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Note

Effect of dopants on the linearity of a d.c. electron-capture detector*

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The use of dopants for electron-capture detectors (ECDs) is certainly not new. The classical example is undoubtedly the addition of methane to the carrier gas argon to slow down epithermal electrons (for a review of classical ECD theory, see ref. 1).

Dopants are introduced for other purposes as well, and sometimes they are introduced unwittingly. An example of the first case would be the addition of small amounts of hydrogen to the carrier gas for keeping the ECD in a clean state[2]; an example of the second case, the presence of column bleed or carrier gas impurities.

Such circumstantial dopants may have beneficial or detrimental effects. Sometimes they have both. For instance, bleed from the column's liquid phase generally decreases sensitivity, but may alleviate deviations sometimes found in the calibration curves of strongly electron-capturing analytes passing at low concentrations through a constant-current pulsed ECD. The presence of oxygen in the carrier gas, as Van de Wiel and Tommassen have pointed out long ago[3], is generally a detriment to sensitive EC detection; however, with certain, mainly mono- or dichloro derivatives of small aliphatics, the presence of oxygen can lead to large increases in sensitivity. These effects have been studied recently with great success by Miller and Grimsrud (ref. 4 and references cited therein). Indications are that the area of "reactive" dopants is presently under increased scrutiny[5].

Another area, at least formally different from the one above, is the addition of various alkanes to the carrier or the purge gas. Clearly the classical use of methane is the antecedent here. Ševčik[6] employed a nitrogen–*n*-pentane mixture as the purge gas and attributed its better performance, compared to argon–methane, to the higher ionization cross section of pentane, faster thermalization of electrons, and the absence of high-energy excited atomic states.

Our group had been interested in the past in such dopants for another reason: the possible changes in the nature or the amount of electron-capturing products formed subsequent to the initial electron attachment to the analyte[7]. The present study, however, came about by a different route. We had been troubled, as no doubt have been other analysts, by the problem of measuring small peaks eluting on the solvent tail. We reasoned that it should be possible to reduce the size of the solvent peak by using the same solvent as a dopant for the carrier gas stream.

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*Material taken from Ph.D. thesis work of K. W. M. Siu.

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Although this approach did not succeed in practice, some incidentals of this investigation are interesting enough to be reported here.

EXPERIMENTAL

Experiments were carried out on a Tracor ^{63}Ni ECD and the column used was a 1 m × 2 mm I.D. borosilicate tube packed with 3% OV-101 on Carbowax 20M–modified Chromosorb W[8]. A Keithley 240A high voltage supply polarized the ECD.

"High-purity" grade nitrogen was used as the carrier gas after further purification by passing through cartridges containing charcoal, silica gel and molecular sieve (Chemical Research Services, Addison, Ill., U.S.A.) and a heated oxygen scavenger cartridge (Supelco, Bellefonte, Pa., U.S.A.). The flow-rates of the carrier gas passing through the column and the purge gas were kept at 30 and 70 ml/min, respectively, throughout the experiments. In the doped modes, the main carrier, and sometimes the purge as well, was made to flow over a pool of the particular dopant (at room temperature) before entering the gas chromatographic system. Typical ECD analytes such as aldrin and lindane were used as test compounds.

RESULTS AND DISCUSSION

Three dopants (*n*-pentane, isooctane and benzene) were studied and all gave similar but rather unexpected results. For constant-voltage, d.c. operation of a regular (meaning: a somewhat "dirty") ECD, the doped mode shows the following differences from the non-doped mode: (1) An increase of the standing current; (2) a decrease of absolute analyte response; (3) a roughly corresponding decrease of the noise level; and (4) an increase of the linear range by about one decade for all electron-capturing analytes investigated. Fig. 1 demonstrates the last effect by a typical linearity plot of aldrin with ± 10% deviation indicated by the dashed horizontal lines.

The picture changes, however, when the detector is carefully cleaned and operated under high-purity conditions. The resulting linearity plots are shown in Fig. 2. There is a shift in the position, but not in the expanse of the linear range.

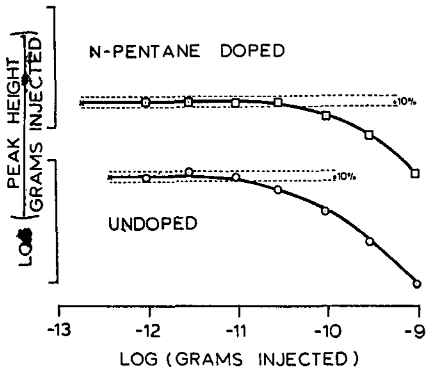

Fig. 1. Linearity plots of aldrin in a regular ECD.

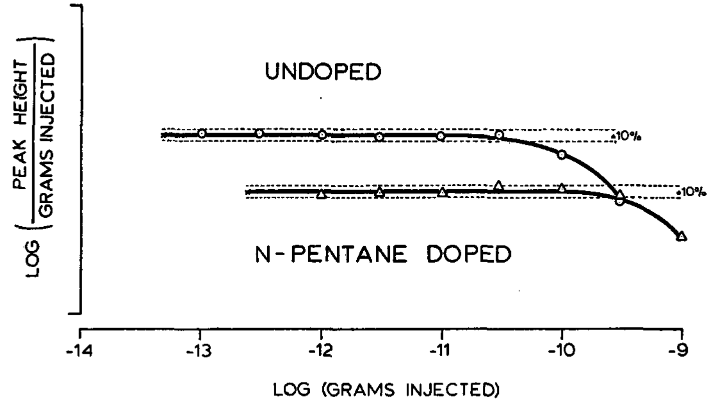

Fig. 2. Linearity plots of aