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CONSIDERATION OF AN ATMOSPHERIC PRESSURE MICROWAVE-INDUCED HELIUM PLASMA AS AN OXYGEN-SELECTIVE GAS CHROMATOGRAPHIC DETECTOR

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SUMMARY

The consideration of an atmospheric pressure microwave-induced helium plasma for oxygen-specific gas chromatographic detection is described. Extensive precautions to exclude oxygen spectral emission produced by impurities in the helium plasma give a reduced elemental background and improved sensitivity. The addition of a small proportion of hydrogen to the helium plasma results in improved gas chromatographic peak shape through reduction of negative sample response segments. Selectivity over carbon of *ca.* 10 is disappointing, however, and precludes direct high precision empirical formula determination.

INTRODUCTION

An important lack in the array of gas chromatographic (GC) detectors is a sensitive and selective oxygen detector. The ability to distinguish oxygenated species such as alcohols, ethers, aldehydes, ketones, and carboxylic acids, from non-oxygenated compounds in high resolution GC eluates is a desirable goal. Mass spectrometry (MS) can afford such information only if resolution is great enough (0.02 *m/e*) to resolve oxygen from NH_2 and CH_4; conventional quadrupole GC–MS systems are inappropriate.

Atomic emission spectrometers equipped with plasma excitation sources have demonstrated much utility as element specific detectors for GC. The atmospheric pressure[1] and reduced pressure[2] microwave-induced helium plasma have been most used because of their high sensitivity and selectivity for both metals and non-metals.

Oxygen-specific detection by GC–microwave-induced atomic emission spectrometry (GC–MIP) was first attempted in 1965 by McCormack *et al.*[3], who investigated both a reduced pressure helium plasma and an atmospheric pressure argon plasma for the analysis of organics and monitored oxygen content by OH molecular emission. Taylor *et al.*[4] had earlier directly determined trace amounts of water present as an impurity in argon by using this 306.7 nm OH emission wavelength.

Since helium, as a plasma support gas, provides an enhancement in atomic

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emission over molecular emission, McLean *et al.*[5] investigated a set of near-infrared OI triplets at 777.19 nm, 777.41 nm, and 777.54 nm using a reduced pressure helium MIP. A 3.0 ng/s oxygen detection limit at 777.19 nm was obtained. It was also reported that oxygen, when present as 0.1–1% of the helium plasma support gas, minimized the formation of carbonaceous deposits in the plasma discharge tube. Since emission from the reduced pressure MIP is viewed by the spectrometer through the walls of a quartz discharge tube, it is critical to avoid any such deposition. In order to detect oxygen specifically, however, nitrogen was substituted as the scavanger gas. Van Dalen *et al.*[6] later demonstrated detection limits for various oxygenated compounds; values were in the range 2.7–12.0 ng/s oxygen for 2-propanone and methanol.

Brenner[7] evaluated the practical limits of a reduced pressure helium MIP for the oxygen-specific detection of GC eluates. A 4.0 ng/s oxygen detection limit, 500:1 oxygen-to-carbon selectivity, and a $1 \cdot 10^3$ linear dynamic range were reported. Using packed columns, he noted that stationary phases such as polyglycol and polyamide caused negative responses to oxygen and nitrogen compounds, but less polar, more thermally stable GC phases did not show this behavior. The empirical formulae for different diols were obtained with reasonable accuracy and precision using nitrogen as a scavenger gas and a multichannel spectrometer to monitor various emission wavelengths.

Yu *et al.*[8] also employed a reduced pressure helium MIP to determine oxygenated compounds at a detection limit of 3 ng/s oxygen and improved this to 300 pg/s oxygen by minimizing air leakage into the GC–MIP and further purifying the helium carrier and plasma gases with a commercial deoxidizer[9]. Besides improving oxygen detection limits, this approach also eliminated the negative oxygen responses observed by Brenner. A $1 \cdot 10^3$ linear dynamic range was reported but no information on oxygen-to-carbon selectivity was provided.

