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INFLUENCE OF THE CARRIER GAS FLOW-RATE ON THE PULSED ELECTRON-CAPTURE DETECTOR

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SUMMARY

The effect of the carrier gas flow-rate on the pulsed electron-capture detector was examined theoretically and experimentally. The results were considered in terms of the standing current and response. Wentworth's kinetic model equations were solved taking into consideration carrier gas flow-rates over the range 30–240 ml/min. An increase in the carrier gas flow-rate resulted in a decrease in the detector response to a sample. These theoretical findings were consistent with the experimental results obtained for sulphur hexafluoride and for technical-grade nitrogen as a carrier gas. The experimental results obtained for high-purity nitrogen were partially inconsistent with the theoretical predictions. It was also shown that the carrier gas flow-rate should be kept at a minimum value that satisfies the greatest chromatographic separation demands in order to achieve good detector performance parameters, irrespective of the kind and purity of the carrier gas.

INTRODUCTION

Many parameters affect the performance of electron-capture detection (ECD), *e.g.*, the pulse period, pulse duration, radioactive foil activity, purity of the carrier gas, detector temperature, concentration and electronic properties of the sample, recombination rate for the electrons and positive ions as well as for ions of both signs, contact potentials and carrier gas flow-rate. The last factor has usually been neglected in the theoretical models of ECD. The experimental data in the literature are frequently confusing and even contradictory.

In 1969, Devaux and Guiochon[1] published a paper on the variations of the ECD response with the carrier gas flow-rate. They used a parallel plate detector with a tritium source, operating in a pulse mode. The carrier gas was a mixture of 95% argon and 5% methane. The carrier gas flow-rate was varied over the range of 10–400 ml/min. Short pulses of 1-μs duration, 50-V amplitude and a fixed pulse period of 70 μs were used. They observed that the background current, I_b, and the electron concentration in the detector increased with the flow-rate, u, tending to saturation for u values exceeding 250 ml/min.

They attributed the latter to the decrease in rate of recombination of thermal

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electrons with positive ions, in accord with the earlier findings of Lovelock[2]. They also found that the ECD response was significantly affected by the carrier gas flow-rate. This relationship was very much dependent on the properties of the sample molecules. They observed that for bromocyclohexane a maximum occurred at a certain value of the flow-rate, whereas for chloroform the response decreased with increasing flow-rate. They concluded that the ECD response could be optimized by a careful optimization of the flow-rate through the detector.

In 1971, Lovelock *et al.*[3] showed that the proportion of the sample ionized decreased with increasing flow-rate, the slope of the relationship depending on the pulse period.

Somewhat confusing results were obtained by Van de Wiel and Tommassen[4] who observed no variation of the ECD standing current with the carrier gas flow-rate. They argued that the earlier results, *e.g.*, those of Devaux and Guiochon[1] or of Scolnick[5], were due to oxygen contamination of the carrier gas. Their detector was placed in an atmosphere of the pure carrier gas. They also proposed that Lovelock's earlier suggestion on the relationship between the rate of recombination of the electron and positive ion and the carrier gas flow-rate, quoted above, was incorrect.

Takeuchi[6], who studied the influence of the carrier gas flow-rate on the ECD response, observed that for short pulse periods no significant influence could be observed, but for pulse periods over 500 μs the standing current increased with increasing flow-rate. He suggested that this could be caused by column bleed. He also found that the electron-capture coefficient increased with increasing flow-rate, assuming its saturation value for $u > 100$ ml/min.

Lovelock and Watson[7], who introduced a simple numerical model of ECD, taking into account the carrier gas flow-rate and the electron-capture reaction with the contaminants present in the carrier gas, showed that the recombination rate could be determined by plotting the relationship between the pseudo-recombination-rate constant and the reciprocal flow-rate.

Connor[8] considered the expanded form of Lovelock's stirred-reactor model of ECD and solved the set of differential equations inherent in this model for a steady-state condition under some clearly defined conditions of ECD operation. He found that for a small sample the positive-ion concentration was not influenced by the presence of the sample at very short as well as very long pulse periods. He suggested that the ECD response at long pulse periods and for small samples was proportional to the reciprocal flow-rate. He[9] also pointed out that at short pulse periods the concentration of the positive ions was proportional to the reciprocal flow-rate.

