ror, one would have a firmware slew-scanning spectrometer of similar concept to the software slew-scanning system presented in Ref. 7. A more exciting concept is a multichannel direct-reading type processor which would incorporate several pairs of MACs and thus would allow parallel processing of an interferogram for several elements. Such a "direct reader" could be instantly reconfigured under firmware control, as the "channels" of direct reader are simply determined by the masks sent to the MACs. Such a system could be based on a modest number of channels, say ten. Based on this concept a versatile and inexpensive real-time correlation-based data processor could emerge for inductively coupled plasma/Fourier transform spectroscopy.

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Laser Fluorescence Detection in Microcolumn Liquid Chromatography: Application to Derivatized Carboxylic Acids*

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A laser-induced fluorescence (LIF) detector is evaluated for use with high-efficiency liquid chromatography columns of capillary dimensions. This detector employs a cw helium-cadmium laser (325 nm, 5–10 mW) as the excitation source, together with a fused-silica capillary flowcell and filter/photomultiplier optical system. The flowcell, which is an integral part of the microcolumn, contributes from 0.06 nL^2 to 0.06 μL^2 variance to the chromatographic system for capillaries of 35 to 330 μm diameter, respectively. The LIF detector is capable of sensing femtogram amounts of coumarin 440, and the response is linearly related to concentration over at least eight orders of magnitude. The potential of this combination of analytical techniques is demonstrated through the analysis of multicomponent mixtures of derivatized fatty acids and prostaglandins at the pico- and subpicomole level.

Index Headings: **Microcolumn liquid chromatography; Laser fluorescence detection; Fatty acid and prostaglandin analysis.**

INTRODUCTION

The separation power of liquid chromatography (LC) can be significantly increased by the use of microcolumns,[1,2] which are generally of three types: narrow-bore packed columns,[3] semipermeable packed capillaries,[4] and open tubular capillaries.[5] However, these microcolumns require the analysis of minute quantities of effluent, and the burden is placed on detection methods to compensate for the reduction in sample mass and volume. The development of sensitive, low-volume detectors appears to be the gating factor in the use of microcolumn LC for routine chemical analysis. It is in this area that laser-induced fluorescence (LIF) has the potential for making an important advance.[6–8] The high power of the laser radiation permits very high sensitivity to be achieved, since the fluorescence signal is proportional to the source intensity. Moreover, the collimated laser radiation can be readily focused into flowcells of nanoliter volume, as required for microcolumn LC, without concomitant loss of radiant power. Other properties of laser sources, such as narrow spectral bandwidth, polarization, and temporal characteristics (pulsed or continuous wave), may be exploited for this purpose as well.

Previous investigations with conventional LC columns have clearly indicated the high sensitivity and selectivity that can be attained with laser-induced fluorescence detection.[9–14] Based on these promising results, several laboratories have undertaken concurrently the combination of microcolumn LC and laser fluorimetric detection. Guthrie, Jorgenson, and Dluzneski[15] replaced the mercury-arc source of a conventional fluorescence detector with a helium-cadmium laser for the analysis of solvent-refined coal samples separated with the use of an open tubular capillary column. Gluckman, Shelly, and Novotny[16] have used a similar system for the detection of derivatized steroids and bile acids separated with the use of a narrow-bore packed microcolumn. In the present study, a sensitive, low-volume LIF detector is de-

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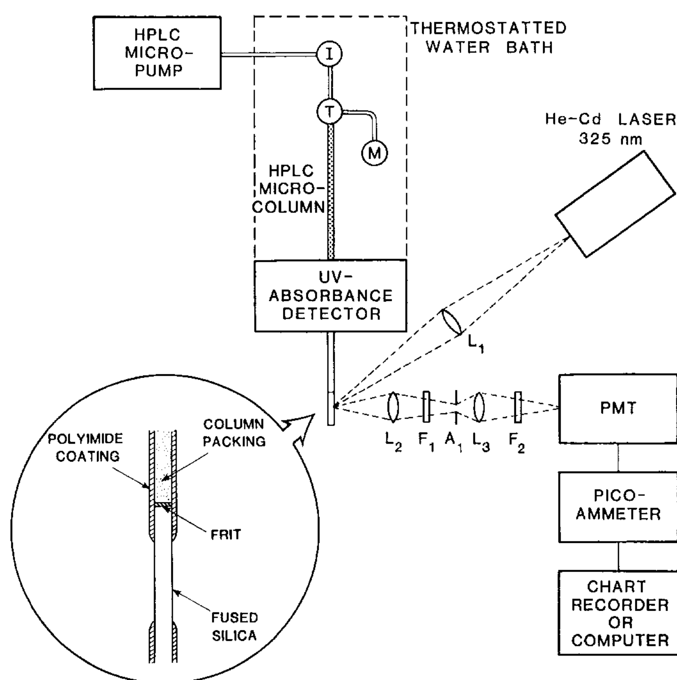

