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Element-selective detection after supercritical fluid chromatography by means of a Surfatron plasma in the near-infrared spectral region

DEBRA R. LUFFER and MILOS NOVOTNY*

Department of Chemistry, Indiana University, Bloomington, IN 47405 (U.S.A.)

ABSTRACT

A microwave-induced plasma, known as the Surfatron, is evaluated as a detector for supercritical fluid chromatography. The spectral range that is investigated is the near-infrared region because of its relative freedom from many spectral interferences, compared to the UV and visible regions. A novel method of heating the column restrictor is described, which is compatible with the very limited space and inaccessibility of the discharge tube configuration in the Surfatron cavity. Sensitivities and selectivities are determined for sulfur, chlorine, and bromine, using both a carbon dioxide and a nitrous oxide mobile phase. The detector is also evaluated in the "universal detection" mode by monitoring the carbon line when a nitrous oxide mobile phase is used. An application is demonstrated through the analysis of a mixture of sulfur-containing pesticides.

INTRODUCTION

During the 1980s, supercritical fluid chromatography (SFC) has gradually realized its potential, as predicted by the pioneering studies of Klesper *et al.*¹, Sie and Rijnders^{2,3}, and Giddings and co-workers⁴⁻⁶. The detection scope of this method had been significantly expanded by the adaptation of "gas chromatography (GC)-like" detectors, primarily because of the advantages inherent in small-bore SFC, both in capillary and packed column systems^{7,8}. The flame-based detectors have proven to be a key to both the universal detection (*i.e.*, flame ionization detection, FID), and element-selective measurements, such as the flame photometric detection (FPD)⁹⁻¹¹ and thermionic detection (TID)¹²⁻¹⁵ principles. A major drawback of both of these detectors is that they are limited to certain specific elements, and therefore lack versatility. For example, an unsuccessful attempt was made¹⁶ to modify TID for selective detection of elements, such as B, Cl, and S. However, electron-capture detection (ECD) was recently successfully coupled with capillary SFC for the detection of halogenated and nitro compounds¹⁷.

Alternatively, consideration of plasma-based devices appears logical due to their increasing technological availability. In principle, the selectivity of plasma detectors should be adjustable to various elements simply by "dialing in" the wavelength by either scanning a monochromator, or selecting an appropriate filter. In addition, these detectors are believed to be less prone to concomitant spectral interferences than the flame-based detectors. For this reason, plasma detection has been investigated in our laboratory^{18,19}, and, more recently by Skelton *et al.*²⁰. Both of these systems exploited the near-infrared spectral region because it is especially suitable for non-metal detection, due to a limited number of molecular bands such as CO and C₂ acting as spectral interferences²¹.

Skelton *et al.*²⁰ adapted radio-frequency plasma detection (RPD) for the detection of sulfur and chlorine, with both CO₂ and N₂O mobile phases; detection limits ranged from 50 to 300 pg/s. Luffer *et al.*¹⁸ evaluated the Surfatron microwave plasma detector for sulfur and a CO₂ mobile phase. The Surfatron had been developed and investigated by others for GC²²⁻²⁴, and recently, a thorough spectroscopic investigation was performed on a He-CO₂ Surfatron plasma; detection limits of 6.3 ng were found for sulfur in the visible region [S(II), 545.3 nm]²⁵.

Based on these results, it seemed promising to evaluate the Surfatron further in the near-infrared region, with respect to the detection of non-metals other than sulfur, such as Cl and Br. In addition, it was suggested¹⁹ that N₂O might be a better choice than CO₂ because it was thought to produce fewer troublesome molecular bands than CO₂, and universal detection possibilities were available through the use of a carbon wavelength channel. The present work summarizes the results of these continued studies, and reports sensitivities and selectivities for S, Cl, and Br. In addition, a pesticide mixture is separated and compared to a similar analysis by SFC-TID¹².

EXPERIMENTAL

Chromatographic equipment

Most of the system has been described previously^{18,19}. The changes that have been made will be noted below.

