a good agreement was obtained with the information values reported by NBS or other workers (7, 17). The relative standard deviation was 3.7% for 11 replicate determinations of a drainage sediment in which gallium content was found to be 10.8 μ g/g.

Registry No. Ni, 7440-02-0; Ga, 7440-55-3.

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Determination of Formaldehyde with the Thermal Lens Effect

Jan A. Alfheim and Cooper H. Langford*

Department of Chemistry, Concordia University, 1455 de Maisonneuve, West, Montreal, Quebec H3G 1M8, Canada

The laser thermal lens analysis of formaldehyde is reported. Two systems were tested, the first using a single laser in combination with a single diode detector and the second using two lasers in conjunction with a photodiode array detector. The formaldehyde solutions were prepared for colorimetry using the NIOSH method based on chromotropic acid. Improved sensitivity over standard absorption techniques is observed with enhancement factors up to 20.0 based on detection of absorptivity as low as 9 imes 10⁻⁵ cm⁻¹ which corresponds to a concentration of 1.5×10^{-8} M. With collection efficiency of 95 % for sampling solutions, this supports facile detection of formaldehyde in the parts-per-billion region in air.

Current interest in the quantitative analysis of formaldehyde stems from its potential as a human health hazard (1). Formaldehyde polymers are used in the fabrication of wood products and home insulation and are known to emit low concentrations of formaldehyde into the surrounding environment (2, 3). A recent trend in pollution analysis is toward decrease of the sample volume by means of an increase of analytical sensitivity. Thermal lens analysis is attractive in this context because it "improves" classic and well-tested methods.

Several methods to analyse formaldehyde have been developed (4-6) using both chromatographic and optical techniques. A close examination of the pararosaniline method (7)has shown it to be pH dependent (8) and seriously effected by SO_2 (9), thus limiting its potential.

In this study the NIOSH method for formaldehyde analysis has been modified to improve its sensitivity from 0.1–2 ppm to the parts-per-billion level where it can compete with GC and HPLC methods (4-6). The modifications to technique include diluting the chromotropic acid solutions 10-fold and then analyzing the samples with a laser thermal lens (LTL) spectrometer rather than a standard absorption spectrophotometer.

A thermal lens works on the principle that the passage of a laser beam through a material with a finite optical absorption generates thermal energy which heats the sample. The temperature gradient causes a refractive index gradient. For a Gaussian laser intensity distribution, a well-defined tranverse gradient in the refractive index will be established. In most materials dn/dt is negative and thus this gradient has the same optical effect on the laser beam as a diverging lens.

It should be noted that a thermal lens is a function of true absorption in the same fashion as other calorimetric techniques and not absorption plus scattering as in transmittance techniques. The intensity of the thermal lens effect is proportional to the absorbed light energy.

LTL is a very sensitive method (10, 11) which has already been used to measure pollutants in the micrograms per liter and lesser regions in both liquid and gaseous samples (12, 13).

In keeping with the goal of minimizing apparatus complexity, both simple single and more complex dual laser systems were used in our experiments to evaluate their detection capabilities for quantitative formaldehvde determination. The admittedly primitive single laser experiments were performed to demonstrate that using the most basic of components to design a system one can still obtain relatively high sensitivity. The dual laser experiments were designed to demonstrate the true potential of LTL as a means of trace pollutant analysis, specifically formaldehyde. We encourage laboratories with one laser available to consider using the thermal lens effect.

EXPERIMENTAL SECTION

Instrument. Figure 1A shows a block diagram for the simplified experimental setup. The optical train and lasers were fixed to a workbench which was isolated from building vibrations with a three-ply "sandwich" consisting of a sheet of cork, a piece of sheet metal, and a layer of sponge rubber. The Coherent CR-6 argon ion laser (A) was used to drive the Coherent CR-590 dye laser (B) which was run at 150 mW at $\lambda = 600$ nm. The power was measured in front of the cell holder to account for power loss due to reflections of preceding optical components. The beam was elevated to the height of the optical train by means of a dual mirror system (C). The lens (D) which brought the light to a focus has a focal length of 23 cm. A manual shutter (E) was used to block the pump beam. The cell holder (F) was placed one confocal