FIG. 1. Schematic diagram of the liquid chromatography and laser fluorescence detection systems. I = injection valve, T = splitting tee, M = metering valve or restricting capillary, L = lens, F = filter, A = aperture, PMT = photomultiplier tube.

scribed that is compatible with all three types of microcolumns, yet is simple and reliable to operate. This detection system is characterized with respect to sensitivity, linear dynamic range, and volumetric and temporal dispersion. The outstanding performance of this detection system is demonstrated by the analysis of subpicomole samples of fatty acids and prostaglandins, derivatized with the fluorescent label 4-bromomethyl-7-methoxycoumarin.

EXPERIMENTAL

A schematic diagram of the liquid chromatography system and laser fluorescence detector is shown in Fig. 1. The key components of this analytical system are described sequentially in what follows:

Liquid Chromatography System. A prototype solvent delivery system (Brownlee Labs, Santa Clara, CA), constructed of two 10-mL stainless-steel syringe pumps, is capable of pulse-free solvent delivery at flowrates from 1 to 1000 μL/min at pressures up to 500 atm. For isocratic separations in which the mobile phase is premixed, the reproducibility of retention times is better than ±0.75% relative standard deviation (R.S.D.) under flow-controlled conditions, and better than ±0.45% R.S.D. under pressure-controlled conditions. The reproducibility of retention times for gradient separations is typically ±1% R.S.D. at flowrates greater than 10 μL/min. By splitting the pump effluent between the microcolumn and a restricting capillary (1:20 to 1:2000), one can reproducibly achieve gradient separations at column flowrates as low as 0.1 μL/min, and isocratic separations as low as 0.005 μL/min.

Narrow-bore packed microcolumns are fabricated from fused-silica tubing (Hewlett-Packard, Avondale, PA) of 0.20 to 0.32 mm inner diameter and 1 to 2 m length. This tubing is packed under moderate pressure (400 atm) with a slurry of the chromatographic packing material (Spheri-5 RP-18, Brownlee Labs, Santa Clara, CA; Micro Pak SP-18, Varian Instrument Group, Walnut Creek, CA) in an appropriate solvent.[17] In this manner, packed microcolumns are reproducibly prepared to yield 150,000 or more theoretical plates.

Samples of 0.5 to 50 nL volume are introduced to the microcolumn by the split injection technique with a 1-μL valve injector (Model ECI4W1, Valco Instruments Co. Inc., Houston, TX). The injection valve, splitting tee, and microcolumn are maintained at constant temperature (±0.3°C) in a thermostatted water bath.

A variable-wavelength UV-absorbance detector (Model Uvidec 100-V, Jasco Inc., Tokyo, Japan) was modified to permit "on-column" detection with fused-silica microcolumns, as described previously.[17-19] The UV-absorbance detector is placed in series before the laser fluorescence detector (see Fig. 1), and is used for comparisons of sensitivity, selectivity, and dead volume.

Laser Fluorescence Detector. A helium-cadmium laser (Model 4240B, Liconix, Sunnyvale, CA) is chosen as the excitation source because of its stability and convenient wavelengths (325 and 442 nm). The UV laser radiation (325 nm, 5–10 mW cw) is isolated with a dielectric mirror and is focused on the miniaturized flowcell with a quartz lens. Sample fluorescence, collected perpendicular to and coplanar with the excitation beam, is spectrally isolated by appropriate interference filters and then focused on a photomultiplier tube (Centronic Model Q 4249 B, Bailey Instruments Co. Inc., Saddle Brook, NJ). The resulting photocurrent is amplified with a picoammeter (Model 480, Keithley Instruments Inc., Cleveland, OH), and finally is displayed on a stripchart recorder (Model 585, Linear Instruments Corp., Reno, NV). For the measurement of detector variance and sensitivity via the statistical moments, the UV-absorbance and LIF detectors are interfaced to an HP-85 computer (Hewlett-Packard, Palo Alto, CA).