In addition to the SE-30 stationary phase, a different column was used in the analysis of the pesticide mixture (SB-Cyanopropyl-50, Lee Scientific, Salt Lake City, UT, U.S.A.); this 10 m × 50 μm I.D. column contained a 0.15-μm film of a 50%-substituted cyanopropyl methylpolysiloxane. The restrictors were of the frit type, obtained from Lee Scientific.

The circulating bath (Haake Buchler, Saddle Brook, NJ, U.S.A.) that replaces the column oven was filled with Therminol 6, a heat-exchange fluid (Monsanto, St. Louis, MO, U.S.A.). All unions were purchased from Scientific Glass Engineering (SGE, Austin, TX, U.S.A.). The gases were CO₂ and N₂O of supercritical fluid grade from Scott Specialty Gases (Plumsteadville, PA, U.S.A.).

The injection volume was 60 nl (without split), which ensured improved quantitation. A 60 cm × 50 μm I.D. fused-silica capillary was used as a retention gap; the capillary was positioned as close to the injection rotor as possible at one end, and connected to the column at the other end. With this configuration, no overloading of the column was noted and the solvent peak did not exhibit significant tailing.

Spectroscopic system

The Surfatron was constructed by our departmental machine shop according to the design of Abdallah *et al.*²⁶. The microwave generator was a Microtron 200 operating at 2450 MHz (Electro-Medical Supplies, Wantage, U.K.). Typical powers used ranged from 110 to 120 W. Since the spectroscopic system was designed for the near-infrared region, a glass lens of 50 mm diameter and 180 mm focal length was used to focus the axial (end-on) image of the plasma with a magnification of 1.2 on the variable entrance slit of the HR-320 monochromator (Instruments, SA, Metuchen, NJ, U.S.A.). The height of the slit was adjusted to match the diameter of the plasma image. The holographic grating was blazed 1 μm and had 1200 grooves/mm. The R632 photomultiplier tube (PMT) from Hamamatsu (Middlesex, NJ, U.S.A.) was biased at -1400 V by a power supply (Products for Research, Danvers, MA, U.S.A.) and mounted in a thermoelectrically-cooled housing (Products for Research). The output from the PMT was converted by a picoammeter (Keithley Instruments, Cleveland, OH, U.S.A.). A 4-pole filter, constructed in-house, was used to filter high-frequency noise by setting the cut-off to 0.5 or 1 Hz. Data were collected on a strip chart recorder.

The helium gas was high-purity (Air Products, Tamaqua, PA, U.S.A.). The model compounds used to evaluate the system (Fig. 1) were obtained from Aldrich (Milwaukee, WI, U.S.A.).

The apex of each emission line was found by scanning the wavelength region with a stepper motor controller (Instruments, SA). A volatile compound containing the element of interest was bled into the plasma by way of a headspace sampling device²⁷. In order to simulate the operating conditions of the system, the appropriate mobile phase gas was doped into the headspace vapor mixture during the scans. The color of the plasma was indicative of the content of the mixture; *i.e.*, a helium-only plasma was pink-orange, a helium-carbon dioxide plasma was blue-green, and a helium-nitrous oxide plasma was purple-pink. These colors agree with those noted for a He-RPD²⁰.

Development of a heated interface

The original interface between SFC and microwave-induced plasma consisted of pre-heating the helium and passing the effluent plus support gas through the aperture of a small nozzle inserted in the discharge tube¹⁸. However, it was determined that, due to the low heat capacity of helium and the low flow-rate of gas, the helium was losing most of the heat by the time it arrived at the tip of the restrictor. The direct consequences of insufficient heating of the restrictor are condensation of the mobile phase and detector "spiking", caused by condensed effluent erratically spurting into the plasma. Work with other SFC detectors has indicated that a restrictor temperature

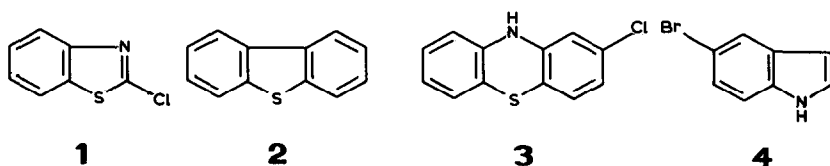


Fig. 1. Model solutes used, and their respective molecular weights. 1 = 2-Chlorobenzothiazole, 170 g/mol; 2 = dibenzothiophene, 184 g/mol; 3 = 2-chlorophenothiazine, 234 g/mol; 4 = 5-bromoindole, 196 g/mol.

