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SELECTIVE ELECTRON-CAPTURE SENSITIZATION OF WATER, PHENOLS, AMINES AND AROMATIC AND HETEROCYCLIC COMPOUNDS

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SUMMARY

A survey of signal enhancements for various classes of compounds was made using selective electron-capture sensitization (SECS) with nitrous oxide-doping. This technique was used to aid in the identification of five phenolic compounds in a complex oil shale waste water fraction. The three-fold difference in the enhancements found for *ortho*- and *para*-toluidine and the twenty-fold difference for benzo[*a*]pyrene and benzo[*e*]pyrene indicate that SECS can be valuable for identifying these isomers. Enhancement factors are presented for other aromatic and heterocyclic compounds. The signal from water was enhanced 260-fold, allowing trace determinations at part-per-million concentrations.

INTRODUCTION

The sensitivity of an electron-capture detector (ECD) to a variety of compounds that do not rapidly attach electrons can be enhanced markedly by the addition of nitrous oxide to the carrier gas stream of a gas chromatograph. The basis of this enhancement is the application of ion-molecule chemistry to reduce electron density in the cell indirectly. For the case when N_2O is added, the reactive ion is O^- (ref. 1). Signal enhancement is observed when the rate of the reaction between O^- and an analyte is faster than direct attachment of electrons. A similar sensitization has been observed by Grimsrud and co-workers[2,3] when O_2 is added to the carrier gas. In that case, O_2^-, which is in equilibrium with neutral O_2 and free electrons, is the reactant with analytes.

The sensitivity of an ECD toward carbon dioxide, carbon monoxide, hydrogen and hydrocarbons can be enhanced by the addition of N_2O to the nitrogen carrier gas stream and we have termed the technique selective electron-capture sensitization (SECS)[4,5]. It has also been shown that SECS with N_2O can lead to an improved sensitive analysis of vinyl chloride in air[6]. In the present paper, we report data for nitrous oxide-induced signal enhancements for various other classes of compounds. Because the magnitude of signal enhancement appears to be quite reproducible for a given compound and varies greatly from one compound to another, these data could

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aid in the qualitative identification of compounds in complex matrices. Analysis of phenolic compounds in an oil shale waste water sample exemplifies this type of application. Studies of aromatic amines and polynuclear aromatic hydrocarbons (PAHs) show substantially differing sensitivities for closely related positional isomers, which, when coupled with comparing retention indices, can be very helpful in confirming isomer identifications. Marked improvement in the detection limit for water by N_2O doping will be demonstrated. Additionally, anomalous responses sometimes occurring in the ECD operated in the SECS mode will be discussed.

EXPERIMENTAL

Instruments

Most of the experiments were carried out with Hewlett-Packard (HP) Models 5730 and 5713 gas chromatographs with 15 mCi ^{63}Ni constant-current ECDs. The Model 5730 gas chromatograph with dual flame ionization detectors (FIDs) and single ECD was equipped with a Grob-type split/splitless capillary injector[7]. The effluent from the ECD was passed through a heated 25 cm × 1/8 in. O.D. stainless-steel tube which was connected to one of the FIDs. This aided in confirming the identity of peaks by allowing simultaneous recording of the ECD and FID responses[8]. The Model 5713 gas chromatograph, equipped with a single ^{63}Ni ECD, a Grob-type capillary injector, and a 10-port Valco gas sampling valve, was also used in these experiments. Both ECDs on these instruments are identical in design and performance. A Tracor Model 560 gas chromatograph equipped with a ^{63}Ni ECD and a Tracor capillary injection system was used for some experiments. The Tracor ECD has a coaxial design with a considerably larger cell volume than the pin-in-cup design of the Hewlett-Packard detector. The Tracor detector also has the capability to be operated at 400°C, compared to a temperature limit of 350°C for the Hewlett-Packard ECD. The higher temperature capability constitutes a definite advantage for SECS experiments with N_2O owing to the temperature sensitivity of the formation of O^- (ref. 4).

The detector pulsing rate of all ECDs was monitored with a frequency counter connected to the detector pulse circuitry. Frequency measurements provide an indication of the relative cleanliness of the electron-capture cell and help determine whether the system is operating properly[9].