Although several researchers have demonstrated the superiority of an "atmospheric pressure" helium MIP for the GC detection of metals and non-metals[10–14], only Tanabe *et al.*[15] have examined its potential for oxygen-specific detection. While the same OI triplets were observed at atmospheric pressure, Tanabe *let al.*[16] reported that the detection of oxygen (as well as nitrogen) was "impossible" as a result of air leakage into the GC–MIP.

Considering other plasma excitation techniques, Brown and Fry[17] and Markey and Abramson[18] have used an inductively coupled argon plasma (ICP) to detect oxygen in GC eluates. A 25-ng oxygen detection limit was obtained by sampling a gas directly into the ICP. However, GC–ICP gave only a 650-ng oxygen detection limit[17] using the 777.19 nm emission line. No oxygen-specific detection has been reported for GC with a direct current plasma (DCP).

Although GC–MIP with a reduced pressure helium plasma has demonstrated some ability to detect oxygen, other researchers, primarily in industry, have reportedly encountered complications in attempting such measurements. In this paper we repoirt investigation of the behavior of an atmospheric pressure MIP as an oxygen-specific detector for GC.

EXPERIMENTAL

Instrumentation

The interfaced GC–MIP system used in this study has been described in detail by Estes *et al.*[19]. It incorporated a Varian 1200 gas chromatograph (Varian Instruments, Walnut Creek, CA, U.S.A.) modified for capillary column split injections, a Heath 703 (McPherson Instruments, Action, MA, U.S.A.) 0.35-m, f/6.8, Czerney-Turner monochromator capable of 0.1 nm spectral resolution, a TM_{010} microwave cavity (J and D, Lexington, MA, U.S.A.) able to induce and sustain a helium plasma at atmospheric pressure, a microwave generator (Microtherm Model CMD5, Raytheon, Lexington, MA, U.S.A.) capable of up to 100-W power output and a heated interface equipped for solvent venting. A coaxial sub-stretcher (Model SL-10N tuner, Microlab/FXR, Livingston, NY, U.S.A.) was attached to the plasma cavity via a UG-58 connector in order to minimize the reflected power level. The photocurrent from the photomultiplier (RCA 4832, 900V) was monitored with an electrometer (Type-600A, Keithley Instruments, Cleveland, OH, U.S.A.) and displayed on a strip. chart recorder (Omniscribe, Houston Instruments, Houston, TX, U.S.A.).

Materials

A 25 m × 0.31 mm I.D., 0.52 μm film thickness, cross-linked SE-30 (methylsilicone) fused silica capillary column (Hewlett-Packard, Avondale, PA, U.S.A.) provided the basis of all chromatographic separations in this study. Ultra high purity helium (99.999%) and hydrogen were obtained from Union Carbide (Linde Division, Somerset, NJ, U.S.A.). Gas purifiers included Oxytrap® (Alltech, Deerfield, IL, U.S.A.), copper catalyst (Catalyst R3-11, Chemalog, South Plainfield, NJ, U.S.A.), and molecular sieve (5 Å)-drierite (Alltech). A fine metering valve (Nupro, Willoughby, OH, U.S.A.) was used to control the hydrogen flow-rate. High-purity boron nitride rods (6.35 mm O.D.) and quartz tubes (6.2 mm O.D. × 4 mm I.D.) were obtained from Union Carbide (Chicago, IL, U.S.A.) and Quartz Scientific (Fairport, OH, U.S.A.), respectively. The chemicals used in this study were all of analytical or laboratory grade. A Brazilian humic acid sample was obtained from Professor Fernando Lances of the Universidade de Saõ Paulo, Saõ Carlos, Brazil.

Analytical method

The first analytical concern was to minimize the level of oxygen atomic emission from impurities in the helium plasma. Four sources of contamination were considered: (1) trace levels of oxygen and moisture from the helium gas tank; (2) air leakage into the GC–MIP system; (3) removal of oxygen from the walls of the quartz (silica) discharge tube at plasma temperature; and (4) column bleed. Ultra high purity helium (99.999%) was further purified by the following series of scrubbers: Oxytrap, molecular sieve-drierite, copper catalyst, molecular sieve-drierite. Air leakage into the GC–MIP system was checked by holding a small piece of "dry ice" (CO_2) at the various connections and monitoring the 247.9 nm carbon emission from the plasma background. Any leaks in the system resulted in a rise in the CI emission. Teflon tape was employed to secure non-heated fittings while graphite ferrules were used for fittings in the gas chromatograph and heated GC–MIP interface. A boron nitride discharge tube was used as a replacement for quartz. (This boron nitride tube (1 mm

I.D.) was in practice sealed inside a larger quartz tube (6.2 mm O.D. × 4 mm I.D.). A high temperature, chemically resistant sealant (Sauereisen Adhesive No. 1, Sauereisen Cements, Pittsburgh, PA, U.S.A.) was utilized to prevent flow leakage between the two tubes. In using this "tube-within-a-tube" arrangement, the plasma gas only came into contact with the oxygen-free boron nitride. The outside quartz tube, because of its different dielectric properties from boron nitride, served to improve the transfer efficiency of microwaves from the generator to the boron nitride discharge tube. A cross-linked methylsilicone fused-silica column was chosen for its preferred thermal and chemical stability in comparison to other GC columns. The column was threaded through the heated quartz tubing (2 mm I.D.) interface to within 5 mm of the plasma cavity. In order to further reduce the level of OI emission in the helium plasma, hydrogen was passed through a molecular sieve-drierite gas purifier and into the GC–MIP interface where it was mixed with the incoming helium gas before entering the plasma. A fine metering valve controlled the hydrogen flow-rate between 0.1 and 0.5 ml/min, or 0.1% (v/v) and 0.4% (v/v) hydrogen-to-helium.

The optimal GC–MIP operating conditions for oxygen specific detection are summarized in Table I. Prior to the addition of any hydrogen into the plasma, 15 ng

TABLE I

GC–MIP OPERATING CONDITIONS FOR OXYGEN-SPECIFIC DETECTION

Chromatographic conditions	
Column	25 m cross-linked SE-30 fused-silica (0.31 mm I.D., 0.52 μm)
Helium flow-rate	1.0 ml/min
Injection split	80:1
Injection size	0.1 μl
Temperatures:	
Column	Dependent on separation needs
Injection	200°C
Interface	200°C
Spectroscopic conditions	
Microwave plasma:	
Cavity	TM_{010} (atmospheric pressure)
Tuning Device	Coaxial strubstretcher
Power	78W at 2450 MHz
Helium flow-rate	130 ml/min
Hydrogen flow-rate	0.1–0.5 ml/min
OI	777.2 nm
Spectrometer	Heath 703, 0.35-m, f/6.8 Czerney-Turner mount
Spectral resolution	0.1 nm
Photomultiplier	RCA-4832, 900 V
Electrometer:	600A, Keithley Instruments
Attenuation	$G \cdot 10^{-8}$A (G = 0.3–3)
Time constant	0.1 s
Entrance and exit	
Slit width	100 μm
Slit height	12 mm
Strip-chart recorder	Omniscribe
Full scale	10 mV
Chart speed	Variable

of oxygen (as 30 ng of methanol) was introduced into the plasma, and its positive response optimized by changing the microwave input power and helium flow-rate via simplex optimization[19]. A positive followed by a negative response was always observed for the methanol peak. Enough hydrogen was then added to the plasma so that only a positive OI response was observed. Increasing the hydrogen flow-rate beyond this level only served to decrease the methanol peak's intensity.

RESULTS AND DISCUSSION

The reduction of oxygen background emission from impurities in the helium plasma was necessary before GC–MIP could be evaluated effectively as an oxygen-specific detector. The steps taken were the use of very high purity helium (99.999%), containing less than 3 ppm water, less than 2 ppm oxygen and less than 5 ppm nitrogen, with the gas scrubbers noted above, confirmation of absence of system air leaks and air entrainment into the plasma and employment of the boron nitride discharge tube. In general, background oxygen signal due to the chromatographic system was minimized by septum purging with 0.5 ml/min of helium, frequent septum replacement and on-column injection, and use of a cross-linked silicone phase to minimize bleed at the column temperatures used.