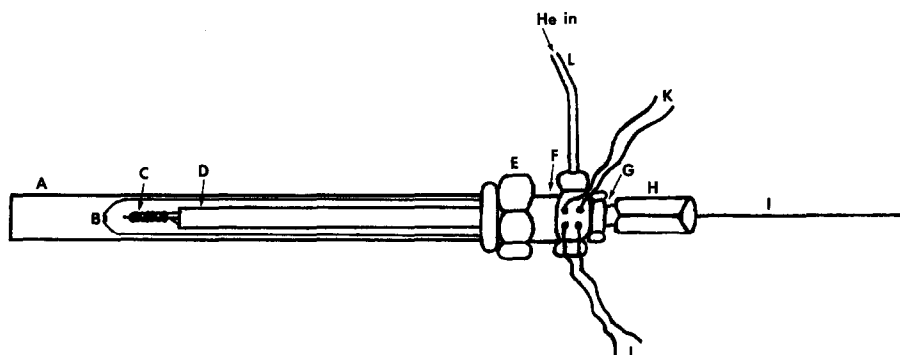


Fig. 2. Schematic diagram of the restrictor heating device (not to scale). A = Quartz discharge tube, 4 mm I.D.; B = quartz nozzle insert, 3 mm I.D.; C = heating coil, 1 cm long, and coated with high-temperature cement; D = ceramic insulating tube with 4 holes; E = Swagelok 1/4-in. nut with PTFE ferrule; F = Swagelok 1/4-in. reducing union; G = SGE 1/16-in. male nut silver-soldered to union F; H = SGE 1/16-in. female nut with Vespel ferrule; I = frit restrictor sleeved through and terminating at C; J = fine gage thermocouple wires exiting F; K = heater wires exiting F; L = 1/16-in. stainless-steel tubing silver-soldered into F.

of at least 300°C is warranted. This minimum operating temperature is also required for the elution of high-molecular-weight analytes. A suggested means of overcoming the heating problem was to increase the mass flow-rate of helium as it passes through an intensely heated length of stainless-steel tubing situated right at the tip of the restrictor. Unfortunately, this attempt was unsuccessful because the plasma does not operate optimally at very high helium flow-rates, and the maximum temperature that could be reached was still only 175°C.

A different approach that was taken involved the coating of the restrictors with a solution of gold in an organic matrix (Liquid Bright Gold), in a manner described elsewhere²⁸. The goal was to attach electrical leads of small dimensions directly to this gold coating, however, the connection proved to be too difficult due to the fragility of the restrictor configuration.

The successful design is based upon the construction of a very small wire coil that is resistively heated, in a manner very similar to that utilized by Reinhold *et al.*²⁹ for direct chemical ionization in SFC-mass spectrometry. The entire assembly is shown schematically in Fig. 2. The coil was prepared by wrapping a length of No. 34 copper-nickel wire (Wilbur Driver, Newark, NJ, U.S.A.) around a post of slightly larger diameter. The strand of wire was doubled, wrapped in one direction for about 1 cm, and then wrapped in the opposite direction until returning to the point of origin. The wire assembly is then removed from the post on which it was wound, producing a coil consisting of two very closely wound layers that becomes a region of very high current density when heated. The wire also possesses a high temperature (260°C maximum) enamel coating, which allows the tightly wound coil to be resistively heated without shorting out; however, the temperature range of the heating coil assembly was targeted to be greater than 300°C. This problem was surmounted by conditioning the coil with slow increments to the applied voltage, which allows the gradual formation of a protective oxide layer capable of sustaining the higher temperatures.