Gas purification and mixing

USP grade nitrogen (General Air, Denver, CO, U.S.A.) was used for carrier gas and make-up gas. Electronic grade nitrous oxide (Scientific Gas Products, South Plainfield, NJ, U.S.A.) was added to the carrier gas. Before use, all gases were passed through 3/8 in. O.D. copper tubing containing molecular sieve 13X which had been activated by passing nitrogen through the sieves while heating at 350°C. The nitrogen carrier gas was passed through an oxygen scrubber composed of 3/8 in. copper tubing packed with R3-11 (Chemical Dynamics, South Plainfield, NJ, U.S.A.), a copper-containing catalyst, before it entered the molecular sieve cartridge. This catalyst must be activated by passing hydrogen through the catalyst while heating to 150°C[11].

Two different devices were used to introduce nitrous oxide into the carrier gas. The first device[10] was a 0.25 mm I.D., type 316 stainless-steel capillary tube that was

crushed nearly flat with a vice and twisted 3 complete turns over a length of approximately 5 cm (see Fig. 1). This flow restricting twisted capillary device was connected to both the HP 5713 and the Tracor instruments through a stainless-steel tee placed in the carrier gas line before it enters the gas chromatograph.

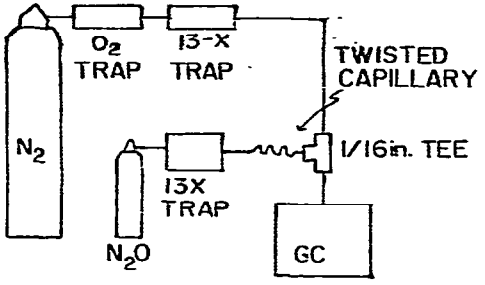

Fig. 1. Twisted capillary method for the addition of N_2O.

A permeation device similar to one used by Goldan *et al.*[6] was constructed by sealing the end of a 1.5 mm O.D., 0.5 mm I.D. PTFE tube by melting the end of the tube in the heated tip of a sealed disposable glass pipet. The sealed end of the PTFE tube extends about 2 cm into a tee interposed into the carrier gas line. This particular permeation device was used with the HP 5730 chromatograph.

The column flow-rate for all packed-column analyses was either 30 or 40 ml min^{-1}; the N_2O level was approximately 20 ppm.

Chemicals

All chemicals analyzed were obtained either from Chem Service (West Chester, PA, U.S.A.) or Aldrich (Milwaukee, WI, U.S.A.). Solvents used for preparing standards were of the highest purity available. Distilled-in-glass hexane and toluene were purchased from Burdick & Jackson (Muskegon, MI, U.S.A.) and Nanograde cyclohexane was obtained from Mallinckrodt (St. Louis, MO, U.S.A.). For those analytes with boiling points less than 120°C, it was necessary to redistill these solvents to remove compounds that produced interfering peaks in the solvent chromatograms[12].

When N_2O was present in the carrier gas, all the analyses performed with the HP gas chromatographs were at 350°C, the detector temperature of maximum sensitivity[5]. Under normal electron-capture mode, most analyses were carried out at 350°C with the exception of the PAHs for which the detector temperatures were either 250 or 350°C. Identifications of compounds were confirmed by retention time analysis using an FID.

Calculations

A signal enhancement value was calculated by dividing the response of the detector in the SECS mode by the response observed with normal electron capture for the same amount of compound.

$$\text{Signal enhancement} = \frac{\text{Peak height with } N_2O}{\text{Peak height without } N_2O}$$

This value reflects the rate of reaction for the analyte with O^- relative to normal electron-capture mechanisms. It is most useful in detector response ratioing or in identification of unknown peaks in the chromatogram.

When 20 ppm N_2O was present in the carrier gas, the noise level normally increased to approximately 4 to 5 times that during normal operation without nitrous oxide addition. To reflect the true improvement in detection limits attainable with N_2O doping, a signal-to-noise (S/N) enhancement must be calculated.

$$\text{Signal-to-noise enhancement} = \frac{\text{S/N with } N_2O}{\text{S/N without } N_2O}$$

RESULTS AND DISCUSSION

Identification of phenols in oil shale waste water

The signal enhancement that is observed when nitrous oxide is added to the carrier gas of an ECD can be used to assist in identifying the compounds giving rise to particular chromatographic peaks in very complex matrices. This approach was used to help identify five phenolic compounds in a waste water sample derived from the pyrolysis of oil shale.

