Colloids" are substances of mainly mineral origin that elute even before  $V_0$  (dead volume of column as determined by Dextran Blue). We assume that this material is mainly "clustered" inorganic material that traveled through the column in specific channels of higher velocity. The "hydrophilics" are natural polyelectrolytes of the type of humic substances. The high-molecular-weight (HMW) fractions eluted first, and the low-molecular-weight (LMW) fractions eluted at higher retention times. In the HMW fraction a good correlation between OC and UV prevails. The unusually sharp peak at around 90 min ("weakly adsorbed LMW fraction") is an artifact. We did not buffer the sample, hence the negative UV responses at around 100 min. The water of the sample itself had a much lower salt content and by this desorbed weakly adsorbed organic material. This material eluted in front of the sample water through the column. Finally, "strongly adsorbed LMW fractions" eluted after  $V_t$  (total permeation volume as defined by phosphate buffer salts).

This interpretation of the chromatogram is based on studies published in ref 13.

## CONCLUSIONS

The experimental data presented here show that a UV thin-film reactor equipped with an active stirring mechanism for the film and combined with high-sensitivity infrared spectrometry can be used for the continuous determination of organic carbon in aqueous solutions in the low  $\mu\text{g/L}$  to mg/L concentration range. In connection with liquid chromatography and further detection principles, the system can be used for the direct quantification (and characterization) of traces of unknown organics which are nonvolatile, nonextractable, and UV-inactive. The excellent performance places the system as a complementary partner to the flame ionization detector (FID).

## ACKNOWLEDGMENT

The study is dedicated to Alfred Graentzel on the occasion of his 83rd birthday. We thank Dr. Spitz of the Max-Planck-Institute of Meteorology in Hamburg, Germany, for the seawater sample.

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RECEIVED for review January 29, 1991. Revised manuscript received June 4, 1991. Accepted July 1, 1991. The study was financially supported by the German Federal Ministry for Research and Technology (Grants BMFT 02-WT-89137 and PWAB PD-90095).