The wire leads of the coil were subsequently threaded through 2 of the 4 holes (1/64 in. diameter) of a ceramic rod (1/16 in. O.D.) made of Omegatite 200 (Omega Engineering, Stamford, CT, U.S.A.) (D in Fig. 2). The leads of an unsheathed fine gauge (0.005 in. diameter) Chromel-Alumel thermocouple (Type K, Omega Engineering) are threaded through the other two holes of the rod. The exit holes for the four wires were drilled through a nut in the assembly (F in Fig. 2), so that the connections can be made far from the area of intense heating. The restrictor is sleeved through one of the four holes and exists just past the end of the coil. It is held firmly in place by an SGE nut and ferrule at the back of the assembly (H in Fig. 2). The ceramic rod is sleeved through a small plug of PTFE (not shown in schematic) that has a hole (1/16 in. diameter) drilled through its side. The PTFE plug (1/8 in. diameter) is placed sideways in the nut and wedged firmly in place, which centers the ceramic rod in the quartz tube (William A. Sales, Wheeling, IL, U.S.A.) while allowing the passage of helium gas around it. A quartz nozzle insert surrounds the coil and rod, as shown in Fig. 2.

Temperature stability of the coil was improved by coating it and the junction of the thermocouple with a high temperature cement (Omega Engineering) and letting it cure for 24 h. A typical coil that is being swept by 300 ml/min of helium easily attains 320°C, requiring only 1.0 A and 13 V from a d.c. power supply. The high flow of mobile phase through the restrictor does not lower the temperature of the coil device, although the helium support gas flow exerts a dramatic effect. Monitoring the temperature at the tip of the coil was accomplished by connecting the leads from the thermocouple to a digital volt meter, which typically reads 12 mV for a temperature of 320°C.

A coil assembly, once conditioned, can last indefinitely, unless a high-voltage spark from a Tesla coil causes it to short out. For this reason, the plasma was ignited by inserting a length of copper wire a short distance into the discharge tube in order to seed the plasma with electrons. This method is superior to the tungsten wire method previously used^{18,19} because the latter leaves a substantial oxide film on the walls of the discharge tube, whereas copper does not.

It may seem surprising that a resistively heated wire coil placed approximately 2 cm from the plasma discharge does not disrupt or degrade the performance of the plasma. However, the additional insulating effects of the quartz inner nozzle and the high-temperature cement coating appear to be sufficient to prevent any problems. The main consequence of including the heating device is a stabilization of the plasma discharge because of the elimination of condensation of mobile phase at the tip of the restrictor, and therefore, a less "noisy" introduction of the heated effluent into the plasma.

It should be noted that this heating device is superior to simply inserting the restrictor into the plasma, as seen in other studies²⁰, because the temperature at the tip of the restrictor is known, stable, and damage to the frit material is virtually impossible. In addition, the very small size of the assembly (< 3 mm O.D.) makes it useful in any type of application where space and accessibility are limiting factors.

RESULTS AND DISCUSSION

It was ascertained in our earlier work¹⁸ that the quartz nozzle inserted into the discharge tube was essential for high-sensitivity detection of sulfur due to the

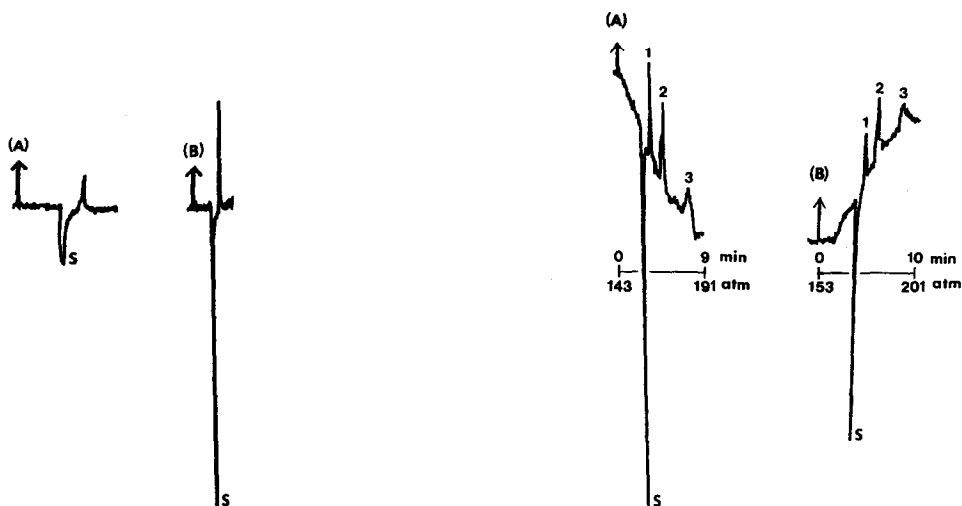


Fig. 3. Sulfur-selective detection of 2-chlorobenzothiazole and methanol solvent (denoted by S). (A) Without nozzle; (B) with nozzle.

