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PARALLEL AND SERIES CONFIGURATIONS FOR ELECTRON-CAPTURE AND OXYGEN-SENSITIZED ELECTRON-CAPTURE DETECTION

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SUMMARY

By use of two electron-capture detectors configured in either parallel or series arrangements where one of the detectors is sensitized with oxygen, the precision of measurement of oxygen-induced response enhancements is significantly improved. The relative standard deviation of repeated measurements is shown to be less than 3% for the parallel and 2% for the series arrangements. Either of these detection schemes will increase the power of oxygen-enhancement measurements for the identification of unknown compounds by gas chromatography. The parallel arrangement may be more generally applicable to broad-range chemical analysis than the series arrangement because with the series arrangement the response of the second detector to some compounds is complicated by the formation of electron-capturing products in the first detector.

INTRODUCTION

The intentional addition of oxygen to the make-up gas of a constant-current electron-capture detector has been shown to provide a useful extension of electron-capture detection (ECD) capabilities for gas chromatography (GC). By use of the reaction of the negative ion, O_2^-, with the analyte the magnitude of the response of the electron-capture detector to numerous compounds can be significantly increased[1,2]. Furthermore, it has been shown that the magnitude of increase in ECD response caused by oxygen is extremely sensitive to differences in molecular structure and may provide a powerful, yet instrumentally simple means for compound verification in analysis by GC–ECD[3–5]. This use may become particularly important for the analysis of structurally similar, EC-active isomers. For example, the ECD responses to the trifluoroacetic anhydride derivatives of the eight possible isomers of aminoanthracene and aminophenanthrene were increased by added oxygen by a continuous range of magnitudes from almost no increase to two orders of magnitude increase[5,6]. In the analysis of these and other environmentally important compounds, a scheme which provides reproducible and precise oxygen-enhanced ECD measurements along with the usual EC response will be of significant assistance in verifying the presence of each suspected isomer.

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The objective of this study was to determine if the precision of oxygen response enhancement (RE) measurements can be improved by the simultanous use of two electron-capture detectors. Previously, all oxygen RE measurements have been made using a single electron-capture detector and a given chromatographic separation which was performed twice, once without oxygen and then with oxygen in the detector. The precision of these measurements has been typically only 6 to 12% depending on the operator's ability to reproducibly inject the sample. While we have shown that this approach is adequate where large differences exist in the individual RE values of the set of compounds under study, the method will be made more widely applicable if the precision of measurement can be increased further. Improved reproducibility as well as increased ease of measurement might be expected if two electron-capture detectors are simultaneously used for each analysis where one detector is operated normally and the other is doped with oxygen. Since the electron-capture detector is thought to be relatively non-destructive to many compounds, a series configuration as well as a parallel configuration might be envisioned and both have been tested here.

EXPERIMENTAL

Parallel detection

The gas chromatograph is a Varian 3700 with constant-current, pulse-modulated operation of its two ^{63}Ni electron-capture detector. The two Varian detectors are mounted side-by-side on the standard Varian detector block. As shown in Fig. 1a, two SE-52 capillary columns (6.0 m × 0.25 mm I.D.) were used with helium as the carrier gas and nitrogen and a nitrogen–oxygen mixture as the make-up gases. The sample is split at the injection port. When desired, oxygen was added to detector B by combining its nitrogen makeup gas with about 6 ml/min of nitrogen containing 2.0% oxygen. An oxygen level of about 0.30% is thereby maintained in the doped detector. A precise level of oxygen is adjusted by fine tuning the oxygen flow until a preselected magnitude of baseline frequency is observed. The total flow-rate of make-up gas to each detector is 40 ml/min. The two detectors were maintained at 300°C. The injector temperature was 210°C. The column temperature was held con-

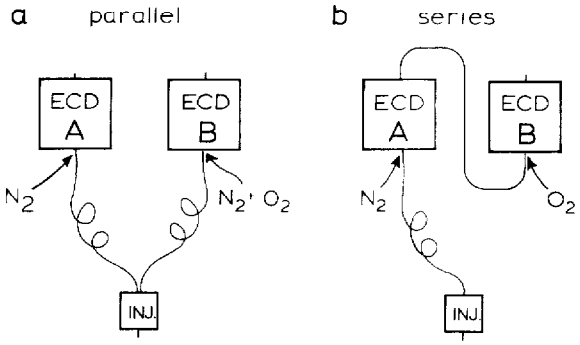


Fig. 1. Two detector configurations used. (a) With parallel detectors, total flow of make-up gas to each detector is 40 ml/min; (b) with series detectors, 40 ml/min nitrogen is added at detector A and 6 ml/min oxygen–nitrogen mixture is added at detector B.

stant at 140°C. A splitless injection of 0.4 μl is used where each injection contains an amount of sample in toluene sufficient to produce small, but easily measured peaks.

