can readily be seen in Figure 6, where DCB fronts at 20 and 30 °C are compared.

The problem of breakthrough of the more volatile CHC on PPF has plagued workers in the field. However, with these frontal experiments it is possible to predict that amount of PPF needed to prevent breakthrough at a given temperature and air volume. This is easily seen in Figure 7 where the results from Figure 3 have been replotted as the cumulative percent of TCB recovered at different air volumes. At 500 m^3, 90% of the TCB is found within the first 4 cm of foam. At 900 m^3, however, 7 cm of foam is required to retain 90% of the TCB. A series of these curves for compounds of differing volatilities would aid the selection of PPF bed volumes and sampling conditions.

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Characterization of the Basic Fraction of Marijuana Smoke by Capillary Gas Chromatography/Mass Spectrometry

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The basic fraction of Mexican marijuana smoke condensate was characterized by combined capillary gas chromatography/mass spectrometry. Enrichment of some trace components was accomplished with high-performance liquid chromatography, permitting tentative identification of nearly 300 nitrogen-containing sample components. A comparison with the basic fraction of tobacco smoke condensate, characterized by the same methodology, revealed that there are both qualitative and quantitative differences between the two condensate fractions.

An extensive use of marijuana together with the related question about its possible hazards to human health have increased scientific interests in these matters. Although much still remains to be learned about the social, pharmacological, and toxicological aspects of marijuana, a number of interesting observations were made over the last 2 decades. While many observed effects of this "drug" relate to its major psychoactive components, Δ^9-tetrahydrocannabinol or other structurally related compounds (cannabinoids) present in the *Cannabis sativa* plant, it has been pointed out (*1–3*) that in certain cases cannabinoids are not toxicologically and pharmacologically synonymous with marijuana. Obviously, other active, as yet unidentified, components must also be present.

The major way of marijuana use is by smoking, yet very little has been known about the chemical composition of the smoke. This situation can now be changed, since relatively standardized ways of smoke condensate preparation together with powerful multicomponent analytical methods (based on chromatographic principles) have become available in the research on tobacco carcinogenesis and related problems. With such methodology, it is quite feasible to separate and identify hundreds of marijuana plant and smoke components. In conjunction with biological testing, even trace components in very complex mixtures can be identified and potentially implicated in toxicity effects.

While glass capillary column gas chromatography and its combination with mass spectrometry are now extensively used in tobacco aroma and smoke research, employment of these techniques in marijuana-related investigations has been considerably less. Thus, smoke profile (*4*) and total condensate and hashish components (*5*) were recorded and further investigated, while a capillary gas chromatographic technique was also used for a forensic "fingerprinting" application (*6*). Maskarinec et al. (*7*) isolated acidic and phenolic components from marijuana smoke condensate and identified numerous components as their methyl and trimethylsilyl derivatives; certain differences between the samples of Mexican and Turkish marijuana were observed. Polycyclic aromatic hy-

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drocarbons in marijuana and tobacco smoke condensates were isolated and characterized qualitatively and quantitatively (*8, 9*); higher amounts of carcinogenic compounds were found in marijuana smoke as compared to tobacco smoke, the fact supporting earlier evidence (*10, 11*) of correspondingly higher mutagenicity of the former with human lung explants.

The present study reports on chemical characterization of the basic fraction of marijuana smoke by combined capillary gas chromatography/mass spectrometry (GC/MS), given the limitations of sample volatility. We estimate that only 15–20% of the isolated basic fraction of the smoke condensate is amenable to gas chromatography. Due to the limited availability of standard compounds, many identifications (out of some 300 components, in total) must still be considered tentative. Tobacco smoke condensate has been used here as a "base line material" to which the marijuana basic fraction can be compared in qualitative and semiquantitative terms.

Interest in the basic fraction of marijuana smoke condensate stems from recent biologial observations (*12–14*). Experimental mice were subjected to a battery of tests encompassing behavioral, neurologic, and autonomic observations following administration of marijuana smoke bases (*12*); the results suggest possible central behavioral effects as well as central or peripheral autonomic effects of this fraction.

Other potentially important observations are related to the observed high mutagenicity of marijuana smoke condensate and the basic fraction in particular (*13, 14*). As the nitrogen containing polycyclic aromatic compounds, so-called aza arenes, have recently provoked interest (*15, 16*) because of their high mutagenicity in a variety of other combustion products, their presence and amounts in marijuana smoke could have additional toxicological implications.

