spectrum. Despite this, the bands in the spectrum are well resolved and allow for easy identification of the three components of the sample.

The identification of impurities in "pure" samples can be attained in this manner. In photoexcitation spectra of fresh samples of naphthalene, we have observed bands attributable to β -methylnaphthalene, indicating its presence as an impurity. Over a period of ~ 7 h of operation, these bands disappear apparently due to degassing of the more volatile β -methylnaphthalene from the sample. In other samples, for instance, β -methylnaphthalene was doped with ~ 250 ppm naphthalene. Photoexcitation spectra of such samples clearly show the presence of the dopant.

The presence of impurities can also be determined from fluorescence spectra. Figure 3 shows the dispersed fluorescence spectrum from excitation of the $32\,458$ cm⁻¹ $\overline{8}^1$ band of naphthalene. This spectrum is unchanged whether obtained from pure naphthalene or from a trace amount of naphthalene in β -methylnaphthalene. If this spectrum represented an unknown impurity in β -methylnaphthalene, it could be identified as such because it is impossible to interpret the spectrum in terms of β -methylnaphthalene vibrations. Together with the photoexcitation spectrum of the sample, an unambiguous identification of the impurity can be made.

The data presented show that even in the photoexcitation mode rotationally cooled spectrometry of a simple mixture can readily distinguish between substitutional isomers of PAHs. This will usually not be possible with solid-state techniques. On the basis of the linewidths in Figure 2 and the earlier discussion of inhomogeneously broadened vibronic bandwidths of PAHs imbedded in solids, it is clear that the selectivity of RC-LIF is significantly superior (10- to 100-fold) to that of fluorescence line narrowing spectrometry in organic glasses (4-6) or laser-excited Shpol'skii spectrometry (9, 10). We hasten to point out, however, that the selectivity of the latter two techniques is high and has allowed for the direct analysis of nonpolar PAHs in real samples (5, 9). Recent work on polar derivatives of PAHs, e.g., amino-PAHs, has shown, however, that application of solid-state fluorescence techniques presents difficulties due to strong analyte-matrix interactions (20). This suggests that RC-LIF spectrometry will be important for the characterization of species prone to strong matrix interactions which obviate fluoresence line narrowing spectrometry.

In the assessment of the analytical utility of RC-LIF spectrometry, its superior selectivity, adequate sensitivity, and absence of matrix effects must be weighed against the fact that quantitation presents a serious problem for real samples. We are now initiating studies to determine whether RC-LIF, as a stand alone technique, can be made semiguantitative. For RC-LIF to be quantitative it will be necessary to couple it with gas chromatography as has been discussed in earlier work (6).

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AIDS FOR ANALYTICAL CHEMISTS

Generation of Dry Formaldehyde at Trace Levels by the Vapor-Phase Depolymerization of Trioxane

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Recent findings that low-level exposures to formaldehyde (HCHO) may produce allergenic effects (1, 2) and that HCHO may be carcinogenic (1, 2) have led laboratories to undertake the measurement of parts-per-billion to parts-per-million



Figure 1. Apparatus for generating ppb-ppm levels of formaldehyde gas. Trioxane vapor emanating from a diffusion cell is swept over a catalyst bed, and the resultant formaldehyde gas is diluted to the desired concentration using clean room air.

(ppb-ppm) concentrations of HCHO in air. A serious obstacle to the development of sensitive sampling and analytical methods has been the lack of an absolute source of gaseous HCHO for generating dynamic, controlled test atmospheres of known concentrations.

Two types of methods have been reported for generating gaseous HCHO, those employing aqueous solutions of HCHO (3, 4) and those based upon the depolymerization of various polymers of HCHO (5-7). Evaporation of aqueous solutions has several obvious shortcomings including: (1) the introduction of H₂O vapor and other impurities into the gas stream (e.g., CH_3OH would be generated if formalin was used), (2) the necessity of assaying the solution for its HCHO content, and (3) the possibility that oligomers and other chemical forms of HCHO may be produced. For generating dry, gaseous HCHO by the depolymerization of various polymers of HCHO, two procedures have been reported. One involves the solidphase depolymerization of paraformaldehyde or of α -polyoxymethylene (5-7) and the other involves the vapor-phase depolymerization of trioxane (8). Experience in our laboratory with the former technique has indicated that the generation rate of HCHO from paraformaldehyde was not constant and that other compounds were also released including water vapor, formic acid, and methyl formate. Godin et al. (7) reported that the depolymerization of α -polyoxymethylene also produced HCHO at yields of less than 100% and that vields varied with temperature. Accordingly, we turned our attention to the depolymerization of trioxane vapor which had been used by Schnizer et al. to produce percent concentrations of HCHO in air (8). The reported procedure involved bubbling air through molten trioxane and sweeping the vapor through a catalyst. Conversions of trioxane to HCHO as high as 89% were reported. The authors suggested that higher yields were possible but were not attained with their apparatus because of the repolymerization of HCHO. We report a modification of this technique to produce ppb-ppm air concentrations of HCHO. Trioxane vapor emanating from a diffusion cell is converted to HCHO with essentially 100% efficiency.

