

CHROM. 12,083

SELECTIVE ELECTRON-CAPTURE SENSITIZATION

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SUMMARY

When nitrous oxide is added to nitrogen carrier gas, certain compounds can be detected with much greater sensitivity than is normally possible. This selective sensitization can be attributed to ion-molecule reactions between analytes being eluted and O^- and NO^- generated *in situ* in electron-capture detectors when the carrier gas contains nitrous oxide. The enhancement of response for various compounds by selective electron-capture sensitization (SECS) using nitrous oxide-doped nitrogen carrier gas has been observed for methane, ethane, *n*-propane, *n*-butane, *n*-pentane, *n*-hexane, benzene, ethanol, methylisobutylketone, hydrogen and carbon dioxide. With SECS, it becomes possible to detect picogram levels of several hydrocarbons with electron-capture detectors. For carbon dioxide the response is sensitized by a factor of 5000 in the presence of nitrous oxide; for methane the peaks are about 10 times larger; and for hydrogen the enhancement is about 40-fold greater than in the absence of nitrous oxide. Examination of the degree of sensitization (or desensitization, in the case of chlorofluorocarbons) may be useful as an indication of the identity of unknown peaks in a chromatogram if identical samples are detected in the presence and absence of a sensitizing gas such as nitrous oxide. Detector stability is not adversely affected by injection of microliter volumes of solvents. SECS has been used to detect hydrogen and methane at the 1-ppm level in samples of ambient air and human breath.

INTRODUCTION

The response of an electron-capture detector (ECD) to selected components may be altered by changing the composition of the carrier gas entering the detector cell¹⁻⁵. Low concentrations of oxygen in nitrogen carrier gas increase sensitivity for butylbromide in a fixed-frequency, pulsed ECD¹. Similar sensitization has been observed with O_2 -doped carrier gas for other halogenated organic compounds^{3,4}. Our recent experiments have shown that the use of nitrogen carrier gas containing

ppm-levels of nitrous oxide enhances ECD response for hydrogen, carbon dioxide and methane in a constant current, variable frequency detector⁵.

We have termed techniques which use modified carrier gases to change electron-capture characteristics selective electron-capture sensitization (SECS). It is apparent that more sensitive electron-capture response is obtained in such instances and that selectivity is determined by various parameters, including composition of carrier gas and detector temperature. In this publication we present data which indicate a variety of compounds for which SECS is applicable when nitrous oxide is used as a dopant.

THEORETICAL

Usually ECD response to a compound results from direct electron attachment causing a decrease in the electron current within the detector cell. At elevated detector temperatures, with O₂ present, the collisional detachment of electrons from O₂⁻ competes with the attachment process, resulting in equilibrium concentrations of both O₂⁻ and electrons^{3,4}. Under these equilibrium conditions, compounds which react with either O₂⁻ or electrons to yield a stable negative ion will reduce the electron concentration in the detector, thus producing a response for that compound. Such a detector is made sensitive for compounds which undergo reactions with O₂⁻.

Addition of N₂O to nitrogen carrier gas causes a different ion chemistry. Steady state concentrations of electrons, O⁻ and NO⁻ are believed to be present in the detector according to reactions 1-3 (refs. 5 and 6).



A compound which reacts with O⁻ or NO⁻ to yield stable negative ions effects a decrease in electron current and a concomitant detector response. In this instance, for a given N₂O concentration and detector temperature, selectivity is determined by the reactivity of a given compound with O⁻ or NO⁻ and sensitivity by the rate constant of the reaction. For example, the reaction of O⁻ with CO₂ is a three-body process⁷:



Reactions such as this, which remove O⁻ and form a stable negative ion, interrupt the sequence in reactions 1-3. This prevents regeneration of electrons in reaction 3, causes a decrease in the free electron concentration in the detector and sensitizes the detector to the analyte.

