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ATMOSPHERIC-PRESSURE MICROWAVE-INDUCED HELIUM PLASMA SPECTROSCOPY FOR SIMULTANEOUS MULTIELEMENT GAS CHROMATOGRAPHIC DETECTION

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SUMMARY

Simultaneous multielement detection for gas chromatography (GC) by atmospheric-pressure microwave-induced helium plasma emission spectroscopy (MIP) is described and evaluated. A valuable application is in the empirical formula determination of unknown compounds. This technique provides the necessary high sensitivity, selectivity and repeatability for detecting both metals and non-metals. Carbon-, hydrogen-, chlorine-, silicon- and phosphorus-containing compounds are investigated. It is shown that, for many applications, GC-MIP is a viable alternative and offers advantages over conventional selective detectors for elements like chlorine (i.e., electron-capture detector) and phosphorus (i.e., photoionization and flame-photometric detectors).

INTRODUCTION

Atomic absorption and atomic emission techniques have been developed for the elemental specific detection of gas chromatographic (GC) eluates. Atomic emission provides the ability to detect several elements simultaneously by employing a multichannel or rapid-scanning spectrometer. A valuable application for this is in the empirical formula determination of unknown compounds. Atomic emission, when used in conjunction with structural information techniques (GC-mass spectrometry, GC-Fourier transform infrared spectroscopy, etc.), can afford a suitable means for speciating unknowns in diverse sample matrices. Atomic plasmas are particularly appropriate vehicles for GC detection. These include the direct current¹ and inductively coupled^{2,3} argon supported plasmas as well as the reduced pressure^{4,5} and atmospheric pressure^{6,7} microwave-induced helium or argon plasmas.

Interfaced GC-atmospheric-pressure microwave-induced helium plasma emission spectroscopy (MIP) has been adopted as a convenient and reliable approach for many applications⁸⁻¹⁴. This technique provides the necessary high sensitivity, selectivity and repeatability for detecting both metals and non-metals as eluates from packed and capillary columns. A microwave plasma is induced and sustained at atmospheric pressure in a "Beenakker" TM₀₁₀ cylindrical resonance cavity⁶. The

cavity can be made of a variety of materials, including copper, aluminum (silver/gold plated), brass and bronze. The plasma is concentrated inside a 6.2 mm O.D. \times 1 mm I.D. quartz discharge tube. Other refractory materials like boron nitride or aluminum oxide have also been used in discharge tubes. Energy fed into the cavity from the microwave generator is at 2450 MHz. Each element has its own set of optimal microwave plasma operational conditions. These include the optimal emission wavelength, spatial viewing of a species in the plasma, as focused onto the spectrometer entrance, total helium plasma flow-rate, microwave input power and entrance/exit slit widths¹¹. Typical input power ranges between 40–100 W and helium plasma gas flow-rates are from 60 to 100 ml/min. Frequency and impedance matching of the microwaves between the generator and cavity is generally performed by using face-plate and stubstretcher tuners¹⁰. Modification to the original Beenakker cavity's coupling and tuning have been examined^{15–17}.

Simultaneous multielement GC-MIP has been examined for specific element detection and as a means for determining empirical formulae. Brenner and co-workers¹⁸ and others^{13,19,20} have used a gas-chromatographic polychromator system (Applied Chromatography System's MPD-850 microwave plasma detector) fitted with a reduced-pressure microwave cavity to determine detection limits and investigate element ratioing. Other multichannel^{19,21} and rapid-scanning²² spectrometers have been applied for GC-MIP, with the aid of both reduced-pressure and atmospheric-pressure cavities. Early investigations have confirmed the value of GC-MIP for determining the stoichiometry of eluted compounds; most of these studies have employed the reduced-pressure cavity. Dingjan *et al.*²³ caution that intercompound element ratioing may deviate for species with large numbers of the analyte atoms per molecule, but that the use of a post-GC-pre-MIP pyrolysis system may minimize any such differences. For many applications, GC-MIP is a viable alternative and offers advantages over conventional detectors. For example, the electron-capture detector, typically used for determining chlorinated species, gives a response which is also dependent on the electronegative atom's environment. A major advantage of GC-MIP is that responses are dependent only on the specific elements, provided that selectivity over matrix or background element emission is sufficiently high. This simplifies the requirement of several standards for calibration purposes. Another advantage, as exemplified in the present study, is the ability to determine such elements as carbon, chlorine and phosphorus simultaneously with high sensitivity, selectivity, and repeatability. Conventionally, a photoionization or flame-photometric detector is used for phosphorus detection, an electron-capture detector for chlorine, and a flame-ionization detector may also be required to evaluate carbon. GC-MIP has the effect of three elemental detectors in one system with a simple analysis.

