regardless of type (Table VIII). A third summary table lists the average molecular weight, carbon number, Z number, carbon atoms in sidechains for the total sample, weight percent C, H, S, O, and atomic H to C ratio as calculated from MS data, and a distribution of the compound types according to the number of aromatic rings and the elements contained (Table IX). This last information can also be normalized. In addition, user oriented computer programs are available to merge the data from the aromatics analysis with those obtained for saturates, yielding conventional parameters such as carbon in aromatic rings, naphthenic rings, or in sidechains and specific correlations related to refinery or pilot plant processes.

These summaries apply at the present only to the 58 types included in the routine procedure; semiquantitative data on additional compound types, such as N compounds or compounds containing more than one heteroatom, can be obtained using manual computations.

CONCLUSION

The methods described have been used for the analysis of approximately 100 complex samples per month during the past 24 months, involving, on the average, the quantitative determination of 300 components in each sample. The method is applicable to all materials derived from petroleum boiling up to 1100 °F, regardless of origin, prior treatment, or width of boiling range interval. No previous separation is essential, and nonvolatile residua can be weighed and taken into consideration. Samples analyzed included petroleum streams, crude oils, and rock extracts, and more recently, coal liquefaction products (*7*). More than 150 compound types containing CH, CHO, CHO_2, CHO_3, CHS, CHS_2, CHSO, $CHSO_2$, $CHSO_3$, CHN, CHNS, and CHNO groups were identified in these samples. Analysis of a sample requires about three hours including instrument time, computer time, and human examination and interpretation of the various computer outputs. The actual computer time expended for data logging on the IBM 1802 varies from 2 to 16 minutes according to the scan rate. The CPU time expended for all successive calculations, including peak recognition, area measurement, formula calculation, and complete quantitative analysis is below 3 minutes on an IBM 360/50 computer. Elapsed time is usually two days. Unmechanized handling of the same type of sample would require about 4 to 8 hours for data acquisition, and a minimum of 24 hours for the computation of a quantitative analysis including only the compound type carbon number distribution. The calculation of the various summary tables would be practically impossible.

ACKNOWLEDGMENT

We thank G. R. Taylor and J. L. Taylor who obtained most of the experimental data, and M. S. B. Munson and H. E. Lumpkin for helpful suggestions in the course of this work.

RECEIVED for review September 22, 1969. Accepted December 19, 1969.

Gas Chromatographic and Nuclear Magnetic Resonance Spectroscopic Studies of 1,3-Dimethylbarbiturates Obtained by Various Methylation Techniques

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The methylation of 5,5-disubstituted barbituric acids by common procedures (dimethyl sulfate, diazomethane) prior to GLC analysis and by recently developed on-column methylation techniques utilizing tetramethylammonium hydroxide (TMAH) or trimethylanilinium hydroxide (TMAnH) has been reviewed and correlated with structural studies of these derivatives by NMR spectroscopy to show that *N*-methylation is predominant by these procedures. GLC retention times for methylated barbiturates derived by any of the above methylation procedures may now be used in full confidence that they arise from the *N*-methyl structures.

NUMEROUS GAS CHROMATOGRAPHIC procedures have been developed for the determination and identification of barbiturates both in pharmaceutical preparations and biological fluids (*1–7*). Unfortunately, the polar nature of the pharmacologically important 5,5-disubstituted barbituric acids, and to a lesser extent the 1,5,5-trisubstituted acids, tends to cause adsorption resulting in loss of material, contamination of the column, and tailing peaks (*8*). These features, which make quantitative work difficult or impossible, especially at the submicrogram level, can often be eliminated if the compound to be gas-chromatographed can be converted to a suitable nonpolar derivative. Although barbiturates do not give stable derivatives with the common silylating reagents (*9*), they can be methylated readily using either diazomethane (*10*, *11*) or