Reactions 1-3 produce the desired steady state concentrations of O⁻ and electrons only at relatively high detector temperatures (*ca.* 350°). Although electron attachment reactions in a conventional ECD can be highly temperature dependent⁸,

the greater sensitivities reported here are in addition to any enhancement caused by increasing the temperature alone.

EXPERIMENTAL

Instruments

Several gas chromatographs with various ECDs were employed in these studies to determine the generality of SECS techniques for different detector designs. Instrument descriptions and operating conditions are given in Table I.

Operating parameters

Operating parameters pertaining to a particular instrument are given in Table I. Experiments in which N_2O -doped carrier gas was used were performed with a mixture containing 20 ppm N_2O in N_2 , prepared by static dilution. Carrier gas impurities were removed by passing the gas mixture through a trap (20×2.5 cm I.D.) containing Molecular Sieve 13X (Union Carbide, South Plainfield, N.J., U.S.A.) maintained at 65° before the carrier entered the chromatographic column. After approximately one day the trap becomes saturated with N_2O and the concentration of dopant entering the chromatograph is constant at approximately 20 ppm.

Standard solutions

All standard solutions were prepared from commercially available reagents in solvents that were doubly distilled in glass. Gas standards were prepared as previously described⁵. Additional gas standards were obtained commercially (Scotty II analyzed gases, Scott Specialty Gases, Plumsteadville, Pa., U.S.A.).

RESULTS AND DISCUSSION

Sensitization of response to selected hydrocarbons

Gaseous test mixtures containing low ppm concentrations of methane, ethane, *n*-propane, *n*-butane, *n*-pentane and *n*-hexane were used to determine the relative ECD responses for these compounds at comparatively low and high temperatures in both the presence and absence of added N_2O in the N_2 carrier gas stream. Data obtained from the H-P (I) instrument (see Table I) indicate only insignificant response changes for these compounds when the detector temperature is raised incrementally from 200 to 350° in the absence of N_2O . However, when N_2O at 20 ppm is added to the carrier gas, detector response increases dramatically with increasing temperature for these compounds. At higher temperatures the rate of reaction 1 is markedly increased^{5,9,10}. The response data, derived from peak height measurements, are shown in Fig. 1. The highest detector temperature used in these experiments is 350° , the operating limit of these detectors containing ^{63}Ni . Corresponding detection limits (signal-to-noise ratio 2) have been determined for these alkanes at 350° with 20 ppm N_2O present in the carrier gas (given as detection limit (numbers in parentheses show ratio of detector response with and without N_2O in the carrier gas)): methane, 30 pg ($\times 13$); ethane, 16 pg ($\times 27$); propane, 15 pg ($\times 31$); butane, 18 pg ($\times 34$); pentane, 35 pg ($\times 29$); hexane, 62 pg ($\times 11$).

TABLE I

CHROMATOGRAPHS AND OPERATING CONDITIONS

Manufacturers abbreviations: H-P = Hewlett-Packard (Palo Alto, Calif., U.S.A.); P-E = Perkin-Elmer (Norwalk, Conn., U.S.A.).

Instrument and model*	⁶³ Ni detector	Detector mode	Detector standing current (nA)	Pulse width (usec)	Pulse height (V)	Pulse frequency (kHz)	Carrier flow-rate (ml/min)	Sample**	Column	Column temp. (°C)
P-E 3920	P-E	Constant current	1	250	-55	Variable	60	G	4 m, stainless steel, Porasil C or Mol. Sieve 5A	50
Portable**	P-E	Variable current	0-2.25	700	-30	1	50	G	2.5 m, stainless steel, Porapak Q or 2.5 m, stainless steel, Porasil D	150 25 70
H-P 5730 (I)	H-P	Constant current	1	-†	-†	-†	40	G or S	1.5 m, stainless steel, Porasil C	70
H-P 5730 (II)	H-P	Constant current	1	-†	-†	-†	30	S	1.8 m, glass, 0.1% SP-1000 on Carboapak C	125
H-P 402	H-P	Variable current	≈1	750	+30	20	40	S	1.8 m, glass, 0.1% SP-1000 on Carboapak C	125

* Roman numerals in parenthesis indicate different instruments of the same model.