Fig. 4. Variation of baseline as a function of helium support gas flow for the separation of compounds 1, 2, and 3 (Fig. 1) using S(I) line and CO_2 mobile phase at 130°C . Helium flow-rate: (A) 100 ml/min; (B) 300 ml/min.

“focusing” of effluent into the plasma. In the present study, however, the use of the heating element directly on the frit restrictor was thought to produce a similar effect, which would preclude the use of a nozzle. In order to test this hypothesis, two injections of a sulfur-containing compound in methanol were performed under identical conditions, except that in one case the nozzle was present and in the other case it was absent. Fig. 3A illustrates the effect of removing the nozzle; both the solvent and solute peaks are severely reduced in intensity, compared to those in Fig. 3B. Hence, in all subsequent work, the nozzle insert was present, as shown in the schematic in Fig. 2.

A major impediment to the acceptance of the Surfatron as a detector for SFC applications was the sloping baseline occurring during density-programmed runs¹⁸. While methods of background correction were originally proposed and attempted, a simpler and more efficient manner of eliminating this effect was discovered and is illustrated by Fig. 4. A separation of model compounds was performed at a low (100 ml/min) and high (300 ml/min) flow-rate of helium. Fig. 4A exhibits the decreasing baseline that we have noted previously¹⁸, while Fig. 4B exemplifies the opposite trend. From this information it seemed likely that an intermediate flow of helium would produce stable baseline during a density-programmed separation. A similar finding has been noted recently for RPD for SFC²⁰. Once the optimum helium flow had been determined, separations were performed to illustrate the sensitivity and selectivity of different lines, initially with a carbon dioxide mobile phase. Fig. 5A illustrates such a separation using the sulfur line (921.3 nm). However, when the same separation was performed using the chlorine line at 837.6 nm, the baseline exhibited a serious decline at this helium flow-rate. Therefore, it was determined that there exists an optimum flow of helium for each line, which probably depends on the background near that line.

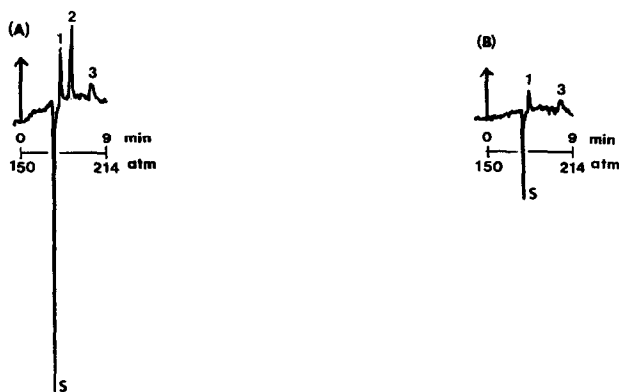


Fig. 5. Selective detection of compounds 1, 2, and 3 (Fig. 1) with CO_2 at 130°C . (A) S(I) line (921.3 nm), 125- μm slits, 180 ml/min He; (B) Cl(I) line (837.6 nm), 125- μm slits, 280 ml/min He.

In addition, this optimum flow is completely different when nitrous oxide is substituted for carbon dioxide, which is further proof that the background determines the ideal support gas flow. For example, the maintenance of the level baseline shown in Fig. 5B required a much higher (280 ml/min) flow of helium than that in Fig. 5A (180 ml/min). The other point to note concerning this separation is the absence of peak 2 in Fig. 5B, which illustrates the good selectivity of this line since this compound contains no chlorine atoms. No comparisons were made with the other strong chlorine line in the near-infrared (912.1 nm) because the signal-to-background and signal-to-noise ratios were rather poor.