In the study described here, a Beenakker cavity has been interfaced to a 75-cm direct reading, multichannel optical emission spectrometer, as used by Brenner¹⁸.

Carbon-, hydrogen-, chlorine-, silicon- and phosphorus-containing compounds are investigated and the system is evaluated for its ability to determine empirical formulae.

EXPERIMENTAL

Instrumentation and design

The interfaced GC-MIP system is depicted in Fig. 1. Energy from the microwave generator (Applied Chromatography Systems, Luton, U.K.) is fed to the Beenakker cavity¹⁰, where helium make-up gas is employed to induce and sustain the plasma. A 12 m \times 0.25 mm I.D. SE-30 fused-silica capillary column (J. and W. Scientific, Rancho Cordova, CA, U.S.A.) is threaded from the Hewlett-Packard 5830A gas chromatograph (Avondale, PA, U.S.A.) through a heated transfer line to within a few millimeters of the plasma region. The transfer line is similar to that used by Quimby⁸. In the current design, the helium plasma make-up gas enters the 1/8-in. stainless-steel transfer line by a 1/4- to 1/8-in. reducing union. A Variac is used for temperature control. The gas chromatograph is modified with a Hewlett-Packard 18835C capillary inlet system for a split-injection mode.

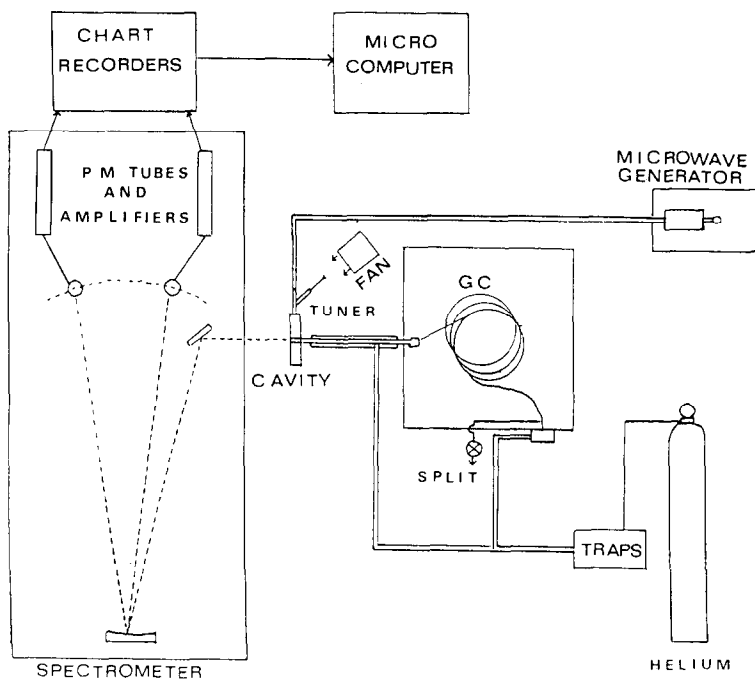


Fig. 1. Diagram of the interfaced multi-channel gas chromatograph-atmospheric-pressure microwave plasma detection system.