** This is a portable chromatograph fabricated by W. C. Kuster, Aeronomy Laboratory, NOAA Environmental Laboratories, Boulder, Colo., U.S.A. The chromatograph is sealed in a box, the atmosphere of which can be controlled.

*** G indicates instruments which have been modified with multiport Valco (Houston, Texas, U.S.A.) gas sampling valves. S indicates injections may be made via syringe.

† These parameters are not adjustable and are not specified in manufacturer's literature.

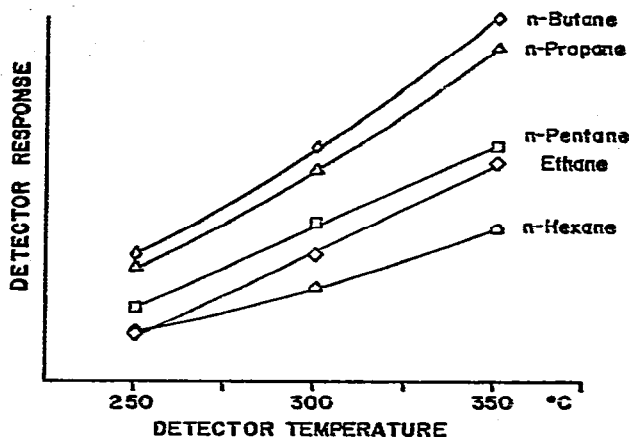


Fig. 1. Temperature dependence of alkane responses in an N_2O -doped SECS detector. Data were determined using the H-P (I) instrument equipped with a 0.1-ml sample loop; sample component concentrations were approximately 15 ppm.

Our calculations indicate that higher concentrations of O^- would be present in the electron capture cell if the detector could be operated at higher temperatures. Presently, safety and licensing requirements for operation of ^{63}Ni -containing detectors limit the operation of the instrument to temperatures not higher than *ca.* 350–400°. We anticipate that even greater sensitization will be found when these experiments are repeated in non-radioactive ECDs which can be operated safely at temperatures above 350°. Such a detector, which employs thermionic emission of electrons from a heated wire, was recently described by Sullivan¹¹ and may soon become commercially available.

The detector on the portable chromatograph described in Table I shows different response to these hydrocarbons, especially with respect to changes in detector temperature. Surprisingly, this detector shows unusual sensitivity for approximately 30-pg quantities of alkanes when the detector temperature is 350°, even in the absence of N_2O -sensitization. Little, if any, additional enhancement of response has been observed for these levels of hydrocarbons when N_2O is added to the carrier gas. For larger amounts of these compounds, however, addition of N_2O to the carrier gas enhances the detector signal. In the portable instrument, addition of N_2O caused the methane signal to increase 11-fold, ethane 8-fold, *n*-propane 6-fold and *n*-butane 5-fold (see Table II). These experiments were performed with peak height measurements under isothermal operating conditions on Porasil D without optimizing chromatographic conditions.

The presence of traces of common atmospheric gases such as O_2 and H_2O as impurities in the chromatographic flow system may affect markedly the ion chemistry. Both O_2 and H_2O react with O^- (ref. 7).



TABLE II
SECS RESPONSE TO SELECTED COMPOUNDS

Compound	Quantity (pg)	Response (mV)	
		N ₂ only	N ₂ + 20 ppm N ₂ O
CH ₄	18·10 ³	56	640
C ₂ H ₆	34·10 ³	116	912
<i>n</i> -C ₃ H ₈	49·10 ³	168	960
<i>n</i> -C ₄ H ₁₀	66·10 ³	180	992
CCl ₂ F ₂	0.91	275	64
CClF ₂ CClF ₂	8.38	115	33
CCl ₃ F	1.27	135	54
CH ₃ CCl ₃	17.9	149	76
CCl ₃ CClF ₂	3.91	111	37
CCl ₄	54.8	491	211
CH ₂ Cl ₂	51.4	65	21
CHCl ₃	10.1	217	87
C ₂ Cl ₄	5.18	238	108

These impurity reactions interrupt the sequence of reactions 1-3 and would be expected to interfere with the SECS response. Experiments performed with the hermetically sealed portable chromatograph confirm this. The instrument used in these studies is sealed in such a way that the composition of the atmosphere surrounding the chromatograph can be controlled. The signal enhancements reported above were obtained when the column, fittings, etc., were bathed in a nitrogen atmosphere. Changing the surrounding gas to oxygen, which allows O₂ to enter the column and detector through any system leaks in much the same way as air might diffuse in, increases the noise level in the detector so that the N₂O-enhanced signals for hydrocarbons are reduced by approximately 10%. This illustrates the importance of controlling the impurity levels, especially of oxygen, in the carrier gas, and insuring that leaks are minimal.

Response to representative halocarbons

A series of halocarbon standards was used to determine the effect of N₂O addition upon compounds that are normally sensitive to electron-capture detection. Data from the experiments are given in Table II. Without exception, these halocarbons show decreased sensitivity when N₂O is present in the carrier gas at 20 ppm. However, the decrease in signal for the halocarbons is not nearly so large as the increase observed for the hydrocarbons. While the magnitude of the sensitization reported for the hydrocarbons detected by the portable chromatograph in Table II is appreciable, the sensitization is seen more impressively in the data reported above for hydrocarbons detected with the H-P (I) instrument. In Fig. 2 chromatographic traces are shown for samples analyzed with and without N₂O in the carrier gas.

From these data one can draw a tentative general conclusion: addition of nitrous oxide can lead to sensitization of response for certain compounds with inherently small rate constants for capture of thermal energy electrons, but there is no sensitization for compounds which are normally sensitively detected (*e.g.*, chloroform), and the competing reactions that occur when N₂O is present in the carrier gas may lead to a

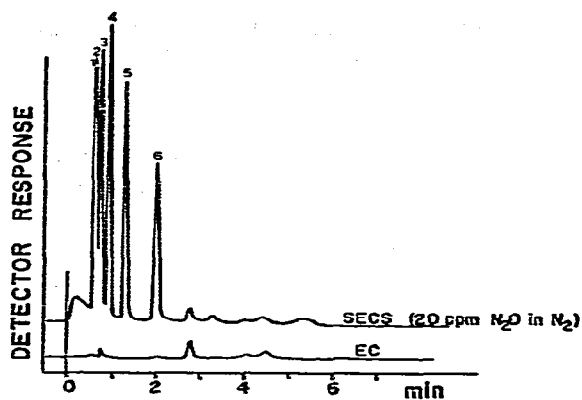


Fig. 2. SECS detection of a mixture of *n*-alkanes. Detector temperature was 350° with a carrier gas flow-rate of 40 ml/min. The analysis was done on a 1.5-m column packed with Porasil C and operated at 100°. A 0.59-ml gas sample loop on the H-P (I) instrument was used to introduce 15 ppm of the hydrocarbons in nitrogen gas standard. Peaks: 1 = methane; 2 = ethane; 3 = propane; 4 = butane; 5 = pentane; 6 = hexane.

decrease in response. Consequently, the practical effect of adding SECS dopant gases may be to convert the relatively selective electron-capture detector into a much less specific, general-purpose detector with no change in instrumentation, simply by switching from one carrier gas source to another. For example, an atmospheric sample chromatographed in the absence of N_2O may give a complex chromatogram showing peaks due to chlorofluorocarbons, other halogenated hydrocarbons and numerous aliphatic and aromatic hydrocarbons. When the same sample is chromatographed in the presence of N_2O , one would expect the aliphatic and aromatic hydrocarbon peaks to be much larger, while the peaks due to the halogenated compounds with high electron-capture cross-sections will not be enhanced. From a comparison of these two chromatograms, specifically the sensitization data coupled with retention data, one can make rapid tentative assignments of compound classes, and perhaps identify the specific compounds.

Response of carbonyl sulfide

Carbonyl sulfide is an important atmospheric constituent, which can be sensitively detected by ECDs. Experiments were performed to determine what effect the presence of N_2O might have on the detector response. No enhancement of COS response was observed at N_2O concentrations up to 5.6 ppm and a detector temperature of 350° in the P-E 3920 instrument using a Porasil C column. Clearly, sensitization is dependent on favorable ion-molecule chemistry for the specific compounds involved and examples exist in which signals are increased, decreased or remain essentially unchanged.

Effects of solvents

Experiments were performed to determine the effect on detector response and recovery of injecting a relatively large mass of various solvents through the detector. Hexane, heptane, benzene and toluene, as available commercially, all contain impurities which give large peaks with an N_2O -doped SECS detector.

Methanol tails severely on the Carbo-pack C column. High purity pentane shows better performance, but generally is an unsuitable solvent in our laboratories, which are located at an elevation of 1660 m, because it vaporizes too rapidly. Detector responses from 1- μ l injections of the solvents are characterized by very large peaks which tail for many minutes after injection on the packed columns used in these exploratory studies. However, the recorder pen returns to the baseline and no apparent solvent-caused anomalies in detector response have been observed when samples are injected immediately thereafter. Repetitive injections in these experiments were possible at 40-min intervals, and this time can probably be greatly shortened by judicious selection and purification of solvents. For the experiments discussed below, we have chosen toluene as the solvent because the components of interest were eluted prior to the solvent, and, therefore, extensive solvent peak tailing is of reduced concern. Additional re-distillation of toluene was necessary to obtain purer samples.

A typical chromatogram of a toluene solution containing 1,1,1-trichloroethane, hexane, benzene and methylisobutylketone is given in Fig. 3. This chromatogram was obtained with N_2O present in the carrier gas. The components of interest are identified in Fig. 2, but several other peaks arise from impurities in the solvent. Without N_2O in the carrier gas, only 1,1,1-trichloroethane and some of the solvent impurities show significant detector response. With N_2O , signals due to the non-halogen-containing compounds increase markedly. The negative response of benzene is a reproducible phenomenon both with and without N_2O in the carrier gas, which we do not yet understand. Larger injections of benzene result in larger negative peaks.

As with the gaseous halocarbon standards, the response for 1,1,1-trichloroethane is slightly reduced when N_2O is present in the carrier gas. Addition of

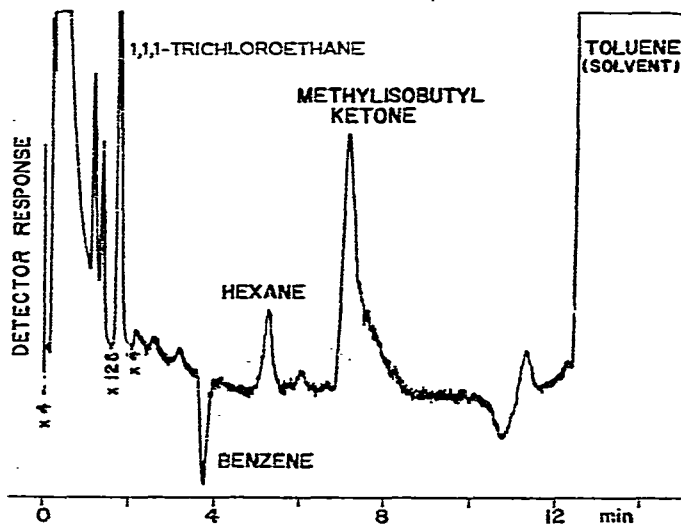


Fig. 3. SECS chromatogram of 1 μ l of a toluene solution containing 0.34 ng 1,1,1-trichloroethane, 44 ng benzene, 3.4 ng hexane and 20 ng methylisobutylketone. Chromatograms were obtained with the H-P (II) instrument. The carrier gas, N_2 , contained 20 ppm of N_2O and the detector was operated at 350°. For conditions, see Table I.

N_2O enhances the response for the other components in the sample, including benzene. Enhancement factors have been estimated for hexane, benzene and methylisobutylketone using the H-P (II) instrument. A sample containing 180 ng of benzene shows an enhancement factor in excess of 100-fold. For 100 ng of hexane, signal intensity is increased by a factor of 200 and for 8 ng of methylisobutylketone the signal is increased 3-fold.

Other studies were performed using the H-P 402 instrument, which differs from all but one of the other instruments of more recent design in that it has a fixed frequency detector. Except for 1,1,1-trichloroethane, a strongly electron-capturing compound, other sample components caused inexplicable, but reproducible, negative detector responses on this particular instrument. This older instrument showed greatly reduced sensitivity when compared with that of newer equipment, but enhancement factors with N_2O were observed for benzene ($\times 8.2$ for 0.35 μg), hexane ($\times 10$ for 0.42 μg) and ethanol ($\times 4$ for 2.4 ng). Small decreases in sensitivity were observed for acetone ($\times 0.9$ for 2.4 μg) and 1,1,1-trichloroethane ($\times 0.3$ for 0.16 ng). It should be borne in mind that the amounts of samples injected were much larger than with the other instruments.

Sensitization of detection of carbon dioxide, hydrogen and methane

We have previously reported the enhancement of electron-capture response for H_2 , CO_2 and CH_4 with an N_2O doped SECS detector⁵. Enhancement factors as great as 5000-fold for CO_2 , 8-fold for CH_4 and 40-fold for H_2 were found. The sensitization for methane can be attributed to the reaction^{5,12}:



We have observed⁵ that the sensitization of response to hydrogen may be affected by the relative importances of reactions 8 and 9:



Since there are two pathways for O^- to be destroyed^{5,13}, the response will depend in a more complicated way than if a single reaction obtained. At elevated temperatures reaction 8 occurs rapidly and causes the expected decrease in free electron density by interrupting reactions 1-3. At lower temperatures, however, the associative detachment process is dominant and in reaction 9 an electron is regenerated, replacing that lost in reaction 1. To the extent that reaction 9 occurs instead of reaction 8, sensitization is accordingly reduced.

The comparative chromatograms in Fig. 4 indicate the usefulness of the technique for determining H_2 and CH_4 in an ambient room air sample. Without N_2O , the measurements are not possible, and, as shown, the sensitization only occurs to a useful extent when the detector temperature is increased to 350°. This is undoubtedly due to the temperature dependence of the sequence of ion-molecule reactions, which occurs at appreciable rates only at higher temperatures. Since hydrogen can be

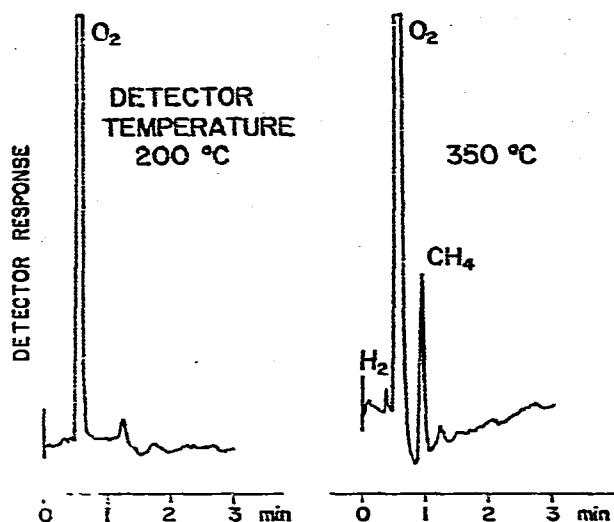


Fig. 4. SECS detection of H_2 and CH_4 in room air. The detector was operated at 200° (left) and 350° (right) with 22 ppm N_2O in the carrier gas using the P-E 3920 instrument with a Molecular Sieve 5A column. Sample size was 5.11 cm^3 at 55 Torr. Replicate samples were injected, but sensitization was sufficient only at 350° to permit detection of H_2 and CH_4 . Ambient air contains approximately 1 ppm of H_2 and of CH_4 . The peaks arise from H_2 (0.4 min), O_2 (0.6 min) and CH_4 (1.0 min).