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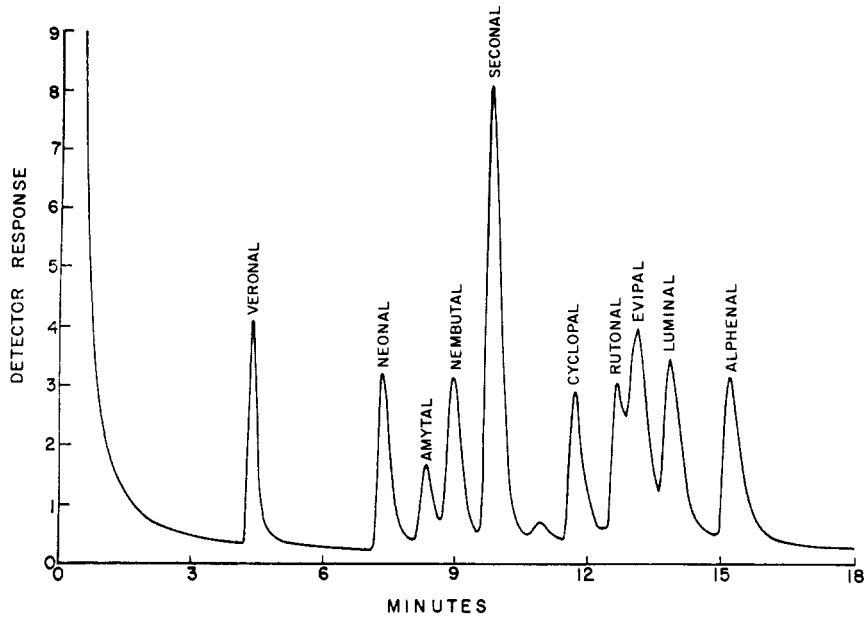

Figure 1. GLC chromatograph of a composite mixture of 1,3-dimethyl derivatives (1 μg of each) of the named barbituric acids

dimethyl sulfate in mildly alkaline media (*12*, *13*) to obtain dimethyl barbiturates which are more volatile than the unmethylated compounds. Recently on-column methylation of barbiturates using tetramethylammonium hydroxide (TMAH) (*14*) and trimethylanilinium hydroxide (TMAnH) (*9*) has been reported as a further aid and simplification for barbiturate analysis.

While methylation greatly facilitates the separation and differentiation of barbiturates by gas chromatography, two aspects of related chemistry require clarification if this combination of techniques can be relied upon for identification purposes. Since the amide portion of barbiturates may tautomerize to give the lactim form, *N*-methylation and/or *O*-methylation may occur resulting in different methyl derivatives with different retention times. The structures of the methylated barbiturates, therefore, need to be established not only for material methylated under normal conditions, but also for those conditions for which on-column methylation has been performed. It is the purpose of this paper to provide unequivocal evidence by nuclear magnetic resonance spectroscopy that *N*-methylation of 5,5-disubstituted barbiturates is exclusive with dimethyl sulfate and predominant with diazomethane, and to relate the GLC retention times derived from these known structures to those obtained by on-column procedures in order to demonstrate that *N*-methylation by a variety of methylating agents is universal.

EXPERIMENTAL

Equipment. Nuclear magnetic resonance spectra were obtained with a Varian A-60A spectrometer from chloroform-*d* solutions (tetramethylsilane used as internal reference) at ambient probe temperature of 40 ± 2 °C. The solutions used were 10–15% by weight in solute and showed no concentration effect on dilution. The chemical shifts are considered accurate to ±0.02 ppm.

A Model 1520B Varian Aerograph gas chromatograph was used with a hydrogen flame ionization detector. A 6-foot long, 1/8-inch stainless steel column packed with 60–80 mesh Chromosorb W coated with 5% SE-30 was conditioned at 250 °C for 48 hours and allowed to equilibrate at 175° for an additional 48 hours. With both the detector and injector at 225°, injections were made at initial oven temperature of 135° after which the oven temperature was programmed to increase at the rate of 4°/min for the first 16 minutes after injection. From 16 to 20 minutes, the oven was maintained at constant final temperature.

Methanolic solutions of the methylated barbiturates (5 mg/5 ml) were injected singly (2 μl ≡ 2 μg solute) and as a composite mixture (1-ml aliquots) of the ten barbiturate solutions. The composite mixture was evaporated and then made up to 1-ml volume with methanol after which 1 μl (10 μg total mixed solute) was injected to obtain the chromatogram shown in Figure 1.

Methylbarbiturates. The methylated barbiturates of Table I were those previously prepared and characterized by Manson and Cloutier (*15*) and held in these laboratories as reference compounds. The combined NMR/GLC re-examination of the analytical grade samples as well as several second and third fractions indicated that no deterioration of any samples had occurred during storage under ordinary refrigeration.