A sample of waste water was obtained from a Colorado oil shale retorting process. This water was steam distilled and the distillate components extracted into hexane with a Nielsen–Kryger apparatus as the condensed steam passed through a layer of this solvent. After removal of most of the hexane by roto-evaporation, 2 μl of the condensed sample were injected (split injection technique) into a gas chromatograph for analysis. A 25-m long fused-silica capillary column (0.25 mm I.D.) coated with Carbowax 20M (Hewlett-Packard, Avondale, PA, U.S.A.) was used to separate the components with the Model 5730 chromatograph. Fig. 2 depicts the analysis of this sample with an ECD operating in the normal and sensitized modes. The complex nature of this sample, even after fractionation, can be seen in both chromatograms. Although the resolution of the capillary column was excellent, there was still a large number of unresolved peaks. Identification of these peaks is ordinarily very difficult without an expensive gas chromatography–mass spectrometry (GC–MS) system. Even with a GC–MS system one may have problems with sensitivity and isomer identification with such a complex sample containing so many overlapping peaks. Indeed, attempts to analyze the sample by GC–MS failed to identify the phenolic components in this sample because of their low concentration and the complexity of the mixture. However, it was possible to identify these components by GC–MS in a different sample (toluene fraction of liquid–liquid extraction) in which the phenols were present in higher concentration than in the distillate.

The identification of the GC peaks by ECD was carried out in a number of ways. Addition of N_2O to the carrier gas produced a large increase in size of a number of peaks in the chromatogram. This allowed more ready location of these peaks from one chromatogram to another. A number of compounds that could possibly be present in this sample were obtained in their pure form and retention times measured in a search for compounds that would match the enhanced sample peaks. When several possible matches were found, each compound was tested to see whether and how much the signal for it was enhanced by SECS (Table I). Finally, a small amount

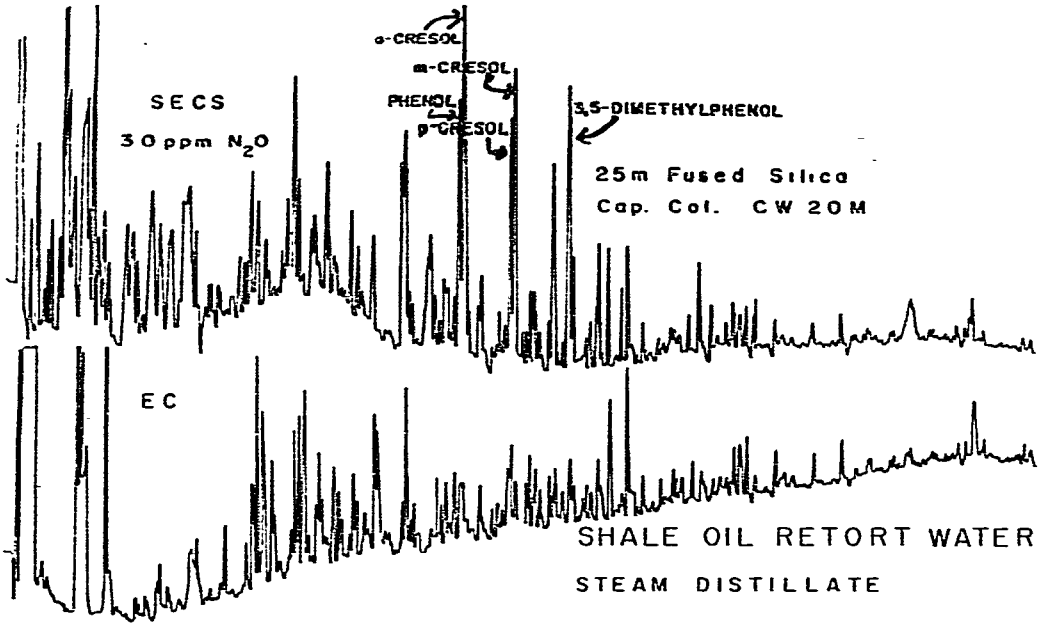

Fig. 2. Identification of phenols in shale oil waste water. 2-μl split injection, temperature program: 50–200°C at 2°C min^{-1} make-up flow-rate, detector temperature 350°C. Top, SECS with 30 ppm N_2O in N_2 carrier gas stream. Bottom, same sample analyzed by ordinary (ECD) without N_2O.

of the pure compound corresponding to each suspected analyte was added to the original hexane sample and the analysis re-run to confirm the identifications. This allowed identification of the peaks with a relatively high degree of certainty. Even higher levels of certainty can be attached if the degree of enhancement matches that of authentic samples. This constitutes a form of signal ratioing. The presence of phenolic components in a sample related to oil shale is not unusual[13], but the identification of these compounds in a very complex matrix at levels too low to be detected with a GC–MS system is significant.