The optimum atomic emission wavelength was found by scanning the near-infrared region while monitoring the oxygen impurity level present in the helium plasma still present despite the various precautions taken. The four most intense oxygen responses, reported in relative terms, were obtained at 777.2 nm (100), 777.4 nm (82), 777.5 nm (16), and 844.6 nm (39). These values were similar to those reported by Tanabe *et al.*[15] except that the 844.6 nm emission line was found to be 10 times less sensitive in that study.

Hydrogen-rich plasma

The effect on oxygen-specific detection of doping the helium plasma with hydrogen is displayed in Fig. 1. Prior to the addition of hydrogen, first derivative-like

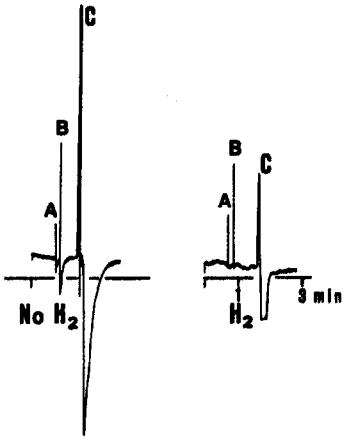


Fig. 1. Oxygen-specific detection showing response differences without and with hydrogen doping. Mixture, 5 vol.% each of pentane (A) and *n*-propanol (B) in toluene (C). Column, 25 m cross-linked SE-30 fused-silica, 40°C. Chromatographic and spectroscopic conditions as in Table I.

peak shapes were observed for both oxygen-containing and non-oxygen-containing compounds. As more and more hydrogen was added to the plasma, this negative response was reduced, but eventually positive response diminished and a bright red hue (656.3 nm) appeared in the plasma. An explanation may be as follows. As an oxygen-containing compound enters the helium plasma, it is fragmented, atomized and ionized, oxygen emission is observed (from background oxygen) and a positive response above the already elevated baseline occurs. Carbon and perhaps hydrogen then interact with any oxygen in the plasma to form species such as CO, CO_2, and OH. Since this interaction involves the oxygen already present in the helium plasma, any consumption of this oxygen gives a drop in the oxygen baseline. The fact that, in Fig. 1, a rapid positive response is followed by a negative response which returns slowly back to the original baseline, supports this "atomic emission-followed-by-molecular emission" mechanism. The addition of hydrogen into the helium plasma consumes background oxygen and forms OH. This behavior was substantiated by monitoring the OH 306.4 nm molecular emission line before and after hydrogen doping. As a non-oxygen containing compound (*e.g.*, pentane) enters the plasma, emission is also observed due to a poor oxygen-to-carbon selectivity of 10:1.

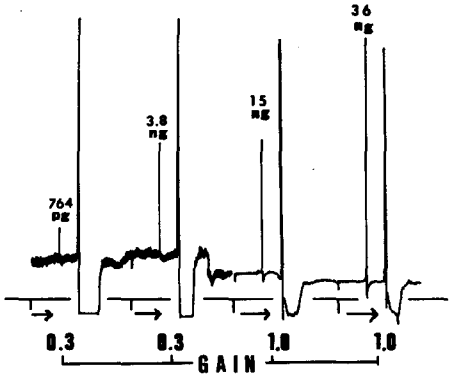
The level of hydrogen added to the helium plasma is important to this oxygen-selective detection scheme. A ratio must be maintained so that enough hydrogen is present to combine with the oxygen-containing impurity gases. However, too much hydrogen will reduce the ionization potential and excitation efficiency of the helium plasma. In this study, the optimum results considering both sensitivity and selectivity were obtained for a ratio of 0.2 ml/min hydrogen to 130 ml/min helium (v/v), corresponding to a 0.15% (v/v) hydrogen-to-helium ratio. At this ratio, 15 ng of oxygen (as methanol or propanol) gave a positive, gaussian peak. After *ca.* 150–200 h, this required ratio had increased to 0.38% (v/v). More background oxygen was now apparently entering the helium plasma due to the copper catalyst exceeding maximum oxygen consumption level.