EXPERIMENTAL

A GCHF 18.3 gas chromatograph (Willy Giede Betriebskontrollgeräte, G.D.R.) was used. A pin-cup electron-capture detector with a ^{63}Ni ionization source with an activity of 10 mCi was built in our laboratory. The detector volume was 1.6 ml. A 1/16-in. stainless-steel pin protruded up to half the height of the cell, and the ionization source formed the outer cylinder. The pulse-voltage generator was also built in our laboratory. It had the following parameters: pulse amplitude, 50 V; pulse period range, 10–50 000 μs; pulse duration range, 1–100 μs. The detector was maintained at 200°C. A stainless-steel 1.5 m × 4 mm silica gel column (100–200 mesh;

Koch-Light Labs., U.K.) operating at ambient temperature was used. The carrier gas was nitrogen, purified by passage through a two-stage filter, packed with activated charcoal and 5-Å molecular sieve. The carrier gas flow-rate through the column was held constant at 30 ml/min, and an additional variable flow of make-up gas was added to the carrier gas at the column outlet. The ECD current was measured by a RFT 6350 electrometer (VEB Statron Fürstenwalde, G.D.R.) and the chromatograms were plotted on a TZ-4100 recorder (Laboratorní Přístroje, Czechoslovakia). Sulphur hexafluoride was obtained from Merck-Schuchardt (F.R.G.) with a specified purity of 99.7%. Mixtures of it in nitrogen were prepared in 2-l stainless-steel bottles by the successive dilution method. On-column injections were made with the help of a six-port valve (Supelco, Switzerland). A *ca.* 0.1-ml sample was injected several times in order to minimize the standard deviation of the ECD response. A pulse duration of 5 μs was sufficient for collection of all the thermal electrons during the pulse. A small potential, E_{bias}, was used to compensate for the effects of the contact potentials[10].

RESULTS AND DISCUSSION

ECD model

The ECD model used here was a combination of the expanded form of Lovelock's stirred-reactor model and Wentworth's kinetic model[11], as proposed by Connor[8], except that the positive-ion diffusion, influenced by the positive-ion space charge was not taken into account. We adopted the notation given by Wentworth and Chen[11] for the concentration of the species present in the detector as well as for the rates of their interaction. The thermal electrons and the positive ions are produced in the ECD volume, V, due to the ionization of the carrier gas molecules by β-radiation at a rate denoted by k_pR_β. The concentrations of the electrons, positive ions, negative ions and sample molecules are denoted as $[e^-]$, $[\oplus]$, $[AB^-]$ and $[AB]$, respectively. The electrons and positive ions as well as the positive ions and the negative ions recombine at rates denoted by k'_D and k'_{N1}, respectively. The rate of the sample input is denoted by B. A non-dissociative type of the electron-capture reaction was assumed to proceed at a rate denoted by k_1. Finally, the total gas flow-rate through the detector was denoted as u. The differential equations describing the change in the concentrations of the species present in the detector are:

$$\frac{d[e^-]}{dt} = k_pR_\beta - k'_D[\oplus][e^-] - k_1[AB][e^-] - [e^-]\cdot\frac{u}{V} \tag{1}$$

$$\frac{d[\oplus]}{dt} = k_pR_\beta - k'_D[\oplus][e^-] - k'_{N1}[\oplus][AB^-] - [\oplus]\cdot\frac{u}{V} \tag{2}$$

$$\frac{d[AB^-]}{dt} = k_1[AB][e^-] - k'_{N1}[\oplus][AB^-] - [AB^-]\cdot\frac{u}{V} \tag{3}$$

$$\frac{d[AB]}{dt} = B - \left(k_1[e^-] + \frac{u}{V}\right)[AB] \tag{4}$$

Numerical analysis

The solutions of eqns. 1–4 were obtained in a way very similar to that given by Wentworth and Chen[11]. We also considered the positive-ion concentration as a variable, assuming that a small fraction, f, of the positive-ion concentration was removed upon completion of the integration over the time of the given pulse period. It was also assumed that all the thermal electrons present at this moment were collected. This mode of integration simulated the action of the pulse. The same mechanism was also assumed for the negative ions due to the fact that their mobility is similar to that of the positive ions, and hence they can be collected during the pulse. We also considered the sample concentration as a variable. The process of integration was repeated until a steady state in the concentration of all the species was achieved, assuming a 10^{-4} change in concentration as a steady-state criterion. The calculations were performed and the figures drawn with the aid of Cyber-70 using the CERN Program Library. The Merson[12] fourth-order integration method was used.