In previous studies, we evaluated the performance of several miniaturized flowcells, including a suspended flowing droplet, an ensheathed effluent stream, and a fused-silica capillary.[20] Because of its operational simplicity, compatibility with many solvents as well as gradient elution, compatibility with a wide range of microcolumn types and sizes, and nondestructive nature, the fused-silica capillary flowcell was judged to be the most versatile and useful among those investigated. This flowcell, shown schematically in the insert of Fig. 1, is formed by the removal of the protective polyimide coating from a short section of fused-silica capillary. When the LIF detector is used alone, the flowcell is simply an extension of the column itself (0.20 to 0.32 mm i.d.), thereby eliminating dead volume from connecting tubes and unions. However, when the UV-absorbance and LIF detectors are employed in series, it is necessary to use a capillary of smaller diameter in order to reduce laminar dispersion between the detectors. In such cases, a fused-silica capillary of 35–100 μm i.d. and 1 m length is attached to the column outlet with PTFE (Teflon®) tubing, and forms the flowcells for both UV-absorbance and LIF detectors. Because fused-silica capillaries can be readily

interchanged to provide a suitable compromise between sensitivity and dead volume, these flowcells are compatible with packed microcolumns as well as the more demanding semipermeable packed capillary and open tubular capillary columns.[20]

Analytical Methodology. Carboxylic acids are derivatized with 4-bromomethyl-7-methoxycoumarin under conditions similar to those of Dünges and coworkers.[21,22] A 10^{-3} M stock solution of 16 saturated and 5 unsaturated fatty acids (Sigma) is prepared in dry acetone. An aliquot of this solution is added (with stirring) to a powdered, anhydrous mixture (1:1) of sodium sulfate and potassium bicarbonate (5 mg), and dibenzo-18-crown-6 (3.6 mg, 10^{-5} mole). The coumarin reagent (2.7 mg, 10^{-5} mole) is added, and the derivatization is allowed to proceed in the dark at 50°C for two hours. The fatty acid standards are used to identify the constituents of commercially available peanut and sesame oils (1 μL), which are saponified and derivatized in a similar manner.

A 10^{-4} M stock solution of nine prostaglandins (Sigma) is prepared in dry acetone, and derivatized with 4-bromomethyl-7-methoxycoumarin as described above. To minimize dehydration of the prostaglandins, which occurs readily in nonaqueous solvents at elevated temperatures, one performs the derivatization reaction at 37°C for six hours.

Organic solvents employed in this investigation are high-purity, distilled-in-glass grade (Burdick & Jackson Laboratories, Inc., Muskegon, MI); water is deionized and doubly distilled in glass (Mega-Pure System, Corning Glass Works, Corning, NY).

RESULTS AND DISCUSSION

Evaluation of LIF Detector Performance. Coumarin 440 is chosen as the test solute for the detector characterization because of its chemical and spectroscopic similarity to the derivatives of 4-bromomethyl-7-methoxycoumarin. This dye is eluted with methanol (k = 0.05) from a fused-silica microcolumn (0.2 mm i.d., 1 m length) containing a 5-μm octadecylsilica packing material. The resulting chromatographic peak is detected sequentially by UV absorbance (λ_{abs} = 254 nm) and laser fluorescence (λ_{ex} = 325 nm, λ_{em} = 430 nm) detectors, which are interfaced to a microcomputer. The sampling rate is selected to accurately reproduce each chromatographic peak, such that 60–100 digitized points are acquired between the limits of integration. The digitized chromatographic data are used to evaluate the sensitivity and variance of the LIF detector via statistical moments, which are calculated by finite summation with the use of the standard equations.[23,24]

Sensitivity and Linearity. By comparison of relative peak areas (0th statistical moment), the fluorescence signal is found to increase linearly with the optical pathlength of the fused-silica flowcell (35–330 μm). However, the background noise level also appears to be nearly proportional to pathlength. Consequently, the signal-to-noise ratio obtained for a standard sample injection is largely independent of the flowcell dimensions within the range investigated. The limit of detection is determined at a signal-to-noise (rms) ratio of seven, which represents the 99.9% confidence level for three replicate