Light emitted from the plasma is focused onto a lens (13.5 cm focal length) before entering a 75-cm direct-reading, multichannel optical emission spectrometer whose secondary slits are situated on a Rowland circle and are aligned at the optimal first- or second-order spectra of the chosen elements (Applied Chromatography Systems, Luton, U.K.). Photomultiplier (PM) tubes are used to measure the emission for the twelve selected elements (Table I). The system employs six operational amplifiers to monitor six elements simultaneously. Element-specific chromatograms are

TABLE I
GC-MIP ATOMIC EMISSION WAVELENGTHS

<i>Element</i>	<i>Wavelength (nm)</i>
Selenium (I)	203.99 (2nd. order)
Arsenic (I)	228.81 (2nd. order)
Bromine (II)	470.49
Chlorine (II)	479.45
Carbon (I)	247.86 (2nd. order)
Phosphorus (I)	253.57 (2nd. order)
Iodine (II)	516.12
Sulfur (II)	545.39
Lead (I)	283.31 (2nd. order)
Silicon (I)	288.16 (2nd. order)
Hydrogen (I)	656.28
Fluorine (I)	685.60

recorded on dual-channel Omniscrite (Houston Instruments, Houston, TX, U.S.A.) chart recorders. An Isaac/Apple data acquisition system (Cyborg Corporation, Newton, MA, U.S.A.) may be employed for data collection. Spectral resolution of approximately 0.1 nm is obtained. The grating's reciprocal dispersion is 13.9 Å/mm (1st order). The wavelength range is 380–800 nm (1st order) and 190–400 nm (2nd. order). Entrance and exit slits are set at 50 μm . Frequency and impedance tuning, described in detail by Estes *et al.*¹⁰ is performed by adjusting a coaxial stub stretcher Model SL-10N (Microlab/FXR, Livingston, NJ, U.S.A.) which is attached to the cavity via a UG-58 connector. A new design for the coupling and tuning of a Beenakker cavity has also been investigated¹⁵. This enhanced cavity provides an improvement in energy transfer efficiency such that 20% lower power levels can be used to maintain a stable plasma. Also, once the cavity is correctly tuned for the operating conditions, it can be shut off and readily reignited without making any changes in the unit. In this enhanced cavity, the fixed coupling loop is replaced with an adjustable plate antenna. A capacitive plate tuning screw is also employed to afford resonant adjustment. The major difference between this enhanced cavity and Van Dalen's modified version¹⁶ is that a plate disc (at the end of the adjustable antenna) is installed in order to provide a wider coupling range.

Procedures

Optimal microwave plasma operational conditions are determined for carbon (62 mA input power and 80 ml/min plasma flow-rate) and phosphorus (52 mA input power and 250 ml/min plasma gas flow-rate). Detection limits for these elements are obtained. For simultaneous multi-element detection, a compromise set of conditions is employed, a microwave input power of 55 mA and a total helium plasma gas flow-rate of 150 ml/min being used. Element ratioing is used to determine the empirical formulae of "unknown" organic compounds containing carbon, hydrogen and chlorine. Organophosphorus compounds are investigated by monitoring carbon, phosphorus, hydrogen and chlorine emission. Organosilicon species are likewise determined by simultaneous monitoring of carbon, silicon, hydrogen and chlorine. All

solution concentrations used are approximately 50 μl of component/ml of solvent. Chromatographic conditions are noted with each figure.

Materials

The following chemicals are used: undecane, undecene, dodecane, dodecene, tridecane, tridecene, tetradecane, tetradecene, chlorotoluene, dichlorobenzene, 1,2,3,4-tetrahydronaphthalene, naphthalene, chloronaphthalene, dichlorophenylphosphine and trimethyl phosphate (Aldrich, Milwaukee, WI, U.S.A.), tetramethylsilane, dichlorodimethylsilane, chlorotrimethylsilane and hexamethyldisilazane (Alfa-Morton Thiokol, Danvers, MA, U.S.A.), 1,2,4-trichlorobenzene (Eastman-Kodak, Rochester, NY, U.S.A.), toluene and phosphoryl chloride (Fisher, Fairlawn, NJ, U.S.A.). Quartz discharge tubes were obtained from Quartz Scientific (Fairport Harbor, OH, U.S.A.) (6.2 mm O.D. \times 1 mm I.D.). Aluminium oxide tubes (6 mm O.D. \times 3 mm I.D. or 3 mm O.D. \times 1.6 mm I.D.) were obtained from Alfa-Morton Thiokol (Danvers, MA, U.S.A.). Commercial grade helium was purified by Molecular Sieve and anhydrous calcium chloride traps.