Figure 1. Block diagram of the laser thermal Lensing systems. Part A shows the pinhole/single laser system. The pinhole (H) was placed 403 cm from the lens (D). Part B shows the modifications to the system including the addition of a second laser (L), an optical flat (G), Nichol prism (H), and photodlode array (K).

distance (5 cm) beyond the focal point (10, 11). The cell used was a Canlab blue label 1-cm square cell. A flat mirror in an adjustable mount (G) was used to direct the beam toward the pinhole detector. The pinhole was 0.1 mm. The photodiode detector (I) behind the pinhole (H) was linked to a Tektronix oscilloscope (J) which had a Type 2A63 differential amplifier, and a 2B67 time base with single sweep capabilities. The lens formation was recorded at various sweep rates to record the initial (I_0) and final steady-state (I_{∞}) intensities following opening the laser beam shutter. The data were then read off the screen and recorded.

Figure 1B is a block diagram of the dual laser thermal lens system. It is comprised of the six first components of the simplified system plus eight new additions. A Siemens 10 mW HeNe laser (L) was used as a probe beam which was directed to and aligned with the pump beam by means of a mirror (M) and an optical flat (G). A polarizing Nicol prism (H) was used to reduce the polarized pump beam intensity to prevent burning of the ensuing filter and polarizer. A 630-nm cuttoff filter (I) separated the pump and probe beams and a rotating film polarizer (J) adjusted the probe beam intensity to maximize the signal from the diode array without saturating the Reticon RL128G selfscanning linear photodiode array detector (K). The signal from the diode array was fed into a Processor Technology SOL computer (N) via 8-bit ADC's for storage purposes. The SOL was interfaced with an IBM personal computer which handled all numerical manipulations. The IBM plotted the beam profile (see Figure 2) and was programmed to fit a best Gaussian curve to the experimental data and to calculate the $(I_0 - I_{\infty})/I_0$ values. A further modification to the initial system was to switch from a square cell to a cylindrical cell to decrease interferences due to solution convection (14).

Reagents. The formaldehyde stock solution was prepared by dissolving 4 4703 g of sodium formaldehyde bisulfite (Eastman Chemicals) in 1 L of deionized distilled water. This solution was standardized against iodine solutions with a starch indicator. Chromotropic acid (Fischer Chemicals)-formaldehyde solutions



Figure 2. Diagram of the HeNe beam profile and the computer-fitted Gaussian profile as seen on the monitor. The signal axis is the scale of 0.256 of the A/D converter. The abscissa is the diode number referenced to the peak centre.

were prepared with doubly distilled H_2SO_4 (American Chemicals) following the NIOSH method (15).

Procedure. All glassware was soaked in an H₂SO₄-HNO₃ acid bath overnight and then rinsed with deionized distilled water before use. The stock formaldehyde solutions were diluted successively to obtain the desired concentrations. Samples prepared following the NIOSH methodology were allowed to stand overnight to ensure full color development although it was noted that 1 h would have been sufficient (15). Before analyzing the samples and blanks using thermal lensing, a further 10-fold dilution was required to reduce the sulfuric acid concentration (vide infra)

All alignments and cell positions were optimized with a concentrated solution of formaldehyde ($\sim 10^{-5}$ M). For the simple system, the flat mirror (G) was adjusted until maximum intensity was observed on the oscilloscope screen. Then the cell was moved along the rail until the thermal lens effect was maximized. The two-laser system required alignment of the probe and pump beams which was performed before each day's run to accommodate any shift in the beams that might have occurred. This was accomplished by using the lens (D) which was on a horizontal and vertical adjustable mount to shift the pump beam in the appropriate direction to maximize the thermal lens signal observed on the monitor.

RESULTS AND DISCUSSION

Dovichi and Harris (16) noted that the sensitivity enhancement that can be realized for a particular laser power is dependent on the thermooptical properties of the solvent in which the sample is dissolved. Solvents that exhibit high dn/dt and low thermal conductivity are desirable for the thermal lens effect. In our experiments it was discovered early that the blank (a mixture of chromotropic acid, sulfuric acid, and water) created such a large lens that the pinhole detector was unable to differentiate between dark signal and the I_{∞} value. Since the blank solution was clear in color, it was assumed that the effect was due in part to absorption by the chromotropic acid and to a great deal of thermal convection in the sulfuric acid.