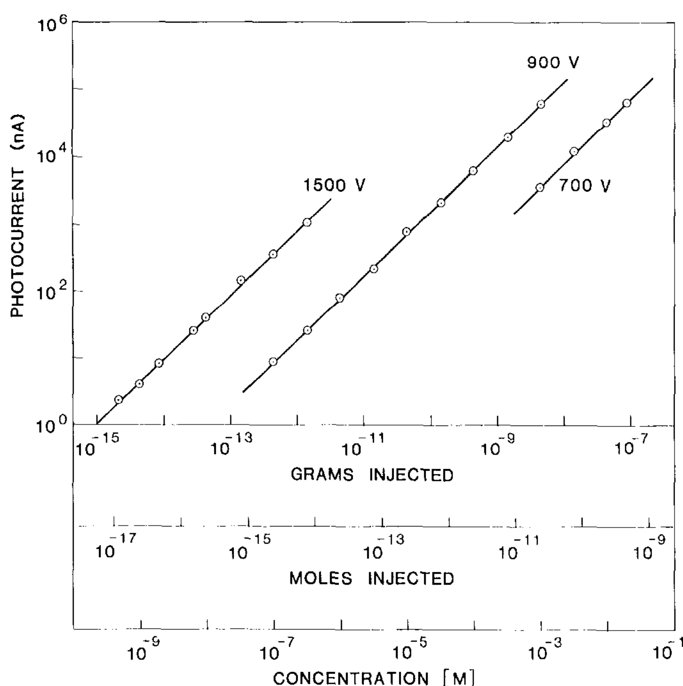

FIG. 2. Linearity of the laser fluorescence detector response as a function of injected sample concentration with varying photomultiplier tube voltage.

measurements.[25] This detection limit is achieved by the injection of 25 nL of 5×10^{-10} M coumarin 440, corresponding to a minimum detectable mass of 2.3×10^{-15} g (1.3×10^{-17} moles). At the detection limit, approximately 115,000 molecules are contained within the optical volume at the maximum of the Gaussian chromatographic peak. The mass flux per unit time is calculated to be 60 ag/s or 204,000 molecules/s at the peak maximum. Whereas detection limits as much as an order of magnitude lower have been reported for laser fluorimetry,[26] such results were achieved under rather rigorous conditions. In contrast, the detection limit demonstrated here is achieved with a relatively low-power laser and simple optical system using a representative solute analyzed under normal chromatographic conditions. Hence, this high sensitivity is indeed typical of that which can be routinely achieved under practical operating conditions.

The fluorescence signal is found to be linearly related to solute concentration over at least eight orders of magnitude, extending from the detection limit (5×10^{-10} M) to the solubility limit (2×10^{-2} M) of Coumarin 440 in methanol. This broad linear range, shown in Fig. 2, is made possible by the varying of the photomultiplier voltage such that the electrical dynamic range is never the limiting factor. While linear ranges of approximately 4–5 decades have been demonstrated previously for fluorescence measurements,[15,16,27] the range established in the present work appears to be unprecedented. It is suggested that the small diameter of the capillary flowcell effectively reduces nonlinear behavior in both the absorption and emission processes, thereby reducing both inner and outer filter effects and extending the linear response into very high concentrations. This extraordinary linear range will facilitate the simultaneous quantitation of both major and minor components in com-

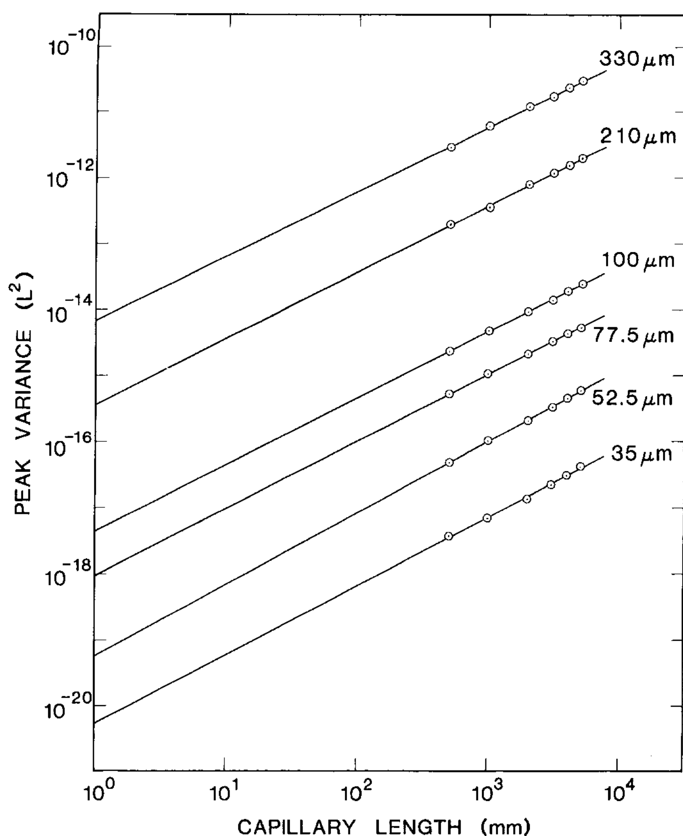

FIG. 3. Volumetric variance of the fused-silica flowcells as a function of inner diameter and length.

plex sample matrices. Moreover, it may ultimately permit the study of solute-solute and solute-solvent interactions at very high concentrations.

Volumetric and Temporal Dispersion. To preserve the inherent separating power of the chromatographic column, the volumetric and temporal dispersion of the detection system must be extremely small. One must assess these contributions independently insofar as possible in order to determine the major sources of band broadening and to minimize their effects.