This analysis of an oil shale waste water fraction exemplifies the use of SECS enhancement to identify compounds in a very complex sample. Because only certain compounds were enhanced, only some peaks showed large changes, making the identification of these compounds much simpler.

TABLE I

SECS ENHANCEMENT OF PHENOLS

Compound	*Signal enhancement*	*S/N enhancement*
Phenol	7	2
o-Cresol	14	4.5
m-Cresol	12	4
p-Cresol	5	1.5
2.6-Dimethylphenol	6	2
3.4-Dimethylphenol	12	4
3.5-Dimethylphenol	12	4

Aromatic amines

The SECS detector response produced by a number of aromatic amines was investigated. For these analyses a 30-m fused-silica capillary column coated with SP-2100 (J & W Scientific, Orangevale, CA, U.S.A.) was used with the HP 5713 gas chromatograph. Samples of 1–100 ng of the amines in hexane were injected (splitless). At low nanogram levels, there appeared to be some irreversible adsorption of aromatic amines in this system. This may be due to the intrinsic acidic nature of the fused-silica surface or to the activity of the wall of the silanized glass injection port insert. Attempts to solve the adsorption problem led us to investigate two other columns: a 2 m × 2 mm I.D. glass column packed with 4% Carbowax 20M + 0.8% KOH on Carbopack B (Supelco) and a 2 m × 2 mm I.D. glass column packed with 5% KOH on Chromosorb 102. Both of these had earlier been reported to be very satisfactory for analysis of amines[14,15]. Due to excessive column bleed and appearance of various ghost peaks from both columns, even after one week of conditioning, we were unable to use these columns for analyses of amines.

All six of the amines studied showed large enhancements and exhibited some interesting isomeric effects. Table II contains the observed signal enhancement values.

TABLE II

SECS ENHANCEMENT OF AMINES

Compound	*Signal enhancement*	*S/N enhancement*	*Boiling point (°C)*
Aniline	70	20	184
N-Methylaniline	46	12	196
N,N-Dimethylaniline	38	9	194
o-Toluidine	100	25	200
m-Toluidine	35	9	203
p-Toluidine	35	9	200

The differences in the toluidine signal enhancements presented an excellent example of how SECS could be a valuable tool for isomer identification. *Ortho*- and *para*-toluidine have the same boiling points, but they can be separated with some columns. The three isomers of toluidine exhibit different enhancement values so these data can be used together with retention data to confirm the identifications. The addition of N_2O to the carrier gas of an ECD makes it possible to determine relative response factors for each analyte. Comparison of these values with values obtained from standards allows ready identification of which isomer is present or indicates that a peak consists of a mixture of two or more compounds.

Polynuclear aromatic hydrocarbons

PAHs were studied to determine whether SECS could be used as a tool to aid in the identification of these compounds. It was also of interest to compare results using N_2O doping with those obtained by the O_2-doping technique of Grimsrud and Miller[16] and Miller *et al.*[17].

Several workers[18,19] have shown that PAH molecules capture thermal electrons in a non-dissociative manner and therefore larger responses for these com-

pounds could be obtained by operating the electron capture detector at lower detector temperatures. For this reason, the responses for PAHs when N_2O is added to an ECD at 350°C have also been compared to the normal ECD responses at 250°C. This is a more realistic measure of the improvement in sensitivity of this new method over one currently in use. The detector temperature, 250°C, was chosen to maintain a detector temperature 50°C above the maximum column temperature.

The results for seventeen PAHs are shown in Table III. These compounds were analyzed with a 1 m × 2 mm I.D. glass column packed with 3% OV-17 on Gas-Chrom Q, that was installed in the Model 5713 chromatograph. The carrier gas was 25 ppm N_2O in nitrogen at a flow-rate of 30 ml min^{-1}. Samples ranging from 1 to 50 ng of PAH per injection were prepared by dilution with toluene.