Preliminary experimentation showed that a 10-fold dilution of the blank was necessary to obtain a signal that was not seriously affected by thermal convection (16). Thus a 10-fold dilution of the color developed solutions of formaldehyde was added to the procedure.

To achieve the maximum sensitivity our system was capable of, the dye laser's most stable wavelength which was closely matched to the absorption maximum of the formaldehydechromotropic chromogen ($\lambda_{max} = 580$ nm) was chosen. The absorptivity of the chromogen at 600 nm was found to be 4.6 $\times 10^3 \,\mathrm{M^{-1} \, cm^{-1}}$. A moderate power of 150 mW was found to be sufficient to pump the samples. Indeed for any greater power the convection problem would have reoccurred.

Our present two-laser system is modeled after the system of Ishibashi et al. (13) in that the HeNe probe laser is not focused before passing through the sample. Ishibashi et al. discuss Sheldon's abherent thermal lens model (17) and calculate enancement factors using his equations. They point out that both the parabolic and abherent models predict linear dependence at lower concentrations. The similarity of the two model's predictions for weak thermal lenses is further discussed by Harris and Carter (18). The analytical curve for formaldehyde from our data based on parabolic lens equations gave the better straight line.

A concentration range of 1.5×10^{-7} M to 50×10^{-7} M formaldehyde in water was studied using the single laser system. Triplicate scans of eight samples at each concentration were averaged, and the average values were used in determining the enhancement factor. The dual laser system was employed for analyzing a concentration range of 1.5 \times 10^{-8} to 50×10^{-7} M. Triplicate scans of five samples at each concentration were averaged and used in the enhancement factor calculations. A detection limit of twice the standard deviation of the blank, where the blank is averaged over all

runs with all sample concentrations, for each system was calculated to be 22×10^{-7} M and 5.6×10^{-7} M, respectively. This corresponds to absorptivity enhancement of 20.0 as defined in ref 10.

Although the standard deviation of the blank value as determined over all runs was quite large, the deviation of each day's blank was much smaller and it was felt that the detection limit reported above was not representative of the best performance achievable. There are several values that lie below the detection limit that appear to be significant. To determine whether these points could be considered to reflect real signals, they were compared to blanks prepared concurrently. At the lowest concentration of 1.5×10^{-8} M a t test indicated signal significance at the 99.9% level. Thus, it was apparent that higher sensitivity than quoted can be achieved with careful control of blanks and the extra effort implied. However, we have not been able to identify the specific chemical causes of the day to day blank variation. This is a problem which is not seen until the LTL technique is exploited because the conventional absorbance measures (1) do not emphasize small blank variations. Also, it should be pointed out that what can be small blank variations in absorption experiments are magnified by the enhancement factor, in our case 20-fold. A referee suggested that the variation is due to the variation in free formaldehyde in the lab environment entering the samples on a day to day basis. This is a very plausible explanation and we thank the referee.

Note that the addition of the second laser into our system proved to be beneficial. The reduction in noise in the probe beam allowed a large improvement in sensitivity.

As the system stands now, thermal lensing analysis of formaldehyde is an attractive alternative to GC an HPLC methods of analysis. GC and HPLC methods have been reported to use from 30 to 500 L of air per sample (29, 30) and/or sampling times from one (6) to several hours (5). Due to the fact that LTL can detect very low concentrations in solution, the amount of gas sample required to detect the same levels of formaldehyde is greatly reduced. With the 5.6×10^{-7} M "detection limit", it would require only 8 L of gas sample at STP to detect formaldehyde in the 10 μ g/L region assuming 95% collection efficiency in the NIOSH system (1). If one accepts the detection of 1.5×10^{-8} M as the statistics have shown to be possible with extra effort in standardization, the volume of sample gas required is reduced to less than 1 L to detect less than 5 μ g/L. This seems a practical target with improved signal processing.