EXPERIMENTAL SECTION

A schematic diagram of the generation system we developed is shown in Figure 1. The diffusion cell, with a diffusion path of 7.9 cm \times 4.9 mm i.d., was maintained at 35.2 \pm 0.05 °C in a thermostatically controlled oven (Model 300, Analytical Instrument Development, Inc., Avondale, PA). By use of a capillary funnel warmed with a heat gun, molten trioxane (Aldrich Chemical Co., purity = 98%, reported mp = 61-62.5 °C) was introduced into the reservoir of the diffusion cell where it was allowed to solidify at room temperature. Dry N₂ flowing at 0.2 L/min swept

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trioxane vapor from the diffusion chamber through the catalyst bed which was held at 160 °C in a tube furnace. The catalyst consisted of 18 g of Carborundum (Fisher Scientific Co.), ground to 40 mesh and coated to saturation with 85% phosphoric acid (Mallinckrodt Chemical Co.), tightly packed into a 7.5-cm section of 1 cm i.d. quartz tubing. To prevent repolymerization of HCHO caused by high concentrations, we immediately diluted the gas stream emerging from the catalyst with air that had been purified with 13X molecular sieve to remove water vapor and any background HCHO. While connected to the vapor source, it was necessary to continuously heat and purge the catalyst with N_2 to prevent the accumulation of HCHO.

Samples of the diluted gas stream were collected over 24 h by bubbling the air through two distilled water bubblers which were connected in series and maintained at 2 °C. Air flow rates through the bubblers were controlled with critical orifices at 0.8 L/min. The collection efficiency of this sampling procedure, verified in our laboratory, has been reported to be approximately 95% (9, 10). Aliquots of the bubbler solutions were analyzed simultaneously by two procedures which have been commonly used for the measurement of HCHO, the chromotropic acid (CTA) method (9, 10) and the pararosaniline (PRA) method (11). We observed that the CTA method stoichiometrically responds both to trioxane vapor and to gaseous HCHO whereas the PRA method responds only to gaseous HCHO (11). A gas sample collected from the effluent of the catalyst with a gas-sampling flask was analyzed by mass spectrometry using a room-temperature inlet system to introduce the sample into the instrument (CEC Model 21-103B).

RESULTS AND DISCUSSION

The generation rate of trioxane from the diffusion cell was determined gravimetrically by weighing the cell periodically on a five place analytical balance. After 1 week, a constant rate of $740 \pm 10 \ \mu g/h$ was observed. This rate was maintained for a period of 5 months until the reservoir became significantly depleted of trioxane whereupon it gradually decreased. We observed that an equilibrium existed between trioxane/HCHO absorbed on the catalyst and HCHO in the N₂ stream. A steady state was established relatively quickly (approximately 1 week).

The generation rate of HCHO from the catalyst, based upon the analysis of 18 samples by the PRA method (which does not respond to trioxane), was $769 \pm 29 \,\mu g$. The corresponding rate based on 65 analyses by the CTA method was 761 ± 28 μ g/h. (These values were corrected for the collection efficiency of the sampling method, which was assumed to be 95%.) The close agreement between these two figures suggests that the conversion of trioxane to HCHO was essentially complete. This conclusion was supported by mass spectrometric analysis which failed to detect the presence of trioxane or of other anomalous compounds in amounts exceeding 2% of the total HCHO present in a gas sample taken downstream from the catalyst. The generation rate of dry HCHO from the catalyst, as indicated by all 83 analyses, was 103% of the gravimetrically determined generation rate of trioxane. The slight positive bias observed is well within the limits commonly achieved with the gas dilution apparatus used in this study (12).

By using the apparatus described above with the double air-dilution system shown in Figure 1, we have produced dynamic, controlled test atmospheres of HCHO at air concentrations between 0.05 and 2 ppm. The generation rate of trioxane vapor and, ultimately, of gaseous HCHO depends upon the temperature and geometry of the diffusion cell, and therefore, a virtually unlimited range of HCHO air concentrations may be produced by modifying these parameters.

This method constitutes a significant improvement over previous HCHO generation techniques. The apparatus is easily assembled and produces a dry gas stream, eliminating potential HCHO losses caused by interactions with water vapor. Most importantly, the generation system produces monomeric HCHO, free from impurities, at air concentrations that can be accurately predicted from gravimetric data and which remain constant for long periods of time.