Series detection

The series configuration of the detectors is shown in Fig. 1b. Chromatographic conditions of the single SE-30 capillary column used here are identical to those of the parallel detection scheme described above. Also, the physical locations of the two detectors are unchanged. For this case, however, pure nitrogen make-up gas (40 ml/min) is added to the first detector and about 6 ml/min of the 2.0% oxygen-in-nitrogen mixture is added to the second detector. The entire contents of the first detector are carried to the second detector by a glass-lined stainless-steel tube (40 cm × 1/16 in. O.D.). This transfer tube is attached to the exit tube (also 1/16-inch diameter) of the Varian electron-capture detector by a short piece of PTFE tubing.

In all experiments the responses of the two detectors were monitored simultaneously by a 2-pen recorder.

RESULTS AND DISCUSSIONS

Parallel detection

In order to ensure that the split ratio at the injector is approximately equal, and in order to determine the relative sensitivities of the two detectors, the chromatograms shown in Fig. 2 were first obtained where both detectors are operated in the normal, oxygen-free mode. In the first three repeated injections the ratio of peak heights observed at detector A and detector B is 1.20. The possibility that the paired ECD responses may differ owing to differing sensitivities of the two detectors is tested by reversing the columns at the detectors. As shown in Fig. 2b, an A to B response

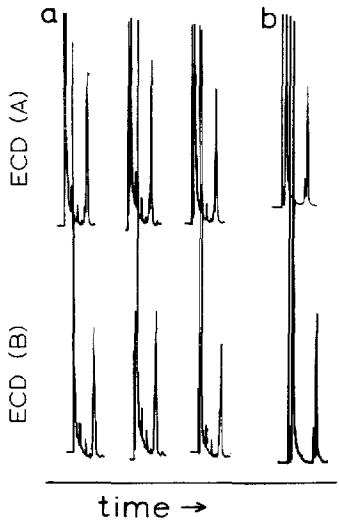
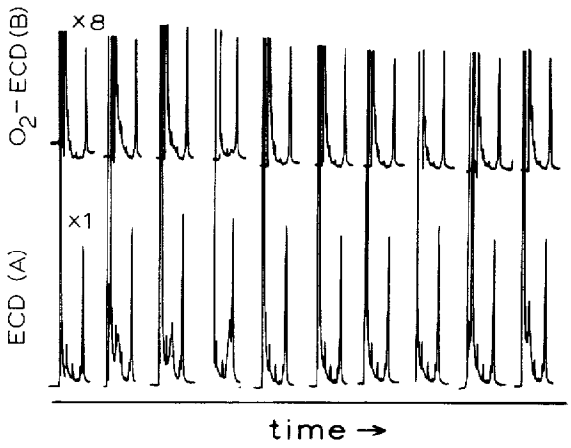


Fig. 2. (a) Parallel ECD responses with dual column analysis of sample containing 12 ng of 2-chloroanthracene, repeated three times with both detectors operated in the normal, oxygen-free mode. (b) Analysis repeated with column–detector connections reversed. Detector temperature 300°C.

ratio of 0.82 is then obtained. This result indicates that our detectors have essentially identical sensitivities and the small difference in normal EC responses seen here is due entirely to the split of sample occurring at the injector. The measurements of oxygen enhancements can now be corrected for the effect of injector split by multiplication of the observed response ratios by 1.20.

In Fig. 3, a single 2-chloroanthracene sample has been analyzed 10 times in repetition. While the peak heights vary noticeably from one injection to the next (due to the difficulty in reproducibly delivering 0.4 μl by syringe), the ratios of the oxygen-sensitized to the normal responses remains very constant. The ratios of the ten dual responses shown are 6.2, 6.2, 6.2, 5.9, 5.8, 6.3, 5.9, 6.0, 6.1 and 6.1. The relative standard deviation of these values is 2.6%. The average of these values, 6.1, times the split ratio, 1.20, indicates that the oxygen-induced RE value for 2-chloroanthracene is 7.3. This value correlates well with the value of 6.9 previously determined in a study also using 0.30% oxygen at 300°C, but by two separate, paired analysis with only one detector[4]. In that study unusually great care was taken to reproducibly inject samples and the relative standard deviation of RE measurements was estimated to be *ca.* 6%. The use of two detectors as described here has significantly reduced the spread of individual determinations and has also greatly relaxed the requirement for precise injections.