Registry No. Formaldehyde, 50-00-0.

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Determination of Structural Characteristics of Saturates from Diesel and Kerosene Fuels by Carbon-13 Nuclear Magnetic **Resonance Spectrometry**

David J. Cookson and Brian E. Smith*

The Broken Hill Proprietary Co., Ltd., Melbourne Research Laboratories, 245 Wellington Road, Mulgrave, Victoria, Australia 3170

Two saturated hydrocarbon fractions, one mainly consisting of n-alkanes and the other containing only branched plus cyclic saturates, have been separated from each of a variety of diesel fuels (approximate boiling range 230-320 °C) and kerosene fuels (approximately 190-230 °C) using silica chromatography and urea clathration. The n-alkane fractions have been simply characterized by using conventional ¹³C NMR spectrometry, yielding average carbon chain lengths. The branched plus cyclic saturates fractions have been characterized by using the gated spin echo (GASPE) ¹³C NMR technique, which yields individual ¹³C NMR subspectra for each CH_n group type (n = 0 to 3) and allows the fractional abundances of CH, groups to be measured. These data have been employed in devising and calculating a number of novel average structure parameters which report on the extent of branching and occurrence of ring structures in the fractions investigated. Spectral data are also used to identify some specific submolecular structures.

Achieving an understanding of the structural characteristics of fossil fuel products is usually a difficult task, primarily because such materials are generally complex mixtures of compounds. This is certainly the case for the diesel fuels (approximate boiling range 230-320 °C) and kerosene fuels (approximate boiling range 190-230 °C) studied in the present work. However, these fuels at least have the simplifying characteristic that they consist almost entirely of hydrocarbons. All of the samples examined here are also olefin free, such that component species can be described as saturated or aromatic. This article is concerned with the saturates class of compounds. Saturates have been isolated chromatographically from whole fuels, and have subsequently been separated into two fractions, one containing mainly *n*-alkanes and the other containing branched plus cyclic (naphthenic) saturates.

Although the composition of n-alkane fractions is relatively simple (see Figure 1, parts A and B) branched plus cyclic saturates fractions are complex mixtures (Figure 1C). This complexity derives from a number of factors. The boiling range of the source fuels allows for a range in the number of carbon atoms per molecule. For example, the diesel cuts studied typically include C_{12} to C_{19} *n*-alkanes. Also the empirical formulas of saturates components may take the form of $C_m H_{2m+2}$ for linear or branched saturates, or $C_m H_{2(m+1-r)}$ for cyclic saturates containing x rings. Finally, species with the same molecular weight may be present in any of a number of isomeric forms.

It is obvious that the identification of each and every compound present in such a mixture would be an exceedingly difficult task, whatever techniques were applied. This is not the objective in the present work. Rather, the intention is to derive average structural information and to identify submolecular structures. Conventional ¹³C NMR spectrometry has previously been applied to fossil fuel saturates (see, for example, ref 1-7) but the structural inferences have been more limited than those derived here. This largely arises from the present application of selected multiplet subspectral ^{13}C NMR analysis, using the gated spin echo (GASPE) technique (8-10). This procedure yields ¹³C NMR subspectra for each CH_n (*n* = 0 to 3) group type. In a conventional ¹³C NMR spectrum of complex materials there is usually substantial overlap of resonances due to C, CH, CH₂, and CH₃ groups leading to spectral congestion. This problem is alleviated with the GASPE subspectral analysis. The accessibility of chemical shift information is consequently enhanced. Further, by identifying the CH_n origin of individual resonances, the prospects for structure elucidation are improved. Also, since the method is quantitative the total abundances of CH_n groups can be obtained and these data facilitate the derivation of average structure information.

From the outset it has been recognized that for average structure information to be credible, it is desirable that parameters devised should be as assumption free as possible. Also, as far as is possible, average structure parameters should not derive from a concatenation of expressions, assumptions, and measurements, that might lead to unacceptable accumulated errors. These factors have been minimized in the present work and the credibility and reliability of structural interferences have been subjected to substantial scrutiny.

A total of nine diesel samples, six of which are petroleum derived and three of which are synfuels, have been studied,