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Pyroelectric Enthalpimetric Sensor

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Thermal methods for investigating material properties require a sensitive and reliable thermal sensor. The two types of thermal detectors generally used are resistance thermometers (hot wires) and thermocouples. The former has been widely employed in katharometry, gas chromatography (1), anemometry (2) and turbulance (3), while thermocouples have been used in differential thermal analysis, calorimetry (4), thermometric titrimetry, enthalpimetry (5), and radiometry (6). For thermal analysis at the microcalorie level it is necessary to use more sensitive thermal detectors. Pyroelectric materials are suitable candidate materials for this purpose. The principal advantages of pyroelectrics over thermocouples are their higher temperature resolution (less than 0.1 °C), lower noise equivalent power ($\sim 10^{-8} \text{ W}/(\text{Hz})^{1/2}$), shorter response time ($\sim 10^{-6}$ s), generally lower sensitivity to ambient temperature change (7), and generally uniform sensitivity over their entire surface (8). Recently there has been growing interest in pyroelectric materials for these various applications (9, 10). One new application has been in anemometry (11). The pyroelectric anemometers have high gas flow rate accuracy (1%, full scale, at flow rate from 0 to 100 cm³/min and near atmospheric pressure) and linear response and can be conveniently fabricated by standard integrated circuit technology.

In the present study, an experiment has been conducted to detect heat exchange due to the melting of alloys. Two different low melting point alloy compositions were chosen for this experiment. Potential application of LiTaO₃ in analytical chemistry is briefly discussed.

DEVICE STRUCTURE AND MEASUREMENT

Czochralski grown, z-cut LiTaO₃ (lithium tantalate) plates, one side polished, were used to carry out the experiment. Gold films 5 μ m thick were evaporated on the polished side to provide two metal electrodes (the sample electrode and the reference electrode) and 0.5 μ m thick Au was evaporated on the back side for the ground contact. The pyroelectric plate used was $6 \times 6 \text{ mm}^2$ and 0.129 mm thick. The finished structure was then mounted on two parallel support wires. These wires were attached to the edges of the back face of the sample using air-drying silver paste. Silver paste was also used to make electric contacts between fine aluminum wires and the two electrodes. A Unitron high-intensity lamp was used to provide roughly uniform irradiation on the back side of the device. The irradiated area was slightly larger than

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the sample area. A 160 Keithley digital multimeter with high input impedance ($\sim 100 \text{ M}\Omega$) was used to measure the pyroelectric response. The resistance of the device was greater than 10 $M\Omega$ (the resistivity of LiTaO₃ is about $10^{13} \Omega$ cm). The output of this meter was connected to a chart recorder.

Two different low melting point alloy compositions: Wood's metal (Bi (50%), Pb (25%), Sn (12.5%), Cd (12.5%) with a melting point of 70 °C) and a ternary eutectic (In (51%), Bi (32.5%), Sn (16.5%) with a melting point of 60.5 °C) with weights of 30 and 17.0 mg, respectively, were placed on the sample electrode. Figure 1 shows schematically (a) the top view and (b) the cross sectional view of the sample.

RESULTS AND DISCUSSION

The pyroelectric voltage response of a pyroelectric material is proportional to the time derivative of the temperature (9). The differential signal of the device is therefore a measure of the average temperature change difference between the two electrodes.

Figure 2 shows the variation of the differential pyroelectric signal vs. time when the light is on (for heating) and off (for cooling). The dashed line is for the case when there was no alloy on the sample electrode. At point "a" on this figure, the sample was exposed to high-intensity light. Consequently the signal rises rapidly from 0 to 0.94 V. A large pyroelectric signal from each electrode upon the sudden exposure of the sample to the light was expected since the pyroelectric response is proportional to the time rate of temperature change. However, the nonzero differential signal during the initial stage of both heating and cooling (see points a and b in Figure 2) is attributed to the different heat capacities of the sample and reference "electrodes" and to the nonuniformities in the incident light. As the sample warms up, two peaks (α and β) appear, which designate the melting of each alloy (with 10 °C temperature difference). About 12 s from the starting point, the sample is at steady state and therefore the electrode response and differential signal vanish. No stationary short circuit current or photovoltaic emf was observed under light illumination. This indicates that there was no anomalous photovoltage in the LiTaO₃ used in this study (12). When the light is turned off, the sample cools down. The two peaks $(\alpha \text{ and } \beta)$ appearing in the cooling curve are due to the solidification of the alloys.

For performance evaluation of the device and for comparison with those of conventional DTA/DSC instruments, quantitative information on the fusion process is needed. This has been left to be determined in further study. However,