TABLE III

SECS ENHANCEMENT FOR POLYNUCLEAR AROMATIC HYDROCARBONS

Compound	*Detector temperature 250°C**		*Detector temperature 350°C*	
	Signal enhancement	*S/N enhancement*	*Signal enhancement*	*S/N enhancement*
Anthracene	3.2	0.8	6.3	1.6
9-Methylanthracene	1.5	0.4	5.9	1.5
Phenanthrene	9.7	2.4	8.1	2.0
Tetracene	1.4	0.4	1.6	0.4
1,2-Benzanthracene	1.3	0.3	3.2	0.8
Chrysene	5.5	1.4	6.5	1.6
Triphenylene	9.5	2.4	17	4.3
Pyrene	6.8	1.7	11	2.8
Benzo[*a*]pyrene	0.6	0.2	1.7	0.4
Benzo[*e*]pyrene	3.5	0.9	34	8.5
Perylene	3.2	0.8	6	1.5
Acenaphthene	4.0	1.0	4.0	1.0
Fluorene	1.2	0.3	1.5	0.4
Dibenzofuran	17	4.3	29	7.3
Dibenzothiophene	18	4.5	25	6.3
Carbazole	3.2	0.8	8.4	2.1
Acridine	3.7	0.9	14.4	3.6

* SECS response at a detector temperature of 350°C divided by the ECD response at 250°C.

The signal enhancements observed for many of these compounds were relatively small. However, there were substantial differences in enhancement factors for a few of the fused ring systems. The most notable effect of structural variation is illustrated in the case of benzo[*e*]pyrene contrasted with benzo[*a*]pyrene, for which the signal enhancement values differed by a factor of twenty. This may be due partly to the fact that at 350°C the normal EC response of benzo[*e*]pyrene is significantly smaller than that of benzo[*a*]pyrene. The enhancement for triphenylene was also significantly larger than those for the other compounds containing four fused aromatic rings. Overall, the more linear fused ring systems tended to exhibit smaller enhancements. Therefore, for certain compounds, it would be possible to use relative enhancement values to differentiate isomers in a difficult analysis of PAHs. This is particularly significant because the mass spectra of isomers of PAHs are very similar, and not of much use in assessing which isomer(s) are present.

Dibenzofuran, dibenzothiophene, carbazole and acridine are heterocyclic molecules in which oxygen, nitrogen or sulfur are included in the ring system. The signal enhancement values differ widely, from 1.5 for fluorene to 28.5 for dibenzofuran. All heterocyclic compounds exhibited much larger enhancements than fluorene, the carbon analog.

From a comparison of our signal enhancements with those reported by Miller *et al.*[17] several interesting features can be noted. Triphenylene and dibenzothiophene exhibited relatively large enhancements with N_2O addition, although they were among the least enhanced compounds when O_2 was added. Substitution of a methyl group at the 9-position of anthracene decreased signal enhancement slightly with N_2O, while the response enhancement values increased by a factor of two with O_2.

For determination of actual improvement in detection limits of PAHs, the SECS response was compared to the response from the ECD operating normally without N_2O at 250°C. The increased noise levels resulting from the addition of N_2O must also be taken into account. The noise level when N_2O was present is approximately four times that without N_2O. The best signal to noise enhancement from our data was achieved with dibenzothiophene, for which the detection limit could be lowered by a factor of 4.5. Of the seventeen PAHs studied, there are only six compounds with signal-to-noise enhancements greater than one. Signal-to-noise enhancement values less than one are actually degradations in sensitivity that are only useful to aid in the identification of compounds if detector-ratioing schemes are employed.

Cyclic heteroatomic compounds

The effect of the presence of a hetero atom on the observed enhancement was investigated further by examining the detector responses for a number of cyclic compounds containing a sulfur, nitrogen or oxygen atom (Table IV). These analyses were performed with the HP 5730 instrument using a 25-m fused-silica capillary column coated with SE-54. Whenever possible, splitless injections were used for sample introduction. For thiophene and other compounds with boiling points below 110°C it was necessary to use split injections under isothermal conditions in order to obtain adequate separation of the analyte from the hexane solvent tail. Furan and tetrahydrofuran proved particularly difficult to resolve from hexane. In the case of furan, it was necessary to use toluene as the solvent and measure the furan response before the solvent was eluted. For tetrahydrofuran, it was necessary to use a 10 ft. × 2 mm I.D. glass column packed with 100–120 mesh Supelcoport with a 10% loading of SP-2250. The last analysis was performed using the Tracor instrument, raising the possibility that the enhancement observed may not be strictly comparable to the results for the other compounds measured with the HP instrument. However, in most cases the responses of the Tracor chromatograph were very similar, if not essentially identical, to those obtained with the HP instrument. It should be noted that the enhancement values reported here are not necessarily a constant for a given compound, but are dependent on detector design and cleanliness and may be dependent on other factors. It is necessary to determine these factors for a given instrument on a periodic basis as detector cleanliness changes.