Results of the numerical integration

The following reaction rate constants were chosen in order to integrate eqns. 1–4: $k_p R_\beta = 1.96 \cdot 10^{-11}$ mol l^{-1} s^{-1}; $k'_D = 2 \cdot 10^{14}$ l mol^{-1} s^{-1}; $k_1 = 1.87 \cdot 10^{14}$ l mol^{-1} s^{-1}; $k'_{N1} = 1.6 \cdot 10^{15}$ l mol^{-1} s^{-1}.

The rate of production of thermal electrons, $k_p R_\beta$, was determined from the experimental data according to the procedure of Wentworth and Chen[11]. The value of the electron–positive ion recombination rate constant, k'_D, was evaluated, assuming that 50% of the nitrogen molecules dissociate to N^+. The values of the electron/N^+ and electron/N_2^+ recombination rate constants were taken from ref. 13. The value of the rate constant for the attachment of electrons to sample molecules, k_1, was taken from ref. 14, and the positive ion–negative ion recombination rate constant was taken from ref. 11. A value of f of 0.03 gave an appropriate k_D (pseudo-recombination rate constant) to simulate the standing current in an nitrogen carrier gas with a ^{63}Ni foil. Numerical solutions were carried out for three values of the sample concentrations, using pulse periods from 40 to 40 000 μs.

Fig. 1 shows the relationship between the concentration of the electrons, b, and the positive ions, $[\oplus_0]$, and the pulse period, t_p, at various values of the ventilation rate constant, u/V, under the no-sample condition. The volume of our detector was 1.6 ml. The carrier gas flow-rate was varied over the range from 30 to 240 ml/min. From the plots, b was almost unaffected by the carrier gas flow-rate, u, for t_p lower than *ca.* 2 ms, which is in accord with Takeuchi's results[6]. However, the maximum concentration of the thermal electrons increased by 50% with increasing u/V. This in turn confirmed the experimental results of Devaux and Guiochon[1]. The concentration of the positive ions, $[\oplus_0]$, was even more affected by u/V than the electron concentration. The effect becomes significant for pulse periods higher than 2.5 ms. A maximum in the relationship between the positive-ion concentration and pulse period near t_p = 10 ms was observed, where the positive ions were lost more efficiently by ventilation than by the electron–positive ion recombination. As u/V increases, this effect becomes more evident, leading to a decrease in the positive-ion concentration and hence to an increase in the electron concentration. The result is that, contrary to the statements of Van de Wiel and Tommassen[4], even in the pure carrier gas there is a notable effect of the carrier gas flow-rate on the detector characteristics.

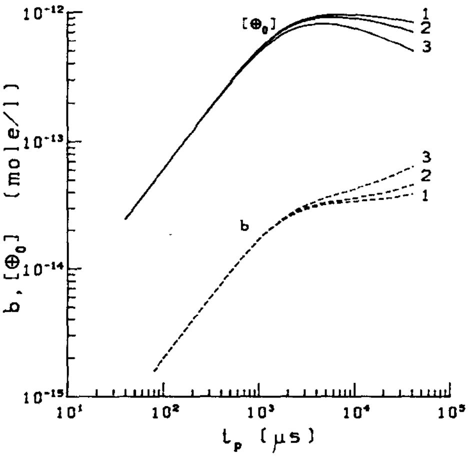


Fig. 1. The electron, b (dashed lines), and positive-ion concentration, $[\oplus_0]$ (solid lines), *versus* the pulse period, t_p, for different values of the ventilation rate constant, u/V (s^{-1}): 1, 0.37; 2, 0.86; 3, 2.56.

Eqns. 1–4 were integrated, assuming three different sample (SF_6) input rates and the same range of variability of the carrier gas flow-rate and the pulse period as in the no-sample case. The calculations were performed assuming an additional flow of make-up gas. The carrier gas flow-rate was fixed at 30 ml/min, giving a ventilation rate constant of $u/V = 0.367$ s^{-1}. Any change in the total gas flow-rate involved a corresponding change in the sample input rate. Introducing a dilution ratio, η

$$\eta = \frac{0.367}{u/V} \tag{5}$$

where u/V is the ventilation rate constant, a knowledge of the dilution ratio allows determination of the actual sample input rate, B, as in eqn. 6