RESULTS AND DISCUSSION

Study of detection limits

The optimal microwave plasma operational conditions and the resulting detection levels have been investigated for carbon and phosphorus as representative elements. The values obtained are compared with literature values in Table II; 14 pg of carbon and 59 pg of phosphorus were detectable with tetradecane and trimethylphosphate as the model compounds. These values are close to those of Estes¹¹, who employed a low-resolution scanning monochromator (Model Heath 703, McPherson, Acton, MA, U.S.A.) and a Beenakker cavity similar to that used here. Brenner¹⁸ used a reduced pressure cavity with the same multi-channel spectrometer and microwave generator as used here.

TABLE II

DETECTION LIMITS FOR CARBON AND PHOSPHORUS BY GC-MIP

	<i>Atmospheric pressure cavity</i>		<i>Reduced pressure cavity</i>
	<i>Present study</i>	<i>Estes¹¹</i>	<i>Brenner¹⁸</i>
Carbon (pg)	14	12	—
(pg/sec)	2.4	2.7	60
Phosphorus (pg)	59	56	—
(pg/sec)	3.7	3.3	5

The optimized conditions for carbon included a helium plasma gas flow-rate of 80 ml/min and 62 mA input microwave power (current). Phosphorus detection was optimized at 52 mA input with 250 ml/min helium gas flow-rate. Since most comparable literature power values are given in watts, a VSWR coaxial power meter (No. 725.3, Raytheon, Waltham, MA, U.S.A.) was placed in series between the mi-

crowave generator's current meter and the cavity. However, the exact correlation between current and power is dependent on each specific percent reflected power level. This, in turn, results from frequency and impedance matching or tuning of the cavity. In general terms, the current reading in mA was approximately equal to the wattage reading on the power meter. In operating the GC-MIP system, it was necessary to employ a 0.12–0.22 mA reflected power level in order to sustain a stable plasma.

Simultaneous multi-element detection

Because each element has its own set of optimized plasma conditions, a compromise must be made for simultaneous multi-element detection. The goal is to maintain as much sensitivity and selectivity as possible for each element. Ideally, simplex optimization^{24,25} may be utilized; multi-element responses may be monitored with regard to four significant parameters: *X* and *Y* positioning of the plasma with respect to spectrometer viewing position, microwave input power, and total helium plasma gas flow. The compromise between the ability to perform analysis close to detection limits and the facility for simultaneous multi-element applications is self-evident.

A carbon-specific chromatogram is similar in appearance to the response obtained with a non-selective flame ionization detector. In general, relative responses for compounds of differing carbon content will be similar, since the flame ionization detector does respond to carbon or, more specifically, CH content; however, flame ionization detector response is not as strictly independent of carbon atom matrix as is that of the MIP. Simultaneous carbon- and chlorine-specific chromatograms are shown in Fig. 2; chlorinated and non-chlorinated organics are readily differentiated. Column efficiency of the capillary peaks is adequate to indicate from relative peak heights of components A, B, F and L the relative number of chlorine atoms in each molecule. As a result of the high quantity of solvent injected (hexane) and the value of chlorine-carbon selectivity, a hexane response is noted at 1.6 min at the chlorine wavelength. The negative response also results from high solvent concentration perturbing the plasma.