Evaluation of the system was repeated using a nitrous oxide mobile phase. A comparison of the sensitivity and selectivity of different lines in the near-infrared region is shown in Fig. 6. The first point of note is the positive solvent peak for methanol on all four lines. This is entirely logical in the case of the C(I) line depicted in Fig. 6A, however, it portends poor selectivity for the other lines. The existence of a large, positive solvent signal can be attributed to the intense CN-band emission throughout the near-infrared region; evidently, the carbon from methanol is combining with the abundant nitrogen from N_2O to produce a large signal. The separation shown in Fig. 6D illustrates high-sensitivity sulfur detection, whereas the separations on the two chlorine lines in Fig. 6A and 6B are discouraging because of the noticeable peak in both cases for dibenzothiophene, which contains no chlorine atoms. Apparently, the CN-band emission is a significant problem when a nitrous oxide mobile phase is used because it is not possible to know how much of the signal is due to analyte emission, and how much is from carbon. This problem was found for all lines examined, except for one; Fig. 7B illustrates the elution of 5-bromoindole using the 889.8 nm line and the corresponding negative solvent peak, in contrast with the same injection using the 827.2 nm Br(I) line, with a corresponding positive solvent peak (Fig. 7A).

Sensitivities and selectivities for all these lines, in conjunction with both mobile phases, are summarized in Table I. The molar selectivities listed in Table I were calculated using naphthalene, unlike some other studies that used an alkane, such as

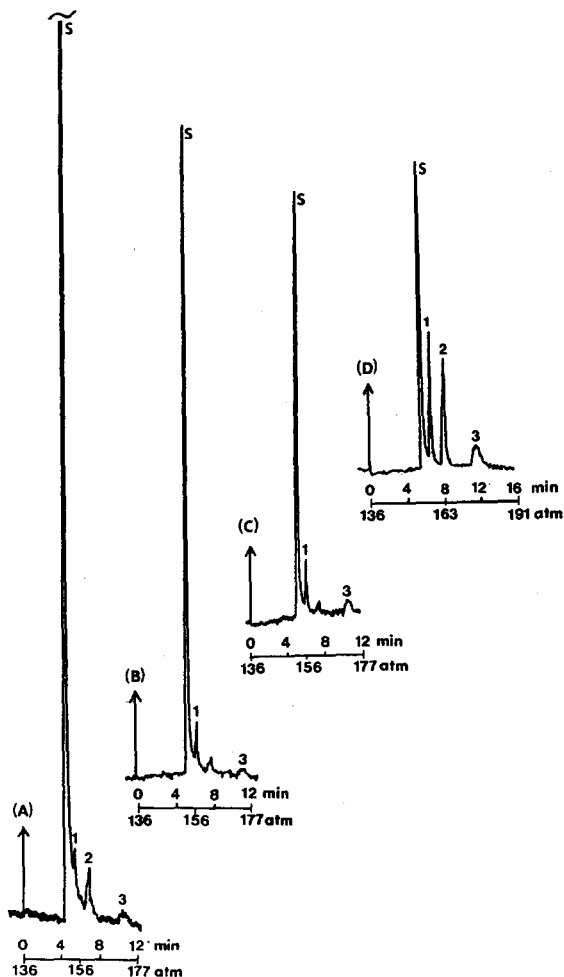


Fig. 6. Selective detection of compounds 1, 2, and 3 (Fig. 1) with N_2O at $130^\circ C$. (A) C(I) line (909.5 nm), 130- μ m slits, 100 ml/min He; (B) Cl(I) line (912.1 nm), 150- μ m slits, 100 ml/min He; (C) Cl(I) line (837.6 nm), 100- μ m slits, 80 ml/min He; (D) S(I) line (921.3 nm), 150- μ m slits, 100 ml/min He.

decane, to determine the carbon signal. This is because naphthalene should more closely approximate the shape, and therefore, the excitation and atomization of the model compounds in the plasma. In all cases, except for Br(I) at 889.8 nm and N_2O , the selectivities for N_2O were significantly poorer than for CO_2 , and therefore, the detection limits determined for the former are somewhat uncertain.