Volumetric dispersion may result from several sources, including laminar and/or irregular flow between the microcolumn frit and the optical region (see Fig. 1), optical integration within the finite detection volume, and other factors. The volumetric dispersion of the LIF detector is examined by the direct injection of samples of coumarin 440 dye into the capillary flowcell. The injection volume is selected so as to cause negligible dispersion, ranging from 0.5 to 30 nL for capillaries from 35 to 330 μm i.d., respectively. The volumetric variance (second statistical moment of the chromatographic peak) is then measured as a function of both the internal diameter of the capillary flowcell and the distance to the illuminated region. As illustrated in Fig. 3, the logarithmic relationship between volumetric variance and capillary length is linear for all flowcell diameters, with slopes determined by linear regression to be from 0.98 to 1.05 and correlation coefficients from 0.9975 to 0.9999. These data correspond very well with the dispersion predicted by the following modification of the Taylor equation:[28,29]

TABLE I. Experimental and calculated variances of fused-silica flowcells.

I.D. (μm)	Experimental variance[a] (nL²)	Calculated variance[b] (nL²)
35	0.0053	0.0084
52.5	0.058	0.096
77.5	0.91	0.99
100	4.5	4.6
210	360	390
330	6700	5900

[a] Determined from the intercept of Fig. 3 at a capillary length of 1 mm.

[b] Calculated from Eq. 1; $L = 0.1$ cm, $u = 0.1$ cm/s, $D_m = 1.4 \times 10^{-5}$ cm²/s.

$$\sigma^2 = \frac{\pi^2 r^6 L u}{24 D_m} \tag{1}$$

where σ^2 is the volumetric peak variance due to laminar spreading in an open tube of radius r and length L, u is the linear solvent velocity in the tube (0.1 cm/s), and D_m is the solute-solvent diffusion coefficient, estimated from the Wilke-Chang equation[30] to be approximately 1.4×10^{-5} cm²/s at 25°C. This close correspondence suggests that laminar dispersion is primarily responsible for the observed peak variance, and that dispersion from irregular flow, longitudinal diffusion, and mixing is negligible.

Under practical circumstances, it is possible to focus the laser radiation within 10 mm of the microcolumn frit. Hence, the total volumetric dispersion of the capillary flowcell can be readily estimated from Fig. 3 at this distance to be between 0.06 nL² and 0.06 μL² for capillaries of 35 to 330 μm diameter. Because variances are directly additive, the volumetric variance of the optical region itself can also be estimated from Fig. 3 at a distance equal to the illuminated length (1 mm). This variance (see Table I) correlates reasonably well with values predicted by calculation using Eq. 1, when based on measurements of the illuminated length and diameter obtained with a microscope objective and reticle. Although this source of dispersion appears to be of little consequence, it might be further reduced by the use of spatial filtering to restrict the length of the capillary flowcell that is viewed by the photomultiplier tube.

Temporal dispersion results predominantly from the finite rate of response of photomultiplier tubes, amplifiers, filters, and other electronic circuitry. Other sources, such as long-lived fluorescence or phosphorescence from solutes of interest or from impurities in the solvents or optical components, may become important when they are of the same duration as electronic time constants. The temporal response of the LIF detector is examined by the periodic interruption of the laser beam with a light chopper at frequencies ranging from 0 to 5000 Hz. The modulated fluorescence signal from a flowing solution of coumarin 440 is observed with an oscilloscope, substituted for the chart recorder in Fig. 1. By the construction of a Bode plot[31] showing the relative signal amplitude as a function of the chopper frequency, the time constant is determined to be 0.7 ms. This time response is sufficiently rapid for almost any chromatographic application, including both high-speed and high-

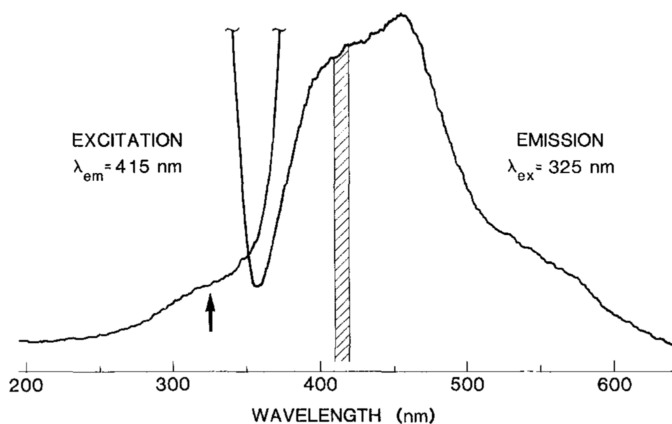

FIG. 4. Fluorescence excitation and emission spectra of 4-bromomethyl-7-methoxycoumarin derivatives of carboxylic acids.