EXPERIMENTAL SECTION

Smoke condensates were obtained by means of a standard smoking machine from 300 cigarettes of either Mexican marijuana obtained from the National Institute on Drug Abuse, Rockville, MD (content of the major cannabinoids: Δ^9-tetrahydrocannabinol, 1.18%; cannabinol, 0.18%; cannabidiol plus cannabicyclol, 0.16%), or standard tobacco (Tobacco-Health Research Institute, the University of Kentucky, Lexington, KY). Puffs of a 2-s duration in 1-min intervals were drawn while the smoke was trapped in pure acetone using a cryogenic trap held at approximately −60 °C. After acetone was evaporated to dryness, the residual condensate weights were determined.

Fractionation of smoke condensates into different compound classes was accomplished according to the previously described solvent partition scheme (*17*). The basic fraction was obtained through solubility adjustment at different pH values. Previous studies with other combustion products (*18,19*) established that most nitrogen-containing substances are effectively extracted into this basic fraction. However, certain compounds of the hydrogen-donor nature (e.g., indole and carbazole derivatives) may end up in the polar neutral fraction (*19*) while using this solvent partition scheme.

At pH 13, marijuana smoke or tobacco smoke bases were reextracted into methylene chloride and, after a suitable solvent evaporation, injected directly onto a 50 m × 0.25 mm i.d. glass capillary column coated with UCON 50-HB-2000 stationary phase. A modified Varian Model 1400 gas chromatograph was used for all gas chromatographic experiments. Column selection and other methodological aspects of the separation of nitrogen-containing compounds were previously described (*18, 20*).

In order to identify the individual chromatographic peaks, we attached the UCON capillary column to the ion source of a Hewlett-Packard Model 5982A combined gas chromatograph/mass spectrometer operating in the electron impact mode. The mass spectra could be acquired only from the major fractions, while the trace components could not be identified from the total chromatograms. Apparently, a comprehensive identification effort and acquisition of spectra from the minor peaks required an enrichment technique.

In order to enhance concentrations of the trace components, we used semipreparative HPLC. The chromatographic fractionations of the total condensate samples were accomplish by using four 90 cm × 1.0 mm i.d. columns connected in series. The packing used was an aminosilane-bonded Porasil C (37–75 μm), as described earlier (*20*). Successive elutions of the smoke condensates had to be made to provide enough material for GC/MS studies. The column outlet was monitored by a Perkin-Elmer LC-55 variable-wavelength detector set at 254 nm, while a Waters Associates Model 6000 pump was used to deliver *n*-hexane through the column at 0.5 mL/min. As there was some evidence of the accumulation of very polar compounds on the column while using *n*-hexane as the mobile phase, the columns were further washed with methylene chloride between the runs until no residual UV absorbance was observed. These fractions were also saved for further identification work.

Individual HPLC fractions were concentrated to appropriate volumes and monitored for efficiency of enrichment by capillary GC. Adequately concentrated samples were further subjected to GC/MS analysis.

RESULTS AND DISCUSSION

Average residual weights from three different smoke collections were 24.8 ± 4.2 and 15.1 ± 3.1 g for marijuana and tobacco, respectively. These weight determinations were carried out after complete evaporation of acetone. Both the uncontrolled variations during smoke collection and losses due to solvent evaporation most likely caused the large deviations from the average. However, in accordance with previous observations (*8, 9*), residue weights were always significantly higher for marijuana smoke. The average yields of the basic fraction from three different experiments were 2.9% and 5.5% for marijuana and tobacco, respectively.

Capillary gas chromatograms of marijuana and tobacco smoke basic fractions are shown in Figure 1, demonstrating the extreme complexity of such mixtures. It is quite evident that the chromatographic profiles of these two samples are quantitatively quite different.

Differences in these two fractions were also indicated by the results of GC/MS. For spectral information on the trace mixture components, HPLC fractionations had to be carried out. As shown in Figure 2 (a course of fractionation monitored for both smoke condensates), quantitative differences between the two materials are also indicated here. Figure 2 shows the sequence of the collected fractions.

Under conditions similar to those in Figure 1, adequately concentrated HPLC fractions were further subjected to capillary GC/MS. Unlike the situation with Figure 1, numerous trace components were now sufficiently enhanced to yield good spectra. While it would be impractical to show the results of all fractionation and enrichment steps, a typical example is demonstrated in Figure 3. Note that quite different peaks are now represented in the two capillary chromatograms. Of course, a minor overlap is understandable.