detected easily by SECS with unprecedented sensitivity, this should greatly facilitate measurement of hydrogen in atmospheric samples.

In related experiments, we have used an N_2O -doped SECS detector to measure hydrogen and methane in samples of human breath. Data from these experiments show that the concentration of hydrogen is from 3 to 20 times higher in exhaled air than in ambient air. The change in methane concentration was negligible in these experiments. A chromatogram obtained from air exhaled by an adult male is presented in Fig. 5, in which the peak at 0.3 min arises from *ca.* 6 pg of hydrogen. This method should prove valuable for determining hydrogen in biological samples^{14,15}. Because hydrogen diffuses very readily, it is expected that hydrogen generated by bacteria or by processes in the body should be rapidly transported by the blood to the lungs where it can be readily partitioned into the air and exhaled. It is expected that such measurements coupled with determinations of numerous other compounds will provide useful diagnostic information for detection of disease states.

CONCLUSIONS

SECS is an effective method for improving the sensitivity with which many compounds can be detected that are not otherwise easily detected. Addition of nitrous oxide to the carrier gas leads to sensitization of the electron-capture response for many compounds, but there is no sensitization for compounds which are already sensitively detected. Therefore, the ECD can be changed from a

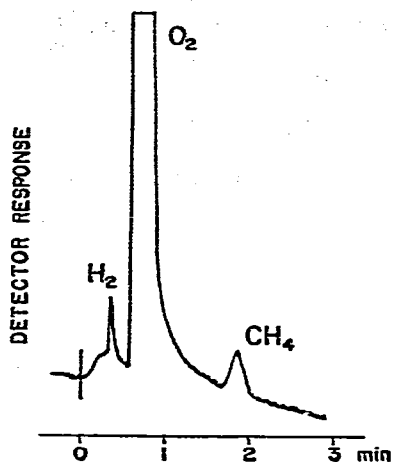


Fig. 5. Measurement of H_2 and CH_4 in human breath. Data were obtained with the H-P (I) instrument using a 1.8-m Molecular Sieve 5A column at 50° . Sample loop volume was $90 \mu\text{l}$. Peak at 0.3 min arises from *ca.* 6 pg of H_2 .

relatively selective detector into a much less specific detector simply by switching from one carrier gas source to another and altering the ion-molecule chemistry. This technique may facilitate identification of unknown peaks. The ion-molecule reactions are in some instances highly temperature dependent; in SECS experiments with 20 ppm N_2O in N_2 , sensitization for most compounds is much greater at 350° than at 250° . Detection of picogram levels of hydrocarbons, hydrogen and carbon dioxide has been demonstrated. Determination of hydrogen in ambient air has been accomplished and this should facilitate global atmospheric measurements. The ease with which sensitive measurements of hydrogen and other compounds in air exhaled by human subjects can be made may lead to new applications in the detection of biological disorders.

ACKNOWLEDGEMENTS

We are grateful to D. W. Denney, J. M. Roberts, E. E. Ferguson, P. D. Goldan, W. C. Kuster and M. L. Green for valuable suggestions and assistance. Support for this work was provided by the United States Air Force Office of Scientific Research (Contract No. F44620-76-C-0031) and the National Science Foundation (Contract No. ENV77-18306). M. P. P. wishes to thank the Graduate School of the University of Colorado for a Colorado Doctoral Fellowship.

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