RESULTS AND DISCUSSION

Structural Characterization by NMR. The *O*-methyl as well as *N*-methyl derivative of 5,5-diethylbarbituric acid (veronal) was claimed by Marotta and Rosanova (*16*) to have been formed during methylation with diazomethane. Their *O*-methylveronal was separated as a noncrystallizing syrup from the crystalline *N*-methyl derivative, but no analytical data were given, although methoxyl determinations were made. This preparation of the *O*-methyl derivative was later questioned by Bush and Butler (*13*), Dox (*11*), and Stuckey (*12*), but these workers relied on chemical and ultraviolet spectroscopic evidence, and reported formation of only *N*-methyl derivatives when using diazomethane and/or dimethyl sulfate as methylating agents. Manson and Cloutier reached the same conclusion from studying infrared spectra of methylated barbiturates (*15*) which showed the absence of N—H stretching bands, the presence of a broad C=O stretching band in the 1650–1750 cm^{-1} region, and a strong band in

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Table I. Nuclear Magnetic Resonance Frequencies for Some 1,3-Dimethylbarbituric Acids

(δ in ppm downfield from TMS in $CDCl_3$)

Compound[a]	Barbiturate C-5	Substitution C-5	*N*-CH_3	CH_3(Et)	CH_2(Et)	ω-CH_3	—CH_2—	$CH_3(CH)\langle$
1(a)	CH_3CH_2	CH_3CH_2	3.33	0.77	2.02	:::	:::	...
2(b)	CH_3CH_2	$CH_3CH_2CH_2CH_2$	3.32	0.77	2.02	0.83	1.8–2.2(α) 1.0–1.3 (β) 0.9–1.2 (γ)	...
3(b)	CH_3CH_2	$(CH_3)_2CHCH_2CH_2$[b]	3.32	0.78	2.03	0.88	1.8–2.2 (α) 0.8–1.1 (β)	0.83
4(a)	CH_3CH_2	$CH_3CH_2CH_2(CH_3)CH$[b]	3.32	0.73	2.10	0.87	1.8–2.3 (β) 1.1–1.5 (γ)	0.96
5(a)	CH_2=$CHCH_2$[c]	$CH_3CH_2CH_2(CH_3)CH$[b]	3.32	...	...	0.88	1.1–1.5 (β) 1.9–2.4 (γ)	0.98
6(b)	CH_2=$CHCH_2$[c]		3.28 3.23	:::	:::	:::	(ring) 1.7–2.5	...
7(b)	CH_3[d]	C_6H_5[e]	3.32	...	...	:::	...	...
8(b)	CH_3[d]		3.32	...	...	...	Cyclohexyl 1.4–1.6 (2H) 1.6–2.3 (6H)	Vinylic CH 5.63
9(a)	CH_3CH_2	C_6H_5[e]	3.33	0.92	2.47	...	...	...
10(b)	CH_2=$CHCH_2$[c]	C_6H_5[b,e]	3.32	...	...	...	...	...

[a] Compound numbering is identical to that used in Table II and Figure 1. Compounds designated (a) were prepared with dimethyl sulfate and (b) compounds were obtained with diazomethane as the methylating agent.
[b] The methine proton signal is seen at 1.38, ~1.3, ~1.3, and ~3.4 ppm in compounds 3, 4, 5, and 10, respectively.
[c] The doublet for the allyl protons is centered at 2.77, 2.82, and 3.17 ppm and the vinylic protons of the allyl group are seen at 4.9–5.9, 4.9–6.0, and 5.0–5.8 ppm in compounds 5, 6, and 10, respectively.
[d] The methyl protons at C-5 resonate at 1.85 and 1.58 ppm in compounds 7 and 8, respectively.
[e] The phenyl protons at C-5 resonate at 7.27, 7.27, and 7.28 ppm in compounds 7, 9, and 10, respectively.

the 1360–1380 cm^{-1} region which they attributed to the N—CH_3 group. None of these techniques permits an assignment of barbiturate structure as unequivocally as NMR spectroscopy.

To the best of our knowledge, no chemical shift data had appeared in the literature for *N,N*-dimethyl-5,5-disubstituted barbiturates when we undertook this work. Such data are given in Table I for the dimethyl derivatives of ten commonly used barbiturates. Table I shows that the same *N*-methyl proton signal is obtained at 3.32 ± 0.04 ppm following methylation by either diazomethane or dimethyl sulfate. In addition, we have also synthesized various *N*-methyl and *N,N*-dimethyl 5- and 5,5-alkylated barbiturates as an extension of earlier structural and spectral investigations (*17*, *18*). From these barbiturates, prepared by the malonic ester and malonic acid/acetic anhydride condensation procedures using monomethylurea and *sym*-dimethyl-urea, respectively, we have observed the same *N*-methyl proton signal at 3.32 ± 0.04 ppm. While writing up this work, we learned of the recent NMR spectroscopic analysis of dimethyl amobarbital, dimethylbarbital, and dimethylphenobarbital employed by Brochmann-Hanssen and Oke (*9*) as confirmation of the expected 1,3-dimethyl structure.