The individual fractions were analyzed, yielding close to 300 nitrogen-containing components which were tentatively identified. Through matching the retention data and mass spectra, the identified components from the individual fraction profiles can be "reconstructed" into the chromatograms of total samples shown in Figure 1. The peak numbering of Figure 1 corresponds to the identified components listed in Table I. Due to unavailability of appropriate retention standards and the small sizes of certain peaks in Figure 1, it has been difficult to provide exact locations of certain constituents. Consequently, many identified components are listed in Table I as being somewhere between the major peaks (e.g., between peaks 6 and 12, 12 and 16, etc). The task of exact peak location proved to be even more difficult with the components at the end of chromatograms as well as those washed with methylene chloride between the HPLC runs. The components yielding recognizable spectra that were difficult

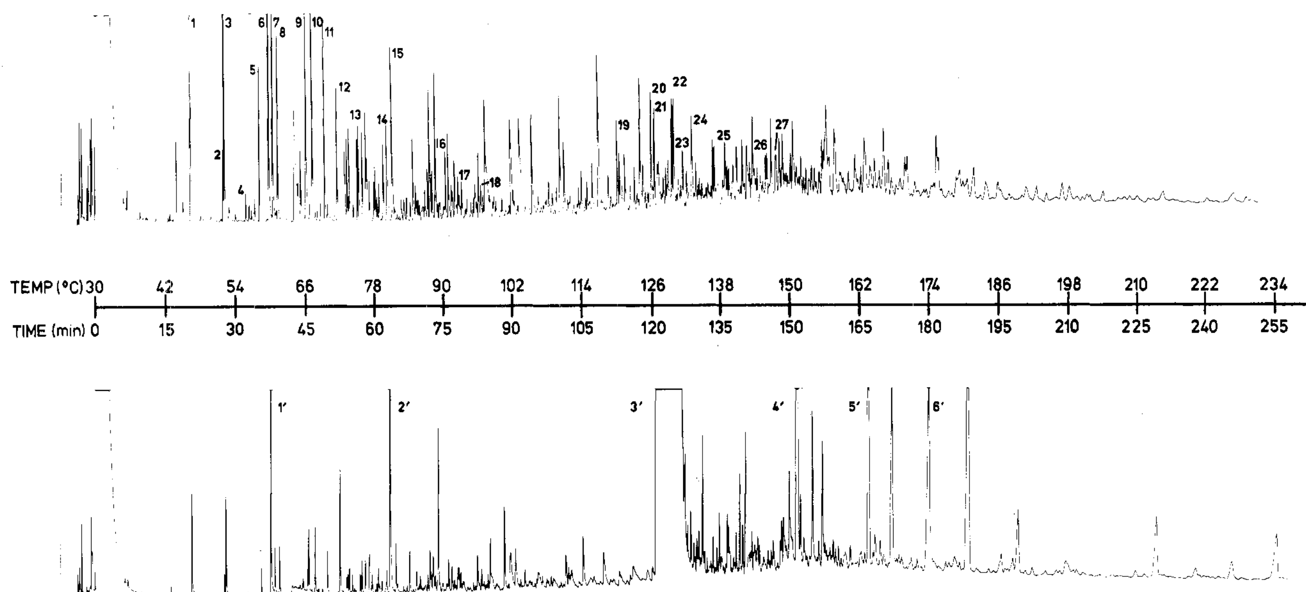

Figure 1. Comparison of chromatograms obtained from the basic fraction of marijuana (above) and tobacco (below) smoke condensates. Column: 50 m × 0.25 mm i.d. glass capillary column coated with UCON 50-HB-2000. For marijuana smoke constituents, see Table I. Tobacco smoke components (bottom chromatogram): 1′, 3-methylpyridine; 2′, 3-vinylpyridine; 3′, nicotine; 4′, myosmine; 5′, nicotyrine; 6′, 2,3′-bipyridyl.