In Fig. 4 chromatograms are shown which indicate that the response ratios are quite constant over a range of different analyte concentrations. In these analyses, RE values of 6.9, 7.0, 7.0 and 7.3 are observed as the analyte concentration is repeatedly doubled. In a previous study, using the single detector method, the RE values of this



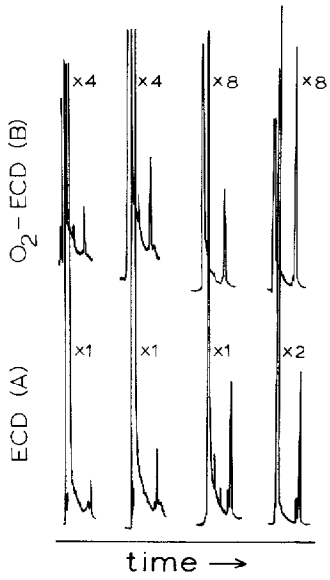


Fig. 3. Parallel ECD and oxygen-sensitized ECD detection of sample containing 12 ng of 2-chloroanthracene, repeated ten times. Oxygen level in detector B is 0.30%.

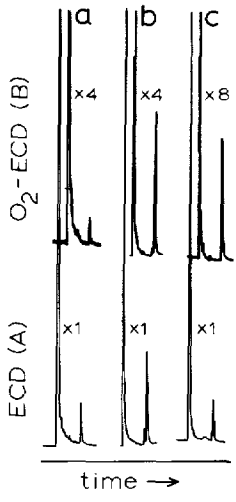
Fig. 4. Parallel ECD and oxygen-sensitized ECD detection of four samples containing 1.5, 3.0, 6.0 and 12 ng of 2-chloroanthracene.

compound and its two isomers were also found to be independent of concentration over a change of two orders of magnitude[4].

In Fig. 5, the dual responses to all three isomers of chloroanthracene are shown. After correction for the injection split ratio of 1.20, the RE values for 1-, 2- and 9-chloroanthracene are determined to be 3.4, 7.3 and 27.0. These values are in reasonable agreement with those previously observed under similar conditions by the single detector method[4]. Since the mass spectra of the three chloroanthracenes are identical[4], their ECD responses as shown in Fig. 5 would seem to offer a particularly useful means for their isomeric identification.

Series detection

A series arrangement of the two detectors as shown in Fig. 1b was also tested. First, several important features of this arrangement are illustrated in Fig. 6a, which shows simultaneous, series responses where both detectors are being operated in the normal, oxygen-free mode. Even with the relatively lengthy transfer line necessary to connect the two detectors used here, it is seen that the chromatographic resolution as perceived by the first detector is reasonably maintained in the second detector. Also, the chromatogram shown in Fig. 6a illustrates that the first detector is, indeed, relatively non-destructive towards the compounds detected. This is to be expected for many compounds which do not have extremely fast electron-capture rates. (We have found that extremely strongly responding compounds such as 2,7-dinitrofluorene, 9-nitroanthracene, and hexachlorobenzene exhibit significantly reduced peaks



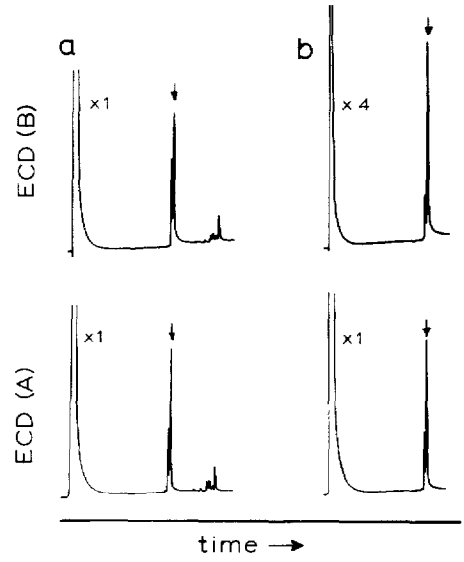


Fig. 5. Parallel ECD and oxygen-sensitized ECD detection of samples containing (a) 5 ng of 1-chloroanthracene, (b) 12 ng of 2-chloroanthracene, and (c) 6 ng of 9-chloroanthracene.