Some additional features of the chemical shift data in Table I are interesting and merit further comment. Only 5-allyl-5-(1-cyclopenten-2-yl)-1,3-dimethylbarbituric acid (compound 6) shows nonequivalence of its *N*-1 and *N*-3 methyl protons. This nonequivalence is most likely due to the unequal anisotropic shielding and deshielding effects arising from the $\Delta^{2,3}$ double bond of the cyclopentene ring on account of the sp^3 geometry at C-1 of this ring. In contrast, the planar sp^2 geometry at C-1 of the cyclohexen-1-yl system of compound 8 results in equal shielding and deshielding anisotropic effects (*17*) to give equivalent *N*-methyl protons. An earlier paper (*17*) demonstrated that the methyl protons of the C-5 ethyl substituents are sensitive probes for detecting anisotropic shielding from the very nearly planar barbiturate ring. The barbiturates 4, 3, and 2 (Table I) bearing the 1-methylbutyl, isoamyl, and *n*-butyl substituents at C-5, respectively, also show this effect where the ω-methyl protons are sufficiently removed from the ring to experience less shielding than the CH_3(Et) protons.

Differentiation and Identification by GLC. Martin and Driscoll (*5*) first employed methylation to simplify gas chromatographic identification and determination of the four most commonly used barbiturates. Using Stuckey's method of methylation with dimethyl sulfate (*12*), Martin and Driscoll assumed that the dimethyl barbiturates have the methyl substituents in position 1 and 3. This assumption for *N*-methylation is based on the observations that the wavelength of maximum absorption at 228 mμ is unaffected by changes in pH (*12*).

Stevenson (*14*) further simplified and extended this technique by using tetramethylammonium hydroxide (TMAH) for on-column methylation of barbituric acids in conjunction with temperature programming by which he was able to resolve and identify thirteen of the eighteen common barbiturates injected as a mixture. Quantitative methylation of barbiturates was reported when the molar ratio of tetramethylammonium hydroxide to barbiturate was at least four

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Table II. GLC Retention Times and Elution Temperatures for Known 1,3-Dimethyl Barbiturates and Correlation with GLC Data Obtained by On-Column Methylation

	Pre-methylated barbiturates				On-column methylation		
Compd	1,3-Dimethyl derivative of[a]	Single R_t (min)	Elution temp. °C	Comp. R_t (min)	Barbiturate methylated[b]	Comp. R_t[c] (min)	Elution temp. °C
1	Veronal	4.50	153	4.37	Barbital	5.0	156
2	Neonal	7.10	164	7.33			
3	Amytal	8.00	167	8.33	Amobarbital	8.2	170
4	Nembutal	8.75	171	9.00	Pentobarbital	8.7	172
5	Seconal	9.75	174	9.90	Secobarbital	9.8	175
6	Cyclopal	11.25	182	11.75			
7	Rutonal	12.50	185	12.66	Methyl phenyl barbituric acid	12.4	183
8	Evipal	13.00	188	13.17			
9	Luminal	13.83	191	13.92	Phenobarbital	13.6	186
10	Alphenal	15.00	195	15.25	Alphenal	15.0	189

[a] Nomenclature used by Manson and Cloutier (*15*).
[b] Nomenclature used by Stevenson (*14*).
[c] Retention times estimated from a composite chromatograph published by Stevenson (*14*) for which elution temperatures were reported.

and the injection port temperature about 240 °C. Like Martin and Driscoll, Stevenson regards the 1,3-dimethyl structure of his methylated derivatives as likely, but he points out that experimental evidence is indirect. Stevenson found that the methylated derivatives of the common barbiturates, prepared according to Martin and Driscoll (*5*), had GLC properties similar to those formed by his on-column methylation techniques. Stevenson also noted that the 1-methyl derivatives of phenobarbital and barbital have considerably longer retention times than the on-column dimethyl derivatives of the parent compounds, but the former compounds give the same derivatives as phenobarbital and barbital when injected with TMAH (*14*).