As expected, the detection limits for the N_2O mobile phase were superior to the corresponding results for CO_2 . The detection limits listed for sulfur and chlorine were determined using compounds 1 and 3 (Fig. 1). These results give an idea of the dependence of sensitivity on molecular weight, which seems to be consistent with the results found previously¹⁸. It is likely that this effect is a result of an increased amount of mobile phase entering the plasma^{18,20}.

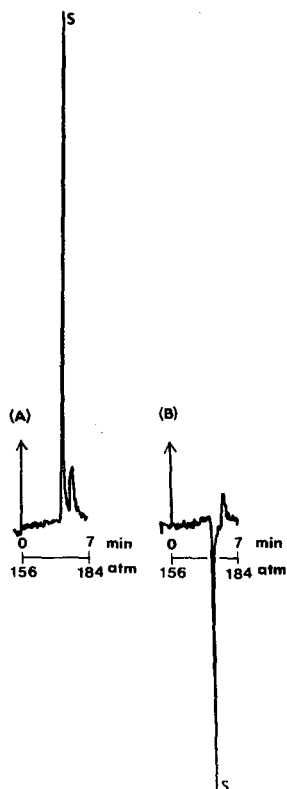


Fig. 7. Injection of 5-bromoindole in methanol, with N_2O at $130^\circ C$. (A) Br(I) line (827.2 nm), $100\text{-}\mu m$ slits, 100 ml/min He; (B) Br(I) line (889.8 nm), $125\text{-}\mu m$ slits, 80 ml/min He.

TABLE I

SENSITIVITIES AND SELECTIVITIES OF VARIOUS ELEMENTS AS A FUNCTION OF MOBILE PHASE

Mobile phase	Element	Line (nm)	Sensitivity ^a (pg/s)		Molar selectivity ^b
CO_2	S(I)	921.3	73	140	325
	Cl(I)	837.6	210	250	100
	Br(I)	827.2	780		110
	Br(I)	889.8	780		165
N_2O	S(I)	921.3	26	85	185
	Cl(I)	837.6	110	400	50
	Cl(I)	912.1	97	550	45
	Br(I)	827.2	300		20
	Br(I)	889.8	520		> 500
	C(I)	909.5	550	2600	—

^a The values listed on the left were obtained from either 2-chlorobenzothiazole or 5-bromoindole; the values on the right were obtained from 2-chlorophenothiazine.

^b Molar selectivities were all calculated from the response of either 2-chlorobenzothiazole or 5-bromoindole over naphthalene.

In general, detection in the near-infrared region does not seem as promising as it was initially for non-metal selective detection with the Surfatron, as evidenced by the results for sulfur¹⁸. In addition, the potential for universal detection with the carbon line and N₂O is limited because of the high detection limits found for the strongest line in this spectral region (909.5 nm), and the decrease in sensitivity as molecular weight of the solute increases (Table I).

As an example of an application, the separation of four pesticides (Fig. 8) is illustrated. Since they contain both phosphorus and sulfur atoms, this permits a comparison with the results obtained with a thermionic detector, in the P-mode, for SFC¹². It was determined in that study that these compounds exhibited only limited solubility in CO₂, so that only a nitrous oxide mobile phase was used. For the sake of comparison, this mixture was separated in N₂O and detected using the sulfur channel. The resultant separation is shown in Fig. 9, where the stationary phase utilized was a 50% cyanopropyl-substituted methylpolysiloxane. As expected, the sensitivity of each compound is dependent on the number of sulfur atoms in each molecule.

A point that has not yet been mentioned explicitly is that the condition of the discharge tube affects the detection limit for each element. This is because the background increases and the baseline becomes much noisier as the discharge tube ages. For this reason, a new length of tubing was used each day. The effect is exemplified by Fig. 10, where Fig. 10A shows the separation of the pesticide mixture at the end of one day, where the discharge tube is quite old and devitrified; Fig. 10B is the same separation performed the next day under identical chromatographic conditions, using a new discharge tube.

By means of comparison, the results recently reported for SFC-TID, SFC-FPD, and SFC-ECD will be briefly described here, and evaluated with respect to the SFC-Surfatron results reported in the present study.