Oxygen specific detection

GC–MIP operation conditions were optimized for oxygen-specific detection, including atomic emission wavelength (777.2 nm), microwave input power (78 W), helium plasma flow-rate (130 ml/min), spatial positioning (optimum emission was viewed at a position toward the walls of the discharge tube), entrance and exit slit widths (100 μm) and hydrogen flow-rate (0.2 ml/min). A 255 pg or 212 pg/s oxygen detection limit but a 10:1 oxygen-to-carbon selectivity was obtained. This was clearly a very poor selectivity by comparison with values obtained at reduced pressure[7].

A $5 \cdot 10^2$ linear dynamic range was obtained for oxygen as methanol. Absolute detection limit was defined as the amount (pg) of oxygen, introduced onto the GC columns, which produces an output response repeatably equal to twice the background mean noise. Mass flow-rate was defined as the absolute detection limit (pg) divided by the oxygen peak's half widths(s). Selectivity was defined as the oxygen response at OI per mole of oxygen divided by the carbon response at OI per mole of carbon.

Oxygen-specific responses at various concentrations are shown in Fig. 2 for *n*-propanol and in Fig. 3 for methanol. It is noteworthy that at the higher oxygen concentrations, a slight negative response starts to occur for *n*-propanol but not for



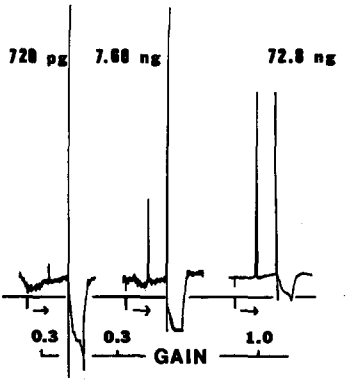


Fig. 2. Oxygen-specific responses for differing amounts of *n*-propanol. Column and conditions as in Fig. 1 and Table I.

Fig. 3. Oxygen-specific responses for differing amounts of *n*-methanol. Column and conditions as in Fig. 1 and Table I.

methanol. If the positive peak height is measured and the negative peak response is disregarded, the calibration curve for *n*-propanol remains linear, as for methanol. Calibration curves for peak height (mm) *vs.* amount of oxygen (ng) for *n*-propanol and methanol showed correlation coefficients of 0.9925 and 0.9980, respectively, although the linear dynamic range for *n*-propanol was finally limited by the negative response at higher concentrations. The lower percent oxygen in *n*-propanol (27%) than methanol (50%) may be the cause of the negative response for the former. For comparison, only a positive, gaussian peak was obtained for a 10-μl injection of carbon dioxide (73% oxygen) into the helium plasma even without the addition of hydrogen.

Oxygen-specific detection, with a hydrogen-doped plasma, of repetitive 15 ng oxygen (as *n*-propanol) injections is shown in Fig. 4. It appears that the negative

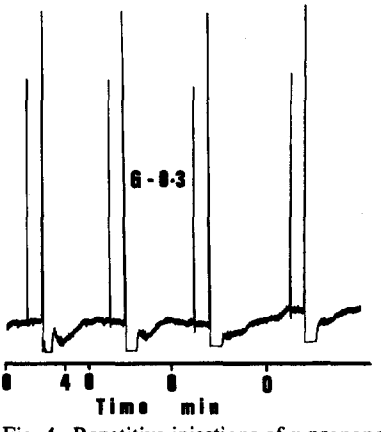


Fig. 4. Repetitive injections of *n*-propanol (15 ng of oxygen), demonstrate a possible solvent effect. Column and conditions as in Fig. 1 and Table I.

response may be due in part to a solvent-effect since it cannot be detected in the first injection but increases for the next few injections before reaching a limit.

The oxygen-to-carbon selectivity was effectively the same for all three atomic emission lines, 777.2 nm, 777.4 nm and 844.5 nm. Higher selectivities could be expected from spectrometers which are equipped for higher spectral resolution. In this work, the spectrometer resolution was 0.1 nm which is considered a moderate value. Brenner[7] reported an oxygen-to-carbon selectivity of 500:1, but for a reduced pressure helium MIP, carbon I emission reaches an intensity level only one tenth that seen in an atmospheric pressure helium MIP. This could partially explain the poor oxygen-to-carbon selectivity observed in this investigation.