Recently, Brochmann-Hanssen and Oke (*9*) described their flash-heater, on-column methylation of barbiturates, phenolic alkaloids, and xanthine bases by means of trimethylanilinium hydroxide (TMAnH). This reagent was found to be superior to TMAH as a methylating agent since *N,N*-dimethylaniline is a better leaving group than trimethylamine. Employing the method of Stevenson, Brochmann-Hanssen and Oke found that most barbiturates gave small second peaks due to incomplete methylation, but they did not observe any degradation reaction with phenobarbital. Structural evidence for the 1,3-dimethyl derivatives of 5-ethyl-5-isoamyl barbituric acid (amobarbital), 5,5-diethyl barbituric acid (barbital), and 5-ethyl-5-phenylbarbituric acid (phenobarbital) prepared by the dimethyl sulfate method (*12*), was reported recently by Brochmann-Hanssen and Oke from NMR spectroscopy. In hexadeuterio-acetone, the methyl proton signal appeared as a singlet at τ6.75, equivalent to six protons for the dimethyl derivatives of the barbiturates above and equivalent to three protons for the monomethyl derivatives: metharbital (5,5-diethyl-1-methyl barbituric acid) and mephobarbital (5-ethyl-1-methyl-5-phenylbarbituric acid). The three dimethyl barbiturates prepared by methylation with dimethyl sulfate had the same retention times as the products obtained by flash-heater methylation.

The structural basis for our series of ten 1,3-dimethyl barbiturates is provided by the chemical shift data of Table I as discussed earlier. The retention times and elution temperatures for this series of compounds, as obtained by programmed temperature GLC studies, by single injection, are given in Table II, and a GLC chromatogram of a composite mixture of 1-μg portion of each of the ten methylated barbiturates is reproduced in Figure 1. A small lag in retention times relative to those in Table II may be seen in Figure 1, presumably due to the composite nature of the sample. The small peak at R_t 11 minutes in Figure 1 was also obtained in the GLC chromatogram of 1,3-dimethylneonal at R_t 10.6 minutes (10% of total area) and is attributed to an impurity in neonal. Consideration was given to the possibility that the minor component in the 1,3-dimethylneonal sample could be a methoxyl derivative of *N*-methylneonal, particularly since NMR spectra showed a minute but significant peak for OCH_3 protons at 4.00 ppm. An impurity, however, is the more likely explanation, and as one reviewer has pointed out, commercial neonal is often impure and gives rise to a second peak of varying intensity in three out of four samples gas chromatographed by flash heater methylation.

For comparison, retention times and elution temperatures for seven of the 1,3-dimethyl barbiturates from Stevenson's data (*14*) are also given in Table II. The overall agreement of both parameters from the two sets of data is very satisfactory, and it should be noted that direct comparison is possible between tabulated barbiturates 1, 4, 5, and 9 since both our derivatives and Stevenson's were prepared from dimethyl sulfate. Although the relative order of retention times for barbiturates methylated by TMAnH by Brochmann-Hanssen and Oke (*9*) parallels the order in Table II, direct comparison is not possible because the former retention time data for dimethyl barbiturates are for isothermal gas chromatography at 130 °C. Brochmann-Hanssen and Oke, however, show that the dimethylamobarbital, dimethylbarbital, and dimethylphenobarbital gave the same retention times under their GLC conditions whether prepared from dimethyl sulfate or by the flash-heater methylation with TMAnH.

From this consideration of NMR spectroscopic evidence for structure and correlation of retention time data from various studies, it is concluded that methylation of the common 5,5-disubstituted or 1,5,5-trisubstituted barbituric acids either by standard techniques (dimethyl sulfate or diazomethane) or by on-column methylation (TMAH or TMAnH) gives 1,3-dimethyl derivatives. One exception may possibly result from the generation of small amounts of *O*-methyl derivatives in addition to the predominant *N*-methyl derivative by the action of diazomethane on 5,5-dialkyl and 1,5,5-

trialkyl barbiturates. NMR spectra on the total products of reaction of 5,5-diethylbarbituric acid and of 5-ethyl-5-methylbarbituric acid with excess ethereal diazomethane do show very small and variable quantities of two *O*-methylated species (OCH_3 proton signals at 4.08 and 4.02 ppm) to be present. The identity of these components is being more fully investigated and will be reported later, together with the structural identity of the various products (with OCH_3 proton signals at 3.86 and 4.00 ppm) arising from the action of excess diazomethane on 1,5-dialkylbarbituric acids.