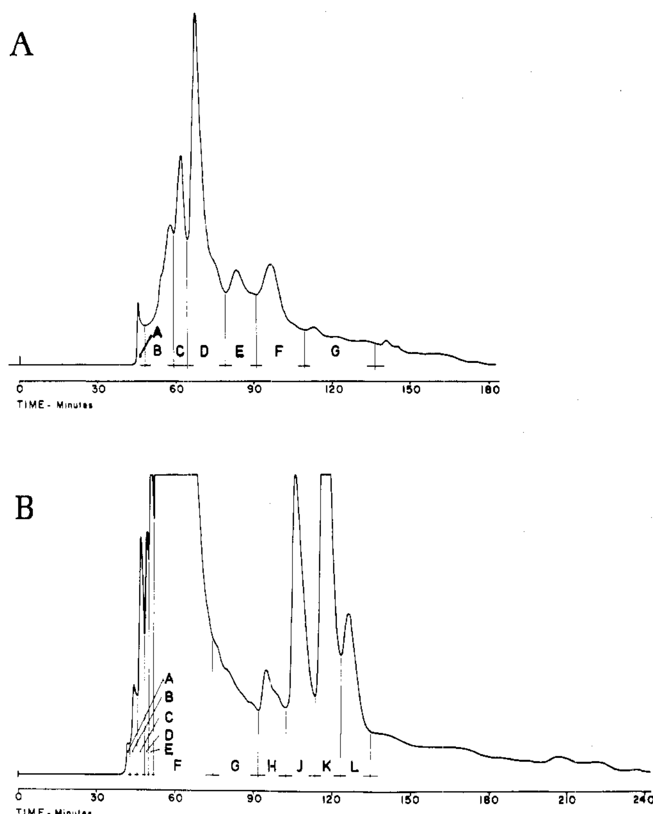

Figure 2. HPLC fractionation of the basic fractions of (A) marijuana smoke and (B) tobacco smoke. Column: Four 90 cm × 1.0 mm i.d. columns (connected in series), dry-packed with an aminosilane-treated Porasil C; conditions as described in the text. The individual fractions were collected and concentrated for capillary GC, as demonstrated in Figure 3.

to insert into the above ranges are *N*-methylacetamide, acetamide, propionamide, isobutylamide, 2-methylbutylamide (?), isovaleramide, valeramide, pyrrolidone, 5-valerolactam, 3-methylvaleramide (?), and 4-methylvaleramide.

Both Figure 1 and the table emphasize that while many similar products of combustion are present in both types of smoke condensate, some definite qualitative and quantitative differences exist.

The solvent partition scheme (*17*) appears highly effective in isolating the basic fraction from these very complex smoke matrices. As indicated by Table I, interferences by non-nitrogen compounds are almost negligible. Although the glass capillary columns provide a great degree of resolution, as evidenced by Figure 1, chemical characterization of the minor components has needed the HPLC fractionation and sample preconcentration (Figures 2 and 3).

Most of the components listed in Table I could not be identified or characterized without the enrichment step. Note the difference between "identification" and "characterization". By "identification" we mean that both mass spectra and retention times of chromatographic peaks coincide with those of corresponding standards or that mass spectra alone are sufficiently characteristic. "Characterization" means here that useful mass spectral information has been acquired to permit a likely structural assignment, such as a molecular formula or even the type of substitution (but not always its position). In many cases, a precise structural assignment will not be feasible without acquiring authentic compounds. However, peak characterization is often useful to decide whether further structural work is profitable or not.

While the state-of-the-art analytical methodologies are now capable of generating a vast amount of data on toxicologically interesting materials, biological interpretation of such data is considerably more difficult. Assays for biological activities in complex mixtures are complicated by possibilities of complex molecular interactions and synergistic effects. In spite of these drawbacks, the analytical information is frequently required to provide better understanding of toxicity at the molecular level. Two general approaches suggest themselves in such investigations: (a) biological investigations of a limited number of fractions (such as, for example, those indicated in Figure 2), followed later by a detailed chemical characterization of the active fractions, or (b) screening materials for the presence of structures that suggest themselves as "toxicologically interesting", drawing from analogies with other toxic substances. Under different circumstances, both approaches could be successfully applied. At any rate, analytical characterization is eventually needed.

Isomerism will frequently play an important role in biological activity. Take an example of a methyl-substituted benz[*a*]anthracene molecule (*21*): while some isomers are highly carcinogenic, the others are virtually inactive. Whether