Examination of the first five entries in the Table IV reveals that responses of all nitrogen-containing compounds were enhanced to a certain extent. The responses of the first four compounds demonstrate that the detection of aromatic compounds was

TABLE IV

SECS ENHANCEMENT FOR HETEROATOMIC COMPOUNDS

Compound	*Signal enhancement*	*S/N enhancement*
Pyrrole	75	15
Pyrrolidine	20	4
Pyridine	45	11
Piperidine	5	1
Quinoline	7.5	2
Furan	—*	—
Tetrahydrofuran	800	120**
2.5-Dimethylfuran	0.8	0.3
p-Dioxane	7	1.5
Thiophene	1.8	0.3
Tetrahydrothiophene	25	5

* Response to 100 ng of furan without and with N_2O = +88 mm peak height.

** Analysis performed with Tracor 560 gas chromatograph at a detector temperature of 400°C; all other measurements made with HP 5730 gas chromatograph at 350°C.

enhanced to a greater degree than that of their saturated analogues. Addition of one or two benzene rings to pyrrole or pyridyl moieties resulted in smaller enhancements. The response enhancements for quinoline, acridine and carbazole demonstrated that the nitrogen-compounds had improved responses over those of the carbon analogues, naphthalene, anthracene and fluorene.

The oxygen-containing compounds produced more unusual responses. Furan produced a small positive response with normal electron capture, but addition of N_2O to the N_2 carrier gas resulted in a large negative response when furan is eluted. This negative response increased with the concentration of furan in the solvent, asymptotically approaching a limit determined by an injection of neat furan. The signal for dimethylfuran was always positive, although not enhanced by N_2O. Tetrahydrofuran displayed a large signal enhancement with N_2O when the Tracor chromatograph was operated with the detector temperature at 400°C. Dibenzofuran exhibits a much larger signal enhancement than that of furan. This effect was the reverse of that observed with the analogous nitrogen heterocycles, carbazole and pyrrole.

The signals produced for SECS of sulfur-containing compounds appear to be intermediate in magnitude to those for the nitrogen- and oxygen-containing compounds. The enhancement of the thiophene signal was very small, but this could be considered intermediate between the negative response for furan and the large enhancement observed for pyrrole. The tetrahydrothiophene signal exhibits an enhancement less than the aromatic analogue thiophene, the reverse of the trend observed for nitrogen compounds. However, the value was greater than that of pyrrolidine and less than that of tetrahydrofuran.

Aromatic compounds

Analyses of aromatic compounds were done on a 3 m × 2 mm I.D. glass column packed with 10% SP-2250 on Supelcoport. Examination of signal enhancement values of these compounds indicates that addition of N_2O to the ECD improved

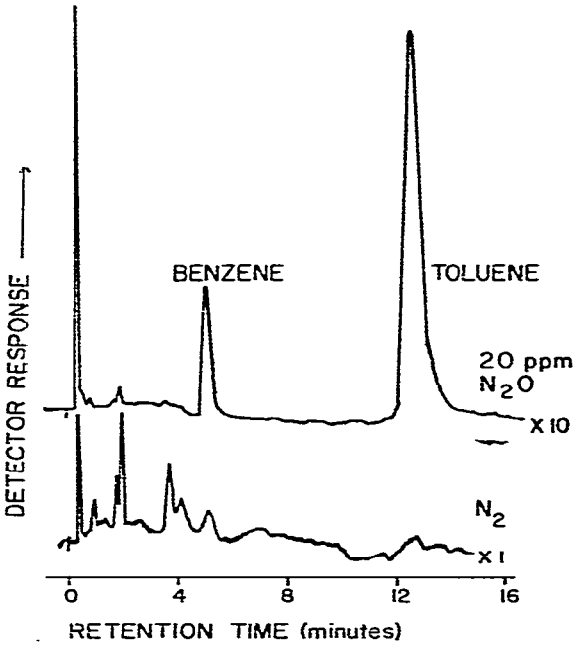

Fig. 3. Response enhancement of benzene and toluene with and without N_2O. Tracor gas chromatograph. 3 m × 2 mm I.D. glass column packed with 10% SP-2250 on 100–120 mesh Supelcoport at 40°C with 45 ml min^{-1} carrier flow, detector temperature 400°C. The sample contained 100 ng each of benzene and toluene.