$$B = B_0\eta \tag{6}$$

where B_0 is the sample input rate in the case of no make-up gas. The results are presented in Figs. 2–5. Fig. 2 shows the relationship between the concentration of the species present in an electron-capture detector and the pulse period, assuming that the rate of the sample input is $1.5 \cdot 10^{-12}$ mol l^{-1} s^{-1}, and the ventilation rate is 0.367. Such plots are influenced by the choice of the sample input rate as well as the ventilation rate, but all possess the characteristic features depicted in Fig. 2. The concentration of the electrons, $[e^-]$, tends to its saturation value for pulse periods exceeding 5000 μs, and this is in agreement with earlier findings of Connor[8]. The concentration of the positive ions is about one order of magnitude greater than that of the electrons, approaching a saturation value for $t_p > 2000$ μs with the plot parallel to the electron concentration plot. The plot of the relationship between the concentration of the negative ions, $[AB^-]$, and the pulse period, t_p, also assumes a maximum value at pulse periods of 500 μs, approaching a steady-state value for longer t_p. The concentration of the sample molecules, [AB], decreases with increasing pulse period

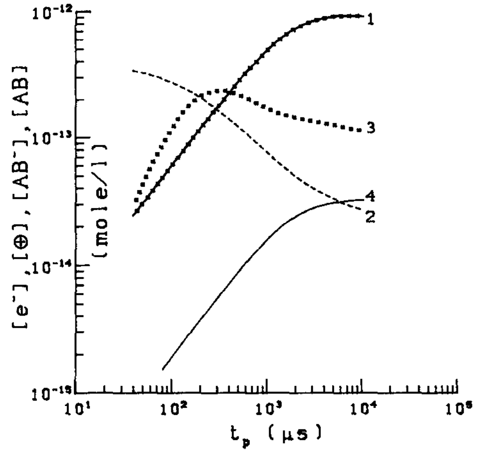


Fig. 2. Concentration of the electrons, $[e^-]$ (4), positive ions, $[\oplus]$ (1), negative ions, $10^2 \cdot [AB^-]$ (3) and sample molecules, $10 \cdot [AB]$ (2), *versus* the pulse period, t_p.

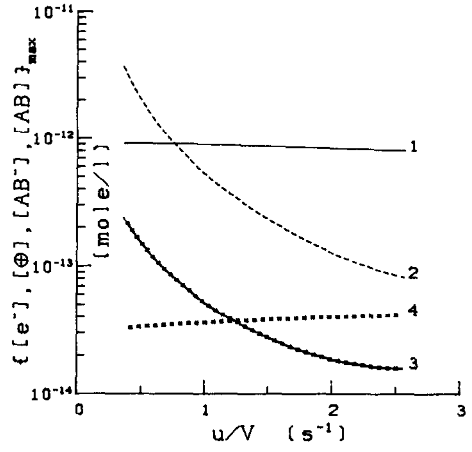


Fig. 3. Effect of the ventilation rate, u/V, on the maximum concentrations of the species present in the detector. Curves as in Fig. 2.

in the manner depicted in Fig. 2. Fig. 3 shows the relationships between the concentrations of the different species present in an electron-capture detector and the ventilation rate, u/V, for the same sample input rate as for the plots shown in Fig. 2.

The ventilation rate affects all the plots in a different manner. The concentration of electrons increases by 30% over the range of variation of the ventilation rate. The concentrations of the other species decrease with increasing ventilation rate. The concentration of positive ions is only slightly affected by the ventilation rate, as was also shown by Connor[9], whereas the concentrations of negative ions and of sample molecules decrease several times over the range of variation of the ventilation rate. The plots shown in Fig. 3 are typical for all three sample input rates which were assumed in the computations.

Fig. 4 shows the effect of the ventilation rate on the relationship between the ECD response and the pulse period. The sample input rate was the same as for the plots shown in Fig. 2. As we showed earlier[14], the ECD response assumes a maximum at a certain value of the pulse period, t_p. The numerical integrations of eqns. 1–4 confirmed this conclusion and showed that the ventilation rate seriously affects the detector response.

Fig. 5 presents the results of computations expressed in terms of the detector response *versus* the ventilation rate, for three sample input rates. It seemed reasonable to expect the ratio of the responses corresponding to the lowest and to the highest ventilation rate constants to equal the dilution ratio. To our surprise, the former was twice as large as the latter.