The thermionic detector has been shown to possess very high selectivities for nitrogen and phosphorus, in conjunction with very low detection limits, *i.e.* < 2 pg/s and < 1 pg/s, respectively¹². In addition, this detector was shown to be extremely useful for detection of biological compounds and their metabolites in physiological fluids, using CO₂ and N₂O (refs. 13–15). FPD has been characterized in the dual-flame mode⁹ as well as in the single-flame mode^{10,11} for a wide variety of organosulfur compounds, with corresponding high selectivity and low detection limits (8 pg/s)

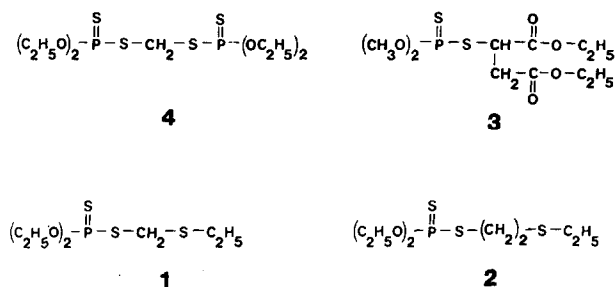


Fig. 8. Pesticides used, and their respective molecular weights. 1 = Phorate, 260 g/mol; 2 = di-syston, 274 g/mol; 3 = malathion, 330 g/mol; 4 = ethion, 384 g/mol.

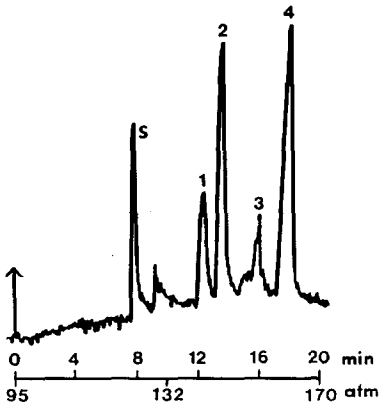


Fig. 9. Detection of four pesticides (Fig. 8) using the S(I) line and N_2O at $110^\circ C$ and a cyanopropyl-substituted stationary phase.

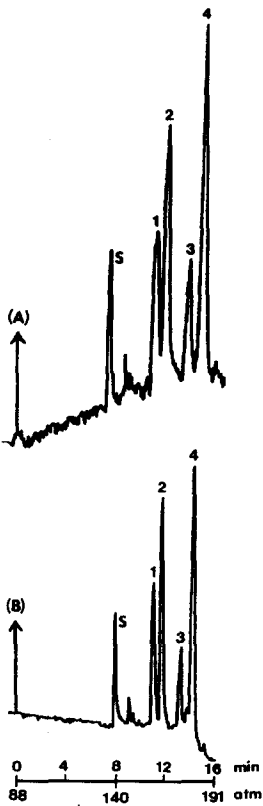


Fig. 10. Separation of four pesticides (Fig. 8) under identical conditions using N_2O at $105^\circ C$ and the S(I) line. (A) Old discharge tube; (B) new discharge tube.

utilizing an improved design¹¹. ECD yields detection limits of high femtograms for halogenated compounds containing chlorine and bromine¹⁷.

The combination of SFC with the Surfatron, in the near-infrared region, demonstrates more versatility than the previous three detection methods because of a theoretically limitless selection of elements. Plasma detection is superior to FPD for the determination of sulfur because the latter suffers from a non-linear response, whereas the former is linear for all elements studied over 2–3 orders of magnitude, and the effective linear concentration range is 10^{-4} – 10^{-2} M, corresponding to an unsplit 60-nl injection volume. More concentrated samples can be detected with larger injection volumes, but the calibration curve would no longer be linear in this range. However, the drawbacks of the Surfatron detector are that sensitivity suffers from a dependence on solute molecular weight, and that selectivity suffers from a dependence on the chosen mobile phase.

The cost of assembling this detection system was approximately US\$ 20 000, which is not as expensive as some laser-based detectors used for LC, especially considering that the plasma detector is capable of simultaneous multielement selective detection, if equipped with a photodiode array. In addition, the detector appears useful for the detection of low nanogram quantities of compounds containing various non-metals, with simultaneous universal detection by FID, if necessary. Further investigation of other plasma sources and spectral regions appears worthwhile.

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