ACKNOWLEDGMENT

The author is grateful to H. W. Avdovich for obtaining the NMR spectra, to G. L. Belec for performing the GLC analyses, and to K. Genest for helpful discussions. The author is particularly grateful to B. C. Flann for making reference samples available for this study.

RECEIVED for review September 11, 1969. Accepted December 22, 1969.

Quantitative Thin-Layer Chromatography Using a Flame Ionization Detector

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A flame ionization detector has been adapted to scan thin-layer chromatographic strips directly and produce a series of signals proportional to the amount of material present for each of the separated organic components. Thin-layer chromatographic separations are carried out on a metal-backed adsorbent strip that is passed directly between the nozzles of a dual-jet flame ionization detector. The signal from the detector is fed to an electrometer, recorder, and digital integrator. The strip is scanned at sufficiently high temperature (300–450 °C) so that all of the sample is removed from the adsorbent by a single scan. Observed background electronic noise is very low and the high detector sensitivity permits use of very small samples. The apparatus is sturdy and easily constructed.

THIN-LAYER CHROMATOGRAPHY (TLC) has many advantages over other chromatographic techniques, but quantitative evaluation of TLC plates has been a difficult task. Quantitative analysis can be made in some cases by densitometry or spot-area measurement, but these techniques require calibration and the relationships are frequently nonlinear. A wide variation in sensitivity is often observed with these techniques.

Cotgreave and Lynes (*1*) developed a technique in which a traveling furnace was passed over a TLC plate and the cracked products were swept into a flame ionization detector (FID) by a stream of gas. F. B. Padley (*2*) described a method whereby a thin quartz rod (0.5-mm diameter) covered with adsorbent (on which TLC separation had been previously made) was passed over the burner of a FID.

In our work, a metal-backed TLC adsorbent strip (on which TLC separation has been made previously) is passed directly between the nozzles of a dual-jet FID. The metal strip provides good physical support for the adsorbent, and it is easier to handle than a coated quartz rod.

EXPERIMENTAL

Apparatus. The main components of the apparatus are the frame with traveling stage, a reversible motor, and a dual-jet FID, as shown in Figure 1, and the TLC-strip assembly as shown in Figure 2.

(1) T. Cotgreave and A. Lynes, *J. Chromatog.*, **30**, 117 (1967).
(2) F. B. Padley, *ibid.*, **39**, 37 (1969).

The frame and traveling-stage portion of the scanner are constructed to provide for the horizontal movement of the TLC-strip through the FID. The traveling stage (holding the TLC-strip with spring-actuated pressure pads) slides on two parallel rails moved by a synchronous reversible motor. The choice of speed of the traveling stage is governed by several parameters of equal importance. These are the detector temperature, which is a compromise of the highest FID temperature at the lowest background noise level; the adsorbent thickness; the type of material used for TLC-strip backing; and the boiling range of the sample. At optimum traveling-stage speed, a sufficiently sharp heat-front exists to give good resolution of closely spaced zones without selective losses of low boiling-point components from the sample. For our work, the major portion of the investigation has been conducted at stage speeds of 9 in./min and a minor portion at 6 in./min. Speeds lower than 6 in./min have also been tested but show poor resolution and some (2–3%) light-end losses.

The traveling-stage speed of the scanner can be varied by replacing the drive pulley or changing the matched gear-set in the drive mechanism. Limit switches reverse the movement of the traveling stage in the automatic mode. Manual switches are provided to override the automatic reverse.

The traveling stage is fabricated of Micarta in order to insulate the TLC-strip electrically from the frame which is maintained at ground potential.

The FID is constructed to provide sufficiently high belt temperatures (300–450 °C) so that all the sample present on the TLC-strip is removed and ionized by a single scan, with low background noise. Pure hydrogen is fed through two individually adjustable platinum-tip nozzles (0.010 inch).

The early work on this project was carried out using a FID, as shown in Figure 3, in which air entered the detector chamber through a number of small holes drilled in a circular plate. The resulting air supply consisted of a group of jets of relatively high velocity. This design was modified (Figure 4) so that air entered through a sintered, stainless steel membrane, giving many more openings to lower the gas velocity. The aim in modifying the air inlet was to avoid losing volatilized sample by venting from the FID chamber. Also, the FID chamber was enlarged to accommodate a larger platinum-collector electrode (2.2-cm diameter). The larger collector is supported at two points to give greater dimensional stability. The ions formed in the flame are collected between the tips of the burners and TLC-strip, both polarized