these responses significantly (see Table V). The detector response for benzene and toluene with and without N_2O in the carrier gas is depicted in Fig. 3.

All aromatic compounds studied produced somewhat unusual responses with the ECD. Benzene signals appeared to be extremely sensitive to impurities in the carrier gas. Under some circumstances, it exhibited negative response with normal electron capture[5]. Styrene, however, always produces a negative response with normal electron capture and positive response when N_2O is added. Biphenyl and naphthalene sometimes produce a "W"-shaped peak, which will be discussed in the section on anomalous responses.

Although the detector responses to all these compounds were increased when N_2O was present, their sensitivities were not superior to those obtainable with an

TABLE V

SECS ENHANCEMENT FOR AROMATIC COMPOUNDS

Compound	*Signal enhancement*	*S/N enhancement*
Benzene	50	10
Toluene	150	30
Naphthalene	9.4	2.4
Biphenyl	44	11
p-Methylbiphenyl	17	43
m-Dimethoxybenzene	26	8.5

FID. However, because SECS makes it possible to detect both *n*-alkanes and aromatic compounds used as retention index standards, this may facilitate compound identification based on retention indices when ECDs are used.

Water

Water exhibited a relatively large enhancement factor, 260 (Fig. 4), and can be sensitively detected with SECS. Unfortunately, the Porapak Q column operating at 110°C exhibited a substantial level of bleed, resulting in a high baseline when N_2O was present in the carrier gas. Therefore, signal-to-noise enhancement with the Porapak column was only a factor of 21. The major problem with the chromatography of water is poor column performance. Porapak Q has been the most common column packing used for GC determination of water; however, recent evidence indicates that these columns cannot be used for the determination of water in most solvents because the solvent can displace the small amount of water adsorbed on the surface of the styrene–divinylbenzene polymeric beads[20]. This could create false peaks if the solvent were eluted before the water. To avoid solvent displacement of water, a 100-μl gas sample loop was constructed from 1/16 in. O.D. PTFE tubing to introduce gas samples containing water. A flowing gas system consisting of a bubbler filled with distilled water, thermostated at 30°C, and a tee to add dry make-up gas (air) was connected to the gas sample loop with 1/4 in. O.D. PTFE tubing. In this way a gas stream saturated with water vapor at 30°C could be diluted to desired levels with dry air. It appears that, with suitable low-bleed columns that give sharp peaks without tailing for water,

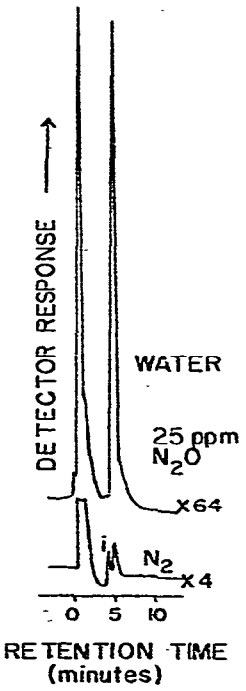

Fig. 4. Response enhancement of water with and without N_2O. Sample was 3 ng of water, 1.8 m × 2 mm I.D. glass column packed with Porapak Q at 110°C. The peak labelled "i" was an impurity.

it should be possible to measure water sensitively by SECS. As a corollary, attention must be paid to drying the carrier gas carefully.

Anomalous responses

The fact that SECS can enhance the detector signal for a compound to which the ECD does not respond has led to the study of many compounds that would not normally be analyzed by electron capture. Some compounds have produced unusual detector responses. The requirement that the detector be operated at a relatively high temperature (350°C) when N_2O is added to the carrier gas has also led to some interesting signals for other compounds that are normally analyzed at much lower detector temperatures with normal electron capture.