Fig. 6 shows the relationship between the electron concentration and the pulse period for high-purity and technical-grade nitrogen at three values of the carrier gas flow-rate. For high-purity nitrogen, the plots are identical to the theoretical ones, depicted in Fig. 1, whereas for technical-grade nitrogen they are not. For the latter case, the maximum concentration of electrons decreases as the flow-rate increases.

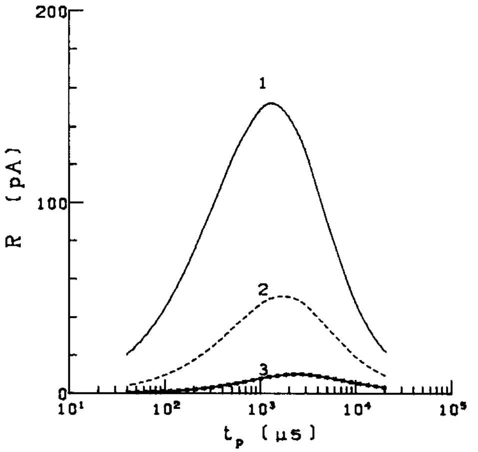
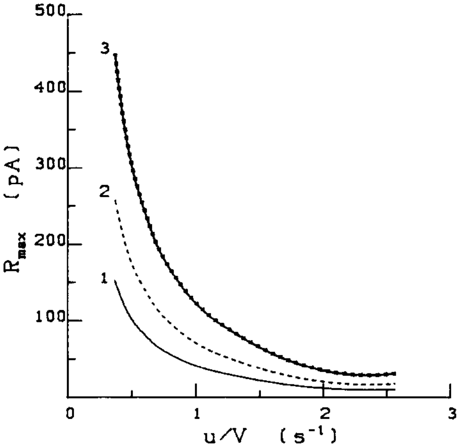


Fig. 4. Effect of the ventilation rate on the relationship between the detector response, R, and the pulse period, t_p. Ventilation rate, u/V, = 0.37 (1), 0.86 (2) or 2.56 s^{-1} (3).

This is certainly due to the electron-capture reaction with the contaminants in the carrier gas. Increasing the carrier gas flow-rate means in this case that more sample molecules are introduced into the detector per unit time and converted into negative ions, and hence the concentration of electrons decreases. This can be regarded as a primary source of certain inconsistencies between the data of other authors[1,2,4,5].

Fig. 7 shows the relationship between the pseudo-recombination rate constant and the inverse flow-rate for high-purity nitrogen. The plot is almost linear, and we are able to determine the recombination rate, $k'_D[\oplus](682\ s^{-1})$, as well as the rate of reactions with the contaminants, $k_{1x}c_x$ ($60\ s^{-1}$), which is in accord with the findings of



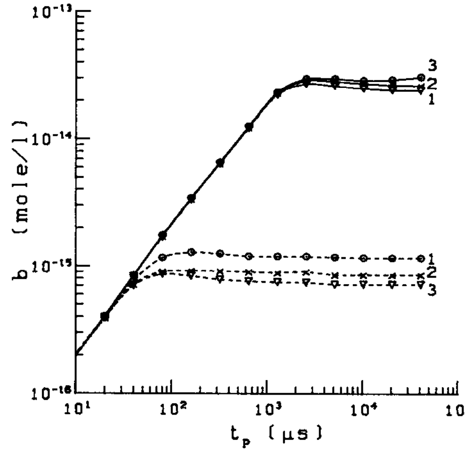
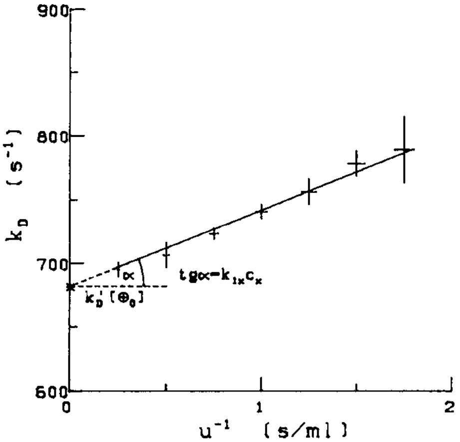


Fig. 5. Effect of the sample input rate, B, on the relationship between the detector response, R, and the ventilation rate, u/V. Sample input rate: $8.0 \cdot 10^{-13}$ (1), $1.5 \cdot 10^{-12}$ (2) or $2.6 \cdot 10^{-12}$ mol l^{-1} s^{-1} (3).