efficiency applications. For comparison, the temporal dispersion may be expressed as an equivalent volumetric variance τ^2F^2, where τ is the observed exponential time constant and F is the volumetric flowrate (typically 1 μL/min).[29,32] When expressed in this manner, the temporal dispersion is equivalent to 1.4×10^{-22} L^2, more than two orders of magnitude less than the smallest volumetric flowcell variance (6×10^{-20} L^2 for a 35-μm flowcell of 10 mm length). Consequently, temporal sources of dispersion appear to be negligible.

Applications. Many molecules of current analytical interest, notably the polynuclear aromatic hydrocarbons, are inherently fluorescent. Although such compounds may occur in very complex matrices, they can be efficiently separated and sensitively detected with the use of the present analytical system.[8,15,20] Many other molecules, however, have low absorption cross-sections or low fluorescence quantum yields. These compounds may be rendered detectable with the use of fluorescence enhancement[33] and fluorescence quenching[34] techniques, or may alternatively be chemically modified to permit fluorescence detection. Derivatization procedures are especially attractive because they introduce an additional dimension of selectivity that can simplify analyses in a predictable and reproducible manner. Because many common UV lasers operate at fixed wavelengths, it is desirable to modify the derivatization label to suit the laser characteristics, rather than the converse. In a previous study,[20] dansyl chloride was demonstrated to be a suitable fluorescence label for excitation by the He-Cd laser (325 nm), and was employed for the detection of amino acids. In this investigation, a coumarin dye is examined as a fluorescent label for carboxylic acids.

The 4-bromomethyl-7-methoxycoumarin (BrMMC) tag is a fairly recent addition to the arsenal of fluorescent molecular probes.[21,22] This dye molecule reacts cleanly and rapidly with a variety of carboxylic acids to form derivatives with excellent spectroscopic and chromatographic properties. Figure 4 shows the fluorescence excitation and emission spectra of these derivatives, which seem well suited for excitation by the He-Cd laser. One collects the fluorescence emission at 430 nm (10 nm FWHM) in order to minimize interference from both the 442-nm laser emission and Raman scattering from the solvent.

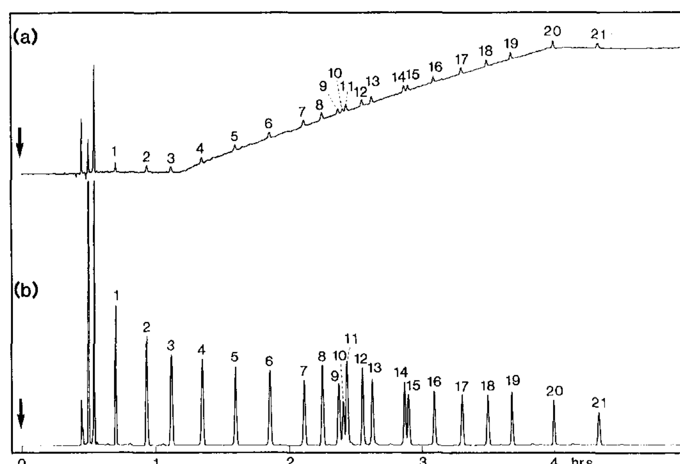

FIG. 5. Chromatogram of standard fatty acids derivatized with 4-bromomethyl-7-methoxycoumarin. Column: fused-silica microcolumn (0.20 mm i.d., 1.2 m length) packed with Spheri-5 RP-18. Mobile phase: A = 62.5% methanol, 22.5% acetonitrile, 15% water; B = 42.5% methanol, 22.5% acetonitrile, 35% ethyl acetate; isocratic for 40 min at 10% B, then linear gradient to 85% B in 170 min; 1.2 μL/min flowrate; 40°C temperature. Solutes: (1) Caproic (6:0), (2) Caprylic (8:0), (3) Pelargonic (9:0), (4) Capric (10:0), (5) Undecanoic (11:0), (6) Lauric (12:0), (7) Tridecanoic (13:0), (8) Linolenic (18:3), (9) Myristic (14:0), (10) Arachidonic (20:4), (11) Palmitoleic (16:1), (12) Linoleic (18:2), (13) Pentadecanoic (15:0), (14) Palmitic (16:0), (15) Oleic (18:1), (16) Margaric (17:0), (17) Stearic (18:0), (18) Nonadecanoic (19:0), (19) Arachidic (20:0), (20) Behenic (22:0), (21) Lignoceric (24:0); 10 picomoles each, 0.031 μL sample injected. Detectors: (a) UV-absorbance, λ_{abs} = 325 nm, 0.02 AUFS; (b) laser fluorescence, λ_{ex} = 325 nm, λ_{em} = 430 nm, 5 μA FS.