GC-MIP is advantageous for the determination of empirical formulae. In Fig. 3 are shown simultaneous carbon, hydrogen, and chlorine chromatograms. In this study, chlorotoluene (peak B) and tridecane (peak I) represent known compounds while the remaining species are considered "unknowns", *i.e.* two effective internal references are used. Element ratioing between carbon and chlorine and between carbon and hydrogen is determined as follows:

$$\frac{C}{Cl} = \frac{\text{Carbon response of unknown}}{\text{Chlorine response of unknown}} \times \frac{\text{chlorine response of known}}{\text{carbon response of known}} \times \frac{\text{carbon atoms in known}}{\text{chlorine in known}}$$

A similar process is repeated for carbon and hydrogen. Experimentally determined empirical formulae are compared with their known values in Table III. Calculated values are in agreement with the predicted values, and repeatability is in the

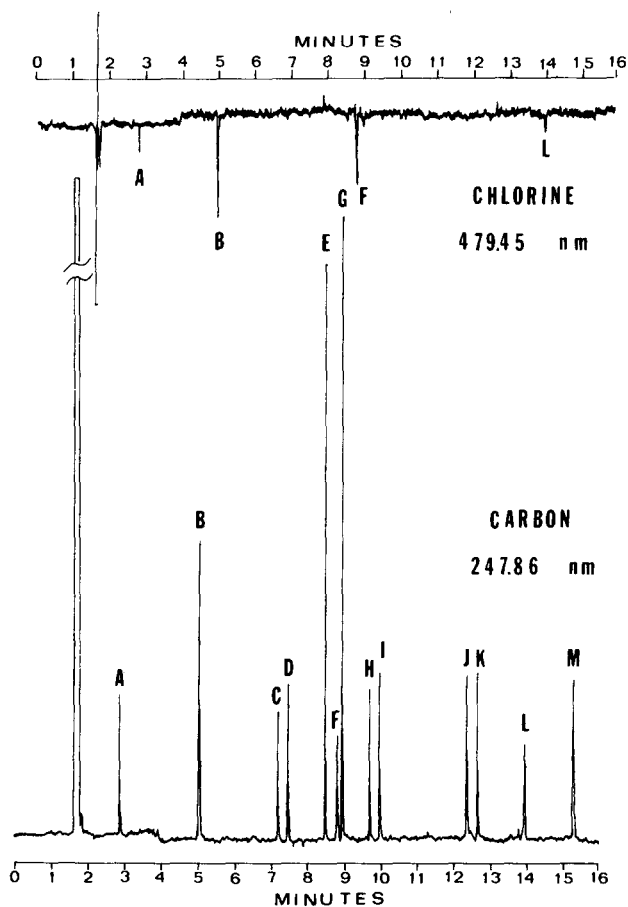


Fig. 2. Simultaneous carbon and chlorine element-specific chromatograms of chlorinated and non-chlorinated organics. Column 30 m \times 0.25 mm I.D. SE-30 fused silica. Temperature 80°C for 2 min then temperature programmed at 5°C/min. Injection temperature 250°C; interface temperature 230°C; column He flow-rate 1 ml/min; plasma He flow-rate 150 ml/min. Injection 0.1 μ l, split 100:1. Peaks: A = chlorotoluene; B = dichlorobenzene; C = undecane; D = undecene; E = 1,2,3,4-tetrahydronaphthalene; F = trichlorobenzene; G = naphthalene; H = dodecene; I = dodecane; J = tridecene; K = tridecane; L = chloronaphthalene; M = tetradecane.

range of 2–4%. The precision and accuracy demonstrated for formula determination of these carbon-, hydrogen-, and chlorine-containing compounds is well inside analytical tolerances. Although plasma stability with regard to fluctuating baseline levels is desirable, the employment of internal or external references aids in element ratioing.