Table I. Compounds Found in the Basic Fraction of Marijuana Smoke Condensate

peak no.	range of elution	mol wt	mol formula	identification	present in tobacco smoke
1		79	C_5H_5N	pyridine	+
2		84	$C_4H_8N_2$	dimethylaminoacetonitrile	+
3		93	C_6H_7N	2-methylpyridine	+
4		94	$C_5H_6N_2$	methylpyrazine	
	4-5	94	$C_5H_6N_2$	a methylpyrimidine	−
5		107	C_7H_9N	2,6-dimethylpyridine	+
6		93	C_6H_7N	3-methylpyridine	+
	6-12	113	C_5H_7NS	dimethyl- or ethylthiazole or -isothiazole (2 isomers)	+
7		93	C_6H_7N	4-methylpyridine	+
8		107	C_7H_9N	2-ethylpyridine	+
	8-10	108	$C_6H_8N_2$	dimethyl- or ethylpyrazine or -pyrimidine (3 isomers)	−
	8-19	121	$C_8H_{11}N$	trimethyl-, ethylmethyl-, or propylpyridine (20 isomers)	+
9		107	C_7H_9N	2,5-dimethylpyridine	+
10		107	C_7H_9N	2,4-dimethylpyridine	+
11		107	C_7H_9N	2,3-dimethylpyridine	+
12		107	C_7H_9N	3-ethylpyridine	+
	12-13	105	C_7H_7N	2-vinylpyridine	+
	12-13	107	C_7H_9N	4-ethylpyridine	+
	12-13	127	C_6H_9NS	a trimethyl- or methylethylthiazole or -isothiazole	−
	12-16	122	$C_7H_{10}N_2$	trimethyl or methylethylpyrazine or -pyrimidine (4 isomers)	+
	12-19	135	$C_9H_{13}N$	butyl-, methylpropyl-, diethyl-, ethyldimethyl-, or tetramethylpyridine (33 isomers)	+
13		107	C_7H_9N	3,5-dimethylpyridine	+
	13-17	110	$C_6H_{10}N_2$	propyl-, methylethyl-, or trimethylpyrazole or -imidazole (15 isomers)	+
14		105	C_7H_7N	3-vinylpyridine	+
15		107	C_7H_9N	3,4-dimethylpyridine	+
	15-19	119	C_8H_9N	methylvinyl- or propenylpyridine, or azaindan (15 isomers)	+
	15-16	136	$C_8H_{12}N_2$	butyl-, methylpropyl-, diethyl-, diethylmethyl-, or tetramethylpyrimidine or -pyrazine (5 isomers)	+
	15-20	149 163 etc.	$C_{10}H_{15}N$ $C_{11}H_{17}N$ etc.	alkylpyridine with five or more carbon atoms in saturated side chains(s) (45 isomers)	+
	15-end	124	$C_7H_{12}N_2$	butyl-, methylpropyl-, diethyl-, dimethylethyl-, or tetramethylpyrazole or -imidazole (16 isomers)	−
16		109	C_6H_7NO	3-methoxypyridine	+
17		121	C_7H_7NO	2-acetylpyridine	+
	17-18	151	$C_9H_{13}NO$	*N*-furfurylpyrrolidine (?)	+
	17-18	123	C_7H_9NO	a methylmethoxypyridine	−
	15-18	106	C_7H_6O	benzaldehyde	−
	15-18	118	$C_5H_{10}OS$	4-methylthio-2-butanone (?)	−
	15-19	135	C_8H_9NO	methylacetylpyridine (4 isomers)	+
18		82	$C_4H_6N_2$	1-methylimidazole	−
	18-19	98	$C_5H_6O_2$	furfuryl alcohol	−
	18-19	133	$C_9H_{11}N$	ethylvinyl-, dimethylvinyl-, methylpropenyl-, or butenylpyridine, or methylazaindan or tetrahydronaphthalene (35 isomers)	+
	18-19	96	$C_5H_8N_2$	ethyl- or dimethylpyrazole or imidazole (5 isomers)	+
	18-19	119	C_7H_5NO	benzoxazole	−
	18-19	121	C_7H_7NO	3-acetylpyridine	+
	18-27	108	$C_6H_8N_2$	methylamino- or aminomethylpyridine (15 isomers)	+
	18-27	147 161 etc.	$C_{10}H_{13}N$ $C_{11}H_{15}N$ etc.	pyridine with five or more carbons in side chains including one double bond, or forming one ring (41 isomers)	+
	18-19	165	$C_{10}H_{15}NO$	a methylfurfurylpyrrolidine (?)	+
	18-19	135	C_8H_9NO	2-propionylpyridine	−
	18-19	121	C_7H_7NO	4-acetylpyridine	−
	18-19	149	$C_9H_{11}NO$	dimethyl- or ethylacetylpyridine (2 isomers)	+
19		94	$C_5H_6N_2$	2-aminopyridine	+
	19-end	138 152 etc.	$C_8H_{14}N_2$ $C_9H_{16}N_2$ etc.	alkylpyrazole or -imidazole with five or more carbon atoms in saturated side chain(s) (42 isomers)	−