A standard mixture of 16 saturated and 5 unsaturated fatty acids (10 picomoles each) is derivatized with the coumarin label. The chromatographic separation is optimized on a fused-silica microcolumn packed with Spheri-5 RP-18 (5 μm), with the use of a complex mobile-phase gradient of methanol, acetonitrile, ethyl acetate, and water. For comparison, the chromatogram is recorded both by UV-absorbance and laser fluorescence detectors. The UV-absorbance chromatogram (Fig. 5a)

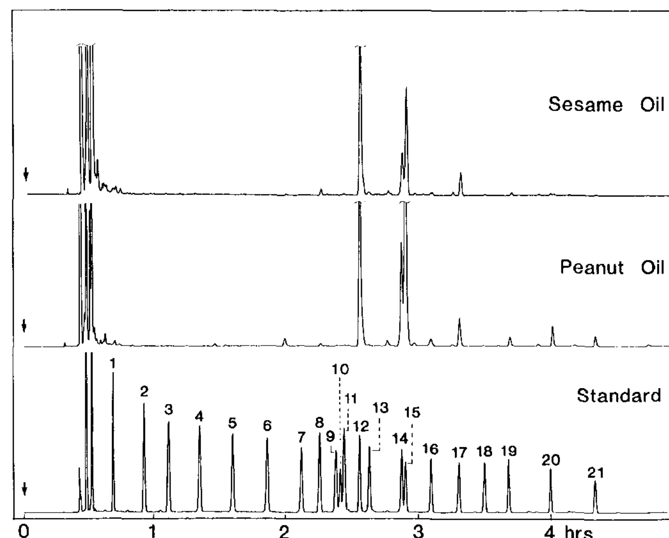

FIG. 6. Determination of fatty acids in saponified peanut and sesame oils. Chromatographic conditions are the same as described in Fig. 5.

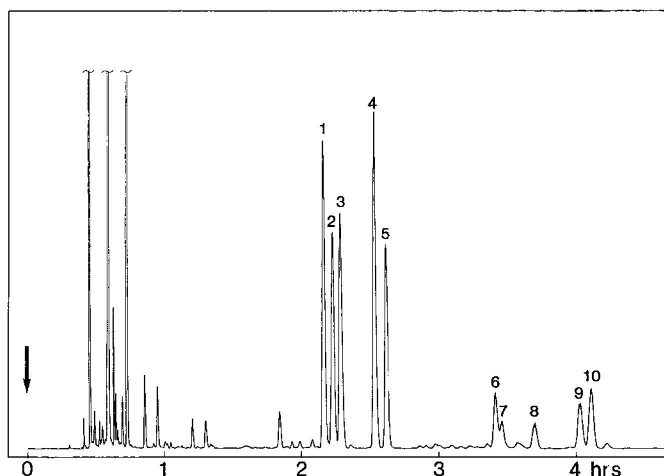

FIG. 7. Chromatogram of standard prostaglandins derivatized with 4-bromomethyl-7-methoxycoumarin. Column: fused-silica microcolumn (0.20 mm i.d., 1.0 m length) packed with MicroPak SP-18. Mobile phase: 24% acetonitrile, 47% methanol, 29% water; 37°C temperature. Solutes: (1) PGE_2, (2) PGD_2, (3) $PGF_{2\alpha}$, (4) PGE_1, (5) $PGF_{1\alpha}$, (6) PGA_2, (7) + (8) PGB_2 and unknown prostaglandin impurity, (9) PGB_1, (10) PGA_1; 0.25–1 picomole each, 0.015 μL sample injected. LIF detector: λ_{ex} = 325 nm, λ_{em} = 430 nm, 2 μA FS.

shows relatively poor sensitivity and selectivity for the fatty acid derivatives. Furthermore, because this detector is highly sensitive to changes in absorbance and refractive index of the mobile phase during gradient elution, the small peaks of interest are superimposed upon a steeply sloping baseline. In contrast, the fluorescence chromatogram (Fig. 5b) shows excellent sensitivity and selectivity for these derivatives, with the peaks of interest superimposed upon a flat baseline.

This methodology is employed to determine the composition of saturated and unsaturated fatty acids in complex lipids, such as triglycerides and phospholipids. Representative chromatograms of saponified vegetable oil samples (1 μL each) are shown in Fig. 6. The peanut and sesame oils contain predominantly unsaturated linoleic and oleic acids, together with lesser amounts of palmitic and other saturated fatty acids. Because of the high sensitivity and broad linear range of the LIF detector, both major and minor components may be accurately quantitated in a single analysis.