Fig. 6. Concentration of the electrons, b, *versus* the pulse period, t_p, for different values of the ventilation rate, u/v, for high-purity nitrogen (solid lines) and for technical-grade nitrogen (dashed lines). Values of u/V as in Fig. 1.



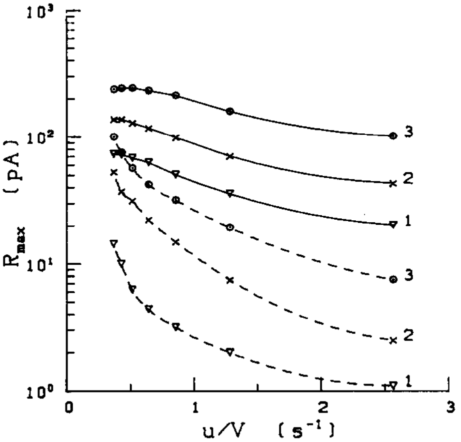


Fig. 7. Pseudo-recombination rate constant, k_D, *versus* the inverse of the carrier gas flow-rate, u^{-1}, for high-purity nitrogen. The error bars shown are equal to two standard deviations (2σ).

Fig. 8. Detector response, R, *versus* the ventilation-rate, u/V, for three different input rates of SF_6, for high-purity nitrogen (solid lines) and technical-grade nitrogen (dashed lines). Input rates (mol l^{-1} s^{-1}); 1, $8.0 \cdot 10^{-13}$; 2, $1.5 \cdot 10^{-12}$; 3, $2.6 \cdot 10^{-12}$.

Lovelock and Watson[7]. The dependence of the pseudo-recombination rate constant with flow-rate is linear, unless the rate of reaction with the contaminants exceeds the recombination rate. We failed in an attempt to construct a similar plot for technical-grade nitrogen. In this case, the pseudo-recombination rate constant was of the order of 20 000 s^{-1}, *i.e.*, almost 30 times greater than for high-purity nitrogen. Perhaps the ratio between the rate of reaction with the contaminants and the rate of recombination can serve as a criterion of purity of a carrier gas. When any ECD model is used for analyzing the experimental data, this ratio should not exceed 0.2.

Fig. 8 shows the relationship of the detector response, R, and the ventilation-rate, u/V, for three sample input rates. The pulse period was selected so as to give the maximum detector response to fulfil the criterion $k_D t_p = 1.79$ (see ref. 14). Fig. 8 shows two families of curves: one (continuous line) corresponds to high-purity nitrogen and the other (dashed line) to technical-grade nitrogen. Surprisingly, the response profiles depicted in this figure were in much better agreement with the theoretical findings for technical-grade than for high-purity nitrogen. It should be noted, however, that there also is a qualitative agreement between the expectations and experimental results for high-purity nitrogen. On the other hand, the discrepancy between the expected and the observed response ratios for the lowest and the highest ventilation rate constants indicates that either the ECD model or its assumptions are incorrect. From the literature and from our own experience, we can find many arguments against the first possibility. However, considering the second possibility, *i.e.*, the correctness of the ECD model assumptions, we can find rather good explanations for the observed discrepancy. We have not considered the positive-ion space charge in our calculations. It seems reasonable to expect that for technical-grade nitrogen a significant number of negative ions will be created, due to severe contamination of that gas with electrophilic molecules, leaving less electrons than in high-purity nitrogen, where they are able to react with the sample molecules. The influence of the positive-ion space charge is smaller in technical-grade than in high-purity nitrogen, as that space charge can be neutralized by a large number of negative ions. Hence, agreement with the theoretical calculations which did not take into account the positive-ion space charge is achieved for techical-grade nitrogen.

CONCLUSIONS

The carrier gas flow-rate has a significant effect on the electron concentration and the ECD response in the pulse mode. This effect becomes even more serious for carrier gases that contain measurable amounts of electron-capturing contaminants. The modified kinetic model of Wentworth proved useful in the qualitative interpretation of the experimental results for high-purity nitrogen. Much better agreement between theoretical calculations and the experimental data was obtained for technical-grade nitrogen, and this indicates that some of the assumptions in the ECD model considered were incorrect. It seems that the positive-ion space charge very strongly influences the ECD performance. The results obtained in this work also indicate that the carrier gas flow-rate should be minimized in order to achieve the best ECD performance, no matter how pure is the carrier gas. This also implies that special care is called for in the preparation of the column, which should allow the best resolution of the compounds under study at minimum carrier gas flow-rate.

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