The oxygen specific detection of a variety of oxygenated compounds (alcohols, aldehydes, ketones, etc.) is shown in Fig. 5, the effect of hydrogen doping being apparent. It is interesting to note that the two compounds which experience the relatively most pronounced negative response, tetrahydrofuran and 2-butanone, are the ones which contain the least oxygen (22%). The addition of hydrogen, in this case 0.5 ml/min, did cause a small decrease in each respective peak height.

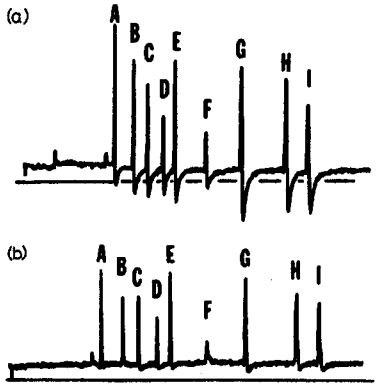


Fig. 5. Oxygen-specific detection of compound mixture without (a) and with (b) hydrogen doping. Methanol (A), ethanol (B), propionaldehyde (C), diethyl ether (D), methyl acetate (E), *n*-propanol (F), 2-butanone (G), ethyl acetate (H) and tetrahydrofuran (I) all at *ca.* 0.5 vol.% in toluene (not shown in chromatogram). Column temperature, 35°C; other conditions as in Fig. 1 and Table I.

The oxygen (777.2 nm) and carbon (247.9 nm) specific element detection of chlorination products of a humic acid material are presented in Fig. 6. Chloral, trichloracetaldehyde, methyl dichloroacetate and methyl trichloroacetate were identified by their retention times. Clearly, the two presently unidentified species eluting between 25 and 30 min contain oxygen.

Although the detection limit obtained is a factor of 10–100 times higher than those obtained for some other elements such as carbon, hydrogen and silicon, this level of sensitivity may still prove valuable for some analytical applications. The selectivity seen in this study must undoubtedly be increased for many wider applications to be feasible. Exploration of other wavelength regions for detection is appropriate as is an "in depth" study of the reasons for the "oxygen" response from non-oxygenated compounds. However if simultaneous carbon-specific detection is

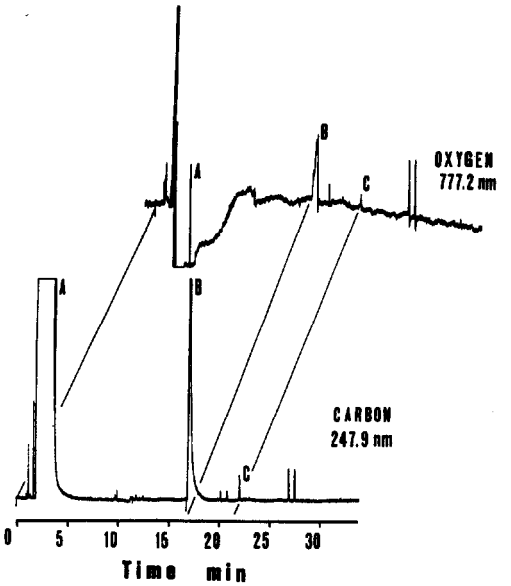


Fig. 6. Oxygen (upper) and carbon (lower) specific detection of chlorination products of humic acid. Column temperature, 35°C for 10 min then temperature programmed to 200°C at 4°C/min. Helium flow-rate 1.4 ml/min, injection split 60:1. Other conditions as in Fig. 1 and Table I. Trichloroacetaldehyde (chloral) (A); methyl dichloroacetate (B); methyl trichloroacetate (C).

available at 247.9 nm, element ratio measurements can be made which correct for the relative selectivities between the elements at the measured wavelengths. Thence empirical formula measurements may be made for compounds including both carbon and oxygen in a manner similar to those reported previously[21,22]. The feasibility of such measurements is currently under investigation.

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