This methodology is also applied to the determination of prostaglandins, the clinically important metabolites of arachidonic acid.[35] Because such compounds are numerous and very similar in chemical structure, their chromatographic separation is a formidable task. Detection and quantitation are similarly difficult, as prostaglandins are present only at trace concentrations in physiological fluids and tissues. The combination of microcolumn LC and laser fluorimetric detection may therefore provide a powerful analytical tool for the determination of these biochemically important molecules. This potential is clearly demonstrated in Fig. 7, in which the coumarin derivatives of nine prostaglandin standards have been separated isocratically and detected at the subpicomole level. This separation is achieved on a fused-silica microcolumn containing MicroPak SP-18 (3 μm), having more than 150,000 theoretical plates under standard test conditions.[17] This promising methodology is currently being employed for the analysis of prostaglandins and leukotrienes in clinical and pharmaceutical samples.[36]

SUMMARY

The development of suitable detectors is currently one of the limiting factors in the routine practical application of microcolumn liquid chromatography. The laser fluorescence detector described herein appears to fulfill the rigorous requirements because of its high sensitivity (a few femtograms of analyte detected), remarkable linearity (greater than 10^8 dynamic range), and readily controlled detection volume (0.06 nL^2 to 0.06 μL^2). Although many improvements are possible, this system can already be applied to a wide variety of interesting analytical problems, of which the demonstrated separations of derivatized fatty acids and prostaglandins are only representative examples. Hence, it would appear that the combination of laser-induced fluorescence detection and microcolumn liquid chromatography shows exceptional promise for the analysis of complex, nonvolatile samples.

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Surface Studies of Coal, Oil, and Coal-Oil-Mixture Ash Using Auger Electron Spectroscopy and Solvent Leaching Techniques*

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Fly ashes produced by the combustion of coal, oil, and a coal-oil mixture have been studied by Auger electron spectroscopy and solvent leaching techniques. The Auger data indicate that the surface concentration of the metal ions Na, Fe, Mg, Ni, V, and Al as well as S and C increases on going from coal to coal-oil mixture and oil ash. The relative surface enrichments of oil and coal-oil-mixture ash are consistent with a simple model of the ash-formation process, and the results confirm that several toxic metals are significantly enriched on the surface of the ash particles. The Auger data are compared to HCl and tris buffer leachate composition analyses, and in neither case does the leachate give an accurate representation of the surface composition. HCl apparently dissolves large oxide deposits and thus overestimates the surface concentrations of Fe, Al, and V. Conversely, several metallic ions are essentially insoluble in neutral aqueous solutions, so their surface concentration is underestimated by the tris leachate.

Index Headings: **Fly ash; Surface analyses.**

INTRODUCTION

A major concern regarding fossil fuel combustion in stationary power sources is the potential for health and environmental effects caused by the ash particles released into the atmosphere. Coal ash, for example, consists of an aluminosilicate core that is coated with a number of toxic heavy metals.[1-4] As a result of this surface enrichment, larger amounts of these toxic elements are available for *in vivo* leaching than would be predicted based on a homogeneous distribution of each element within the particle.

The most direct evidence of ash surface enrichment is provided by analyses using ion microprobe mass spectrometry (IMMS),[5,6] and similar results have been obtained with the use of x-ray photoelectron spectroscopy (XPS)[7,8] and Auger electron spectroscopy (AES).[5] In all cases, these studies have used ion etching techniques to obtain chemical depth profiles of the particles and, consequently, to establish surface enrichment. Unfortunately, well-defined depth profiling is essentially precluded for heterogeneous particles such as fly ash. This is due to several factors including variations in particle size, uncertainties in etch rates, and cross-contamination effects.[9] In addition to these analytical difficulties, current data on surface enrichment is limited essentially to coal ash.

To date, only limited data is available on the surface composition of fly ash from oil-burning plants;[10,11] thus, the purpose of the work described here was to extend the surface composition data base by reporting data for fly ash from a commercial oil-burning power plant and for ash obtained from the combustion of a coal-oil mixture. For completeness, corresponding analyses were performed on fly ash obtained from a pulverized coal combustor. The surface composition of each ash was determined with the use of AES techniques. In order to avoid uncertainties associated with ion etching, we determined the characteristic bulk composition of each ash by atomic absorption measurements, and the surface enrichment of each element was then calculated from the ratio of the surface to bulk concentration. In addition, the surface analysis of each ash was compared with HCl and tris buffer leachate analyses.

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