Table I (*Continued*)

peak no.	range of elution	mol wt	mol formula	identification	present in tobacco smoke
	19-end	109	$C_5H_7N_3$	methylamino- or aminomethylpyrazine or -pyrimidine or diaminopyridine (4 isomers)	
	19-end	122	$C_7H_{10}N_2$	aminoethyl-, ethylamino-, aminodimethylamino-, or methylaminomethylpyridine (13 isomers)	+
	19-20	131	C_9H_9N	divinylpyridine, azadihydronaphthalene or methylazaindene (2 isomers)	+
20		129	C_9H_7N	quinoline	–
21		162	$C_{10}H_{14}N_2$	nicotine	+
	21-27	130	$C_8H_6N_2$	diazanaphthalene (2 isomers)	+
	20-25	124	$C_6H_8N_2O$	a methoxyaminopyridine (?)	–
22		129	C_9H_7N	isoquinoline	–
	22-end	118	$C_7H_6N_2$	indazole or pyrrolopyridine (3 isomers)	+
	22-end	123	$C_6H_9N_3$	aminoethyl-, ethylamino-, aminodimethyldimethylamino-, or methylaminomethylpyrazine or -pyrimidine or methyldiaminopyridine (5 isomers)	+
23		143	$C_{10}H_9N$	8-methylquinoline	
24		143	$C_{10}H_9N$	2-methylquinoline	
25		143	$C_{10}H_9N$	7-methylquinoline	
26		143	$C_{10}H_9N$	4-methylquinoline	
	22-end	143	$C_{10}H_9N$	other methylquinolines and -isoquinolines (10 isomers; 14 in all)	+
	22-end	132	$C_8H_8N_2$	methylindazole, -benzimidazole, or -pyrrolopyridine (12 isomers)	+
	22-27	145 159 etc.	$C_{10}H_{11}N$ $C_{11}H_{13}N$ etc.	pyridine with five or more carbon atoms in side chains including two double bonds or containing one ring and one double bond (11 isomers)	+
	22-27	150	$C_{10}H_{14}O$	2-*tert*-butylphenol	–
27		157	$C_{11}H_{11}N$	2,4-dimethylquinoline	
	22-end	157	$C_{11}H_{11}N$	other dimethyl- or ethylquinolines or -isoquinolines (19 isomers; 20 in all	+
	25-end	144	$C_9H_8N_2$	methyldiazanaphthalene (3 isomers)	+
	25-end	146	$C_9H_{10}N_2$	dimethyl- or ethylindazole, benzimidazole, or pyrrolopyridine (23 isomers)	+
	25-end	136	$C_8H_{12}N_2$	aminopyridine with three carbon atoms in saturated side chain(s) (8 isomers)	+
	27-end	137	$C_7H_{11}N_3$	an aminopyrazine or -pyrimidine with three carbon atoms in saturated side chain(s) or a dimethyl- or ethyldiaminopyridine	+
	27-end	155	$C_{11}H_9N$	vinylquinoline or phenylpyridine (3 isomers)	+
	27-end	169	$C_{12}H_{11}N$	methylvinylquinoline or methylphenylpyridine (6 isomers)	+
	27-end	122	$C_6H_6N_2O$	2-pyridinecarboxamide	+
	27-end	150	$C_9H_{14}N_2$	aminopyridine with four carbon atoms in saturated side chain(s) (3 isomers)	–
	27-end	133	C_8H_7NO	an azaindanone (?)	–
	27-end	136	$C_7H_8N_2O$	a methylpyridinecarboxamide	–
	27-end	133	$C_7H_7N_3$	methylpyrrolopyrimidine or -pyrazine (?) (2 isomers)	–
	27-end	147	$C_8H_9N_3$	a dimethyl- or ethylpyrrolopyrimidine or -pyrazine (?)	–
	27-end	171	$C_{12}H_{13}N$	propyl-, methylethyl-, or trimethylquinoline or -isoquinoline (4 isomers)	+
	27-end	185 199	$C_{13}H_{15}N$ $C_{14}H_{17}N$	quinoline or isoquinoline with four or more carbon atoms in saturated side chain(s) (2 compounds)	–

similarities with this case exist within the nitrogen compounds studied in this work is presently not known but certainly cannot be ruled out. The point of interest is, however, that capillary GC is capable of resolving virtually all possible positional isomers with such compounds. The number of isomers listed in Table I means that they were actually recorded as individual peaks.

A survey of Table I reveals in many cases the presence of compounds that are to be expected in various tar products or fuels. For example, methylated pyridines and quinolines in tobacco smoke were already investigated (*22, 23*), and a number of other small nitrogen-containing molecules were found by Schumacher et al. (*24*) in the same material. The presence of alkylated quinolines in both marijuana and tobacco is of interest, as these substances have recently been implicated as environmental cocarcinogens (*16*).