A good example of this is the negative response observed for some PAHs and aromatic hydrocarbons. This negative response was not simply an inverted peak, as Grimsrud and Miller[16] have reported, but rather a "W"-shaped peak. The leading edge of the negative response was very sharp, but the bottom of the peak was generally rounded and the return to the baseline was very slow. As more of the compound was injected, a positive peak would appear, superimposed on the negative component of the peak. The mirror image (positive peak) would appear to tail very badly. If a very large amount of analyte were injected, the negative component would appear as a slight drop in the baseline just before the large positive peak. The negative component was observed with pure nitrogen and sometimes with N_2O in the carrier gas and when using either packed or capillary columns. The size of the negative peak seemed to be influenced largely by the cleanliness of the septum and the amount of column bleed. Therefore, avoidance of negative and other anomalous responses depends in part on maintaining as clean a chromatographic flow system as possible. It appeared that whenever a compound produced a very poor detector response, there was a strong possibility of observing negative peaks.

For the purpose of estimating enhancements, only the positive component of the peak was used. The peak height was measured from the base of the negative signal to the top of the sharp positive peak.

A second type of negative peak was observed for olefin compounds. This was truly a negative peak, reasonably symmetrical, similar to that recorded for hydrogen at low detector temperature[4]. There was no positive component, and the magnitude of the peak increases in the negative direction (decreasing frequency) with increasing amount of analyte injected. Hexene and octene are examples of compounds that produce such negative peaks with or without N_2O present in the carrier gas.

ACKNOWLEDGEMENTS

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REFERENCES

1 R. Marx, G. Mauclaire, F. C. Fehsenfeld, D. B. Dunkin and E. E. Ferguson, *J. Chem. Phys.*, 58 (1973) 3267.
2 E. P. Grimsrud and D. A. Miller, *Anal. Chem.*, 50 (1978) 1141.
3 E. P. Grimsrud and R. G. Stebbins, *J. Chromatogr.*, 155 (1978) 19.

4 M. P. Phillips, P. D. Goldan, W. C. Kuster, R. E. Sievers and F. C. Fehsenfeld, *Anal. Chem.*, 51 (1979) 1819.
5 R. E. Sievers, M. P. Phillips, R. M. Barkley, M. A. Wizner, M. J. Bollinger, R. S. Hutte and F. C. Fehsenfeld, *J. Chromatogr.*, 186 (1979) 3.
6 P. D. Goldan, F. C. Fehsenfeld, W. C. Kuster, M. P. Phillips and R. E. Sievers, *Anal. Chem.*, 52 (1980) 1751.
7 K. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 57.
8 A. Södergren, *J. Chromatogr.*, 160 (1978) 271.
9 C. Burgett, *Hewlett-Packard Service Note 5700A-6, Gas Purity Check and Standing Frequency Measurement*, Hewlett-Packard, Avondale, PA, 1972.
10 V. Pretorius, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 10078.
11 *Technical leaflet on BASF Catalyst R3-11*, Chemical Dynamics Corp., South Plainfield, NJ, 1971.
12 W. D. Bowers, M. L. Parsons, R. E. Clements, G. A. Eiceman, F. W. Karasek, *J. Chromatogr.*, 206 (1981) 279.
13 J. S. Stanley, *Investigation of Trace Elements and Organic Ligands in Oil Shale Waste, Ph.D. Thesis*, University of Colorado, Boulder, CO, 1981.
14 F. Raulin, P. Price and C. Ponnamperuma, *Amer. Lab.*, 12 (1980) 45.
15 K. Kazuhiro, Y. Yamazaki and M. Uebori, *Anal. Chem.*, 52 (1980) 1980.
16 E. P. Grumsrud and D. A. Miller, *J. Chromatogr.*, 192 (1980) 117.
17 D. A. Miller, K. Skogerboe and E. P. Grimsrud, *Anal. Chem.*, 53 (1981) 464.
18 J. E. Lovelock, A. Zlatkis and R. S. Becker, *Nature (London)*, 84 (1962) 540.
19 W. E. Wentworth and R. S. Becker, *J. Amer. Chem. Soc.*, 84 (1962) 4263.
20 C. P. M. G. A'Campo, S. M. Lemkowitz, P. Verbrugge and P. J. van den Berg, *J. Chromatogr.*, 203 (1981) 271.