The value of GC-MIP is also shown in simultaneous carbon-, hydrogen-, phosphorus-, and chlorine-specific chromatograms. In more typical GC, the latter elements are determined by separate detectors. Simultaneous detection of these elements will simplify speciation of organophosphorus and chlorine compounds used as pesticides. In Fig. 4 is depicted the chromatography of a range of compounds, which present some challenge in gas chromatography, phosphoryl chloride, trimethyl phos-

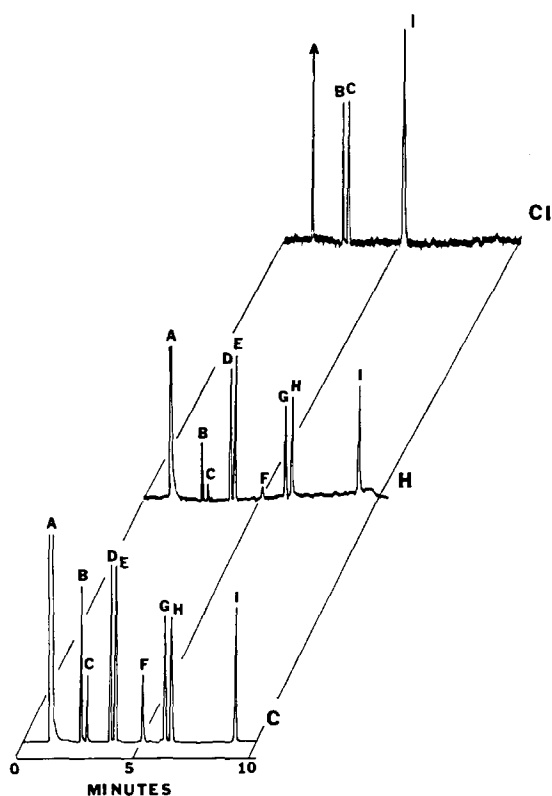


Fig. 3. Simultaneous carbon-, hydrogen- and chlorine-specific element chromatograms for the determination of empirical formulae. Column 12 m \times 0.25 mm I.D. SE-30 fused silica. Temperature 95°C for 5 min then temperature programmed at 5°C/min. Injection temperature 250°C; interface temperature 200°C; column He flow-rate 1 ml/min; plasma He flow-rate 150 ml/min. Injection 0.1 μ l, split 90:1. Peaks: A = toluene; B = chlorotoluene; C = dichlorobenzene; D = undecene; E = undecane; F = trichlorobenzene; G = dodecene; H = dodecane; I = tridecane.

TABLE III

EMPIRICAL FORMULA DETERMINATIONS OF CHLORINATED AND NON CHLORINATED ORGANICS BY GP-MIP

Compound	Empirical formula (known)	Empirical formula (calculated)
Chlorotoluene	C ₇ H ₇ Cl	Reference
Dichlorobenzene	C ₆ H ₄ Cl ₂	C ₆ H _{4.05} Cl _{1.96}
Trichlorobenzene	C ₆ H ₃ Cl ₃	C ₆ H _{3.03} Cl _{3.04}
Undecane	C ₁₁ H ₂₄	C ₁₁ H _{24.03}
Undecene	C ₁₁ H ₂₂	C ₁₁ H _{21.90}
Dodecane	C ₁₂ H ₂₆	C ₁₂ H _{26.39}
Dodecene	C ₁₂ H ₂₄	C ₁₂ H _{24.11}
Tridecane	C ₁₃ H ₂₈	Reference