A number of compounds found in the smoke condensates in this work not been previously reported in such materials. Compounds with polar substitutions, such as aminopyridines, acetylpyridines, aminoalkylpyridines, aminopyrazines, pyridinecarboxamides, etc. might be worth testing for biological activity.

Comparisons between tobacco and marijuana smoke constituents are interesting. Although many observed differences

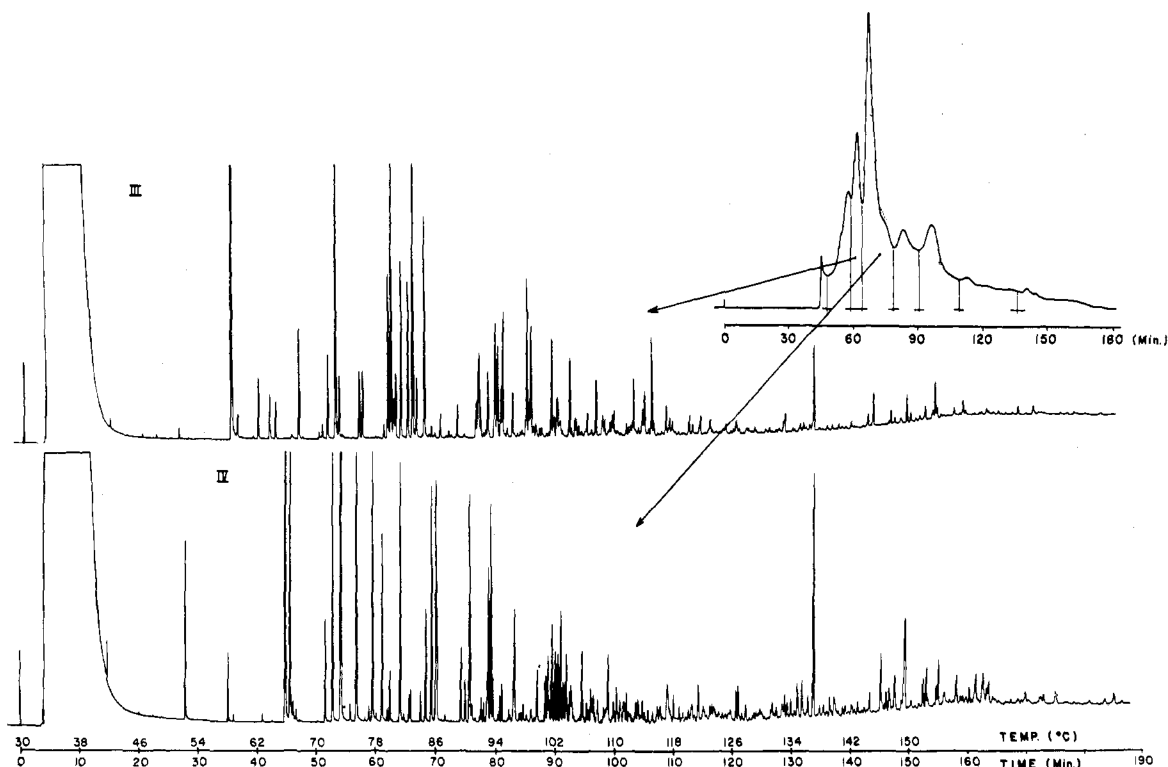

Figure 3. A typical analysis of HPLC fractions by capillary HPLC. Columns and conditions: same as Figures 2 and 3, and as described in the text.

are primarily quantitative in nature, the amounts can be strikingly different and may well have toxicological significance. The trivial case in point is nicotine, which exists as a trace component in the smoke or even the marijuana plant extract (*25*), while it accounts, naturally, for the majority of the tobacco fraction.

The total profiles of marijuana and tobacco smoke bases are strikingly different. To see a large array of structures would be more logical for tobacco than marijuana due to the possible pyrolytical decomposition of nicotine and the related bases. Precursors of the many components of varying structures in marijuana are a bit of a puzzle: our preliminary results (*25*) indicate that only some 0.2–0.7% of the plant extract is basic. Although some marijuana alkaloids were tentatively identified in an earlier work (*26*), they are only trace components of the plant. The same is true for other (mostly "trivial") nitrogen compounds (*27*) of *Cannabis sativa*. A reasonable assumption can also be made that the content of proteins and nucleic acids in both types of plant should be roughly comparable. Why does then the marijuana smoke contain to so many basic pyrolytical fragments? Although only quantitative differences exist among numerous profile components, a number of peaks appear to be "typical" of the marijuana smoke condensate. Benzoxazole, substituted thiazoles, pyrazoles, or imidazoles come closest to meeting such conditions; if present in tobacco smoke at trace levels, they are below the sensitivity limits of the described methodology. Of course, "typical" tobacco smoke components of basic nature are known (*28*) that also appear in the respective chromatogram (Figure 1).