Fig. 6. Series configuration of detectors. (a) without addition of oxygen to detector B; (b) with addition of oxygen to detector B. Arrows mark point of elution of 2-chloroanthracene. Peak just prior to arrow is due to 9-chlorophenanthrene. Multiplet of peaks included in chromatogram (a) are due to impurities of unknown identity.

in the second detector.) The three chloroanthracenes appeared to be well-behaved in that nearly equal peak heights are observed in both undoped detectors. The small (9%) reduction in the second peak height for 2-chloroanthracene in Fig. 6a is probably due to a slight loss of chromatographic resolution occurring in the first detector and the transfer line.

In Fig. 6b, the series responses to the same sample is shown where the second detector is now sensitized with oxygen. The response enhancement for 2-chloroanthracene measured directly from the ratio of peak heights in Fig. 6b is 5.4. This enhancement value is lower than the value of 7.3 measured with the parallel configuration. This difference can be attributed entirely to the combined effects of chromatographic broadening and the further dilution of analyte by the addition of 15% additional make-up gas at the second detector. The response enhancements for 1-chloroanthracene and 9-chloroanthracene were 2.5 and 21, respectively, with the series configuration and, therefore, were also reduced by about 25% relative to the enhancement measured with the parallel configuration.

Upon repeating the analysis shown in Fig. 6b fifteen times, excellent reproducibility is observed. The relative standard deviation of these enhancement measurements was *ca.* 2.0%. Also, the enhancement values measured for 2-chloroanthracene were found to be relatively independent of analyte concentration. This important point is illustrated in Fig. 7 where three samples containing 3 ng, 8 ng and 100 ng of 2-chloroanthracene produced enhancements if 4.4, 4.8, and 4.9, respectively.

For the chloroanthracenes, the series configuration of detection appeared to function at least as well as the parallel configuration. However, with the series configuration anomalous responses to some compounds have been noted. These appear

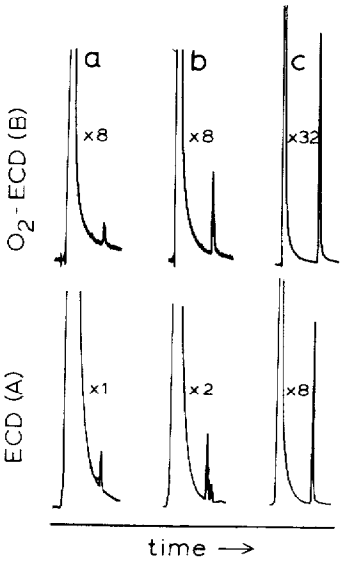


Fig. 7. Series ECD and oxygen-sensitized ECD of three samples containing (a) 3 ng, (b) 8 ng, and (c) 100 ng of 2-chloroanthracene.

to be due to the production in the first detector of EC-active products which affect the response of the second detector. For example, also shown in Fig. 6a is a peak just prior to the 2-chloroanthracene peak which is due to the presence of 9-chlorophenanthrene. Without added oxygen in either detector the response of the second detector to this compound is observed to be 1.6 times the response of the first. This behavior for other weakly responding compounds has been previously observed[7], in a study in which tandem electron-capture detectors were also used. In that study, also, this behavior was attributed to the formation of EC-active products in the first detector. In Fig. 6b, the oxygen-induced enhancement of the series detector to 9-chlorophenanthrene is 3.1. This is about twice as large as the corresponding measurement previously reported[3]. Therefore, anomalous oxygen enhancement measurements might also be expected for 2-chlorophenanthrene when a series configuration is used. The generality of this type of behavior is not known and is under further investigation.

In summary, by the use of simultaneous EC and oxygen-sensitized EC detection the reproducibility of enhancement measurements is greatly improved. The parallel configuration of detectors has been shown to provide a high level of reproducibility without adding any accompanying complexities. The series arrangement also functioned very well for the chloroanthracenes studied here, but has caused anomalous behaviour for some compounds, presumably due to the production of EC-active products in the first detector which are passed on to the second.

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