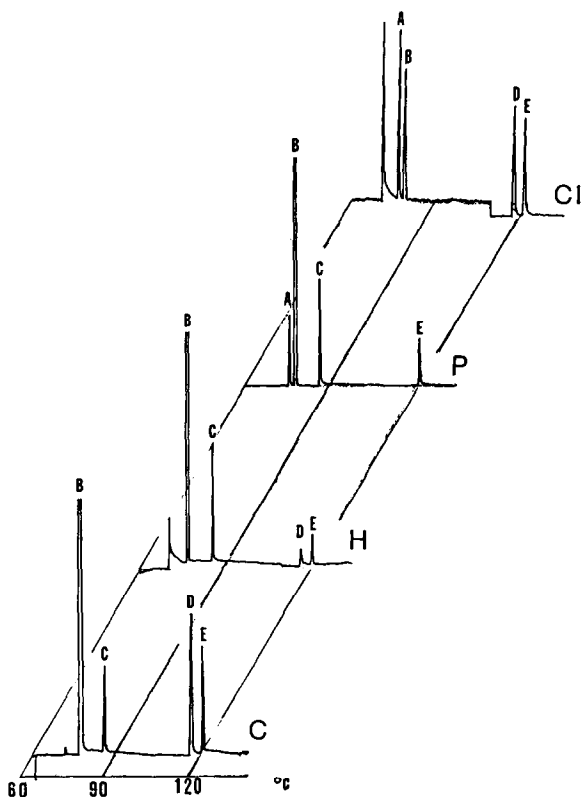


Fig. 4. Simultaneous carbon-, hydrogen-, phosphorus-, and chlorine-specific element chromatograms. Column as in Fig. 3. Temperature program from 60°C at 10°C/min. Injection temperature 180°C, interface temperature 150°C. Column and plasma He flow-rates and injection as in Fig. 3. Peaks: A = phosphoryl chloride; B = toluene; C = trimethylphosphate; D = 1,2,4-trichlorobenzene; E = dichlorophenylphosphine.

phate and dichlorophenylphosphine, as well as trichlorobenzene. The good peak characteristics evident for each elemental monitoring confirm the integrity of elution from the fused-silica column. The unmarked peak eluted prior to phosphoryl chloride is considered to be hydrogen chloride, resulting from the breakdown of dichlorophenylphosphine in the presence of water. It shows in the hydrogen and chlorine channels, unlike the high level of toluene solvent which again appears in each channel due to insufficient selectivity at high sample levels.

Chromatograms of a range of organo silicon compounds is shown in Fig. 5. Simultaneous detection affords a way to distinguish silanes from chlorosilanes and to determine the empirical formulae of unknowns. A problem with silicon detection, which is under more exhaustive investigation²⁶, is that at plasma temperatures silicon is stripped from the walls of the quartz discharge tube, resulting in a high background signal and diminished repeatability. Alternative discharge tubes are under investigation for silane and chlorosilane applications; accordingly, an aluminum oxide discharge tube was used for this particular chromatogram.

Following this initial investigation of the validity of the GC-atmospheric-pres-

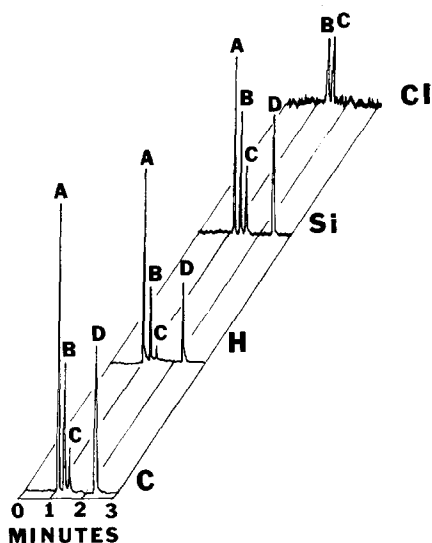


Fig. 5. Simultaneous carbon-, hydrogen-, silicon- and chlorine-specific element chromatograms of silanes and chlorosilanes. Column, flow and injection conditions as in Fig. 3. Column temperature 35°C isothermal. Injection and interface temperatures 80°C. Peaks: A = $\text{Si}(\text{CH}_3)_4$; B = $\text{SiCl}(\text{CH}_3)_3$; C = $\text{SiCl}_2(\text{CH}_3)_2$; D = $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$.

sure MIP for elemental formula determination, the most useful immediate enquiry focuses on nitrogen- and oxygen-specific detection. Inherent problems involve air entrainment in the cavity and plasma gas purity. Brenner¹⁸ obtained 3-ng detection limits for these elements under reduced pressure, but it remains to be seen what sensitivity and precision levels may be determined at atmospheric pressure. The key requirement for useful elemental formula determinations in oxygen- and nitrogen-specific element detection needs no emphasis, but, if successful, will serve to establish the validity of this technique for practical microanalysis.

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