Whereas the identification and chemical characterization work described here concerns nearly 300 nitrogen-containing compounds within the volatility restrictions up to 2-ring structures inclusive, biological testing can now be performed on both HPLC fractions or individual substances of "interesting" structures. Naturally, possible toxicity or synergistic effects of larger nitrogen-containing compounds that were extracted from marijuana smoke condensate (not appearing in our chromatograms due to volatility limitations) cannot be excluded.

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CORRESPONDENCE

Effects of Major Ions on the Determination of Trace Ions by Ion Chromatography

Sir: The most obvious problem associated with the use of ion chromatography (*1*) in the determination of the principal ions in seawater is that of linearity of response, since the latter is electrolytic conductivity of acids or hydroxides. A second phenomenon, potentially a problem to be confronted in the same area of use, has not been addressed. Is there a range of concentration of one species which will affect the response of a second species *even though* the two elution peaks are well separated? This problem was addressed and we wish to report our result since it will be of general use to those users of ion chromatography who are making determinations of a minor constituent species in the presence of a very large amount of a second constituent species.

EXPERIMENTAL SECTION

The two anions chloride and sulfate were chosen for the study because: (i) their elution peaks are well separated, (ii) they are easily obtainable as reagent grade salts of the same cation, and (iii) chloride is of most general interest in view of its concentration in seawater.

A Dionex Model 14 ion chromatograph (Dionex Corp., Sunnyvale, CA) was used, equipped with a 3 × 150 mm anion precolumn, a 3 × 500 mm anion separator column, and a 6 × 250 mm anion suppressor column. Standard anion eluent, 0.0024 M Na_2CO_3/0.0030 M $NaHCO_3$, was used. The sample loop was ca. 100 μL and a flow rate of 130 mL h^{-1} was used for all of the study. Test results of chloride and sulfate were prepared in standard eluent as the solvent, eliminating the complication of the dip which precedes the chloride elution peak (*2*). No more than six test samples were run between suppressor regeneration cycles. The order of test solution loading was varied as a further precaution to prevent the suppressor state from becoming a variable. A two-pen recorder, together with the multiscale instrument output, permitted the record of response on effective scales of 30–1000 μS cm^{-1}. All responses have been converted to the scale of 100 μS cm^{-1}. Peak heights on the chart paper were used as measure of response. Three series of experiments were conducted:

Series 1. Eight test solutions were prepared, each of which contained 100 ppm sulfate while the chloride was varied from 0 to 400 ppm.

Series 2. Six test solutions were prepared, each of which contained 100 ppm sulfate while the chloride was varied from 500 to 16000 ppm.

Series 3. Six test solutions were prepared, each of which contained 4000 ppm chloride while the sulfate was varied from 0 to 80 ppm.

RESULTS AND DISCUSSION

Each result reported represents the mean of three runs of an identical test solution, but run on different days. The results of series 1 are shown in Table I. The chloride response in series 1 was linear with chloride concentration. The results of series 2 are shown in Table II. The scatter in peak height measurements within one series is just about what we have experienced over a 3-year period. The difference between the peak heights in Table I and Table II is not due to random error. The series are run at quite different times and we routinely recalibrate at regular intervals. Within an interval instrument response is checked for constancy of response with one or more standards. Clearly the response of 100 ppm sulfate is not affected by up to 4000 ppm chloride, but the response is very much affected at the higher chloride concentrations. The data shown in Table III were subject to a

Table I. Response of 100 ppm SO_4^{2-}

sample	ppm of Cl^-	SO_4^{2-} peak height, cm
1	0	2.18
2	10	2.16
3	20	2.14
4	50	2.14
5	75	2.17
6	100	2.18
7	200	2.16
8	400	2.15

Table II. Response of 100 ppm SO_4^{2-}

sample	ppm of Cl^-	SO_4^{2-} peak height, cm
1	500	2.23
2	1000	2.22
3	2000	2.22
4	4000	2.19
5	8000	2.09
6	16000	1.49[a]

[a] Average of two runs, the peak in the third run did not return to base line.

Table III. SO_4^{2-} Response in 4000 ppm Cl^-

sample	ppm of SO_4^{2-}	SO_4^{2-} peak height, cm
1	0	
2	10	0.22
3	20	0.46
4	40	0.95
5	60	1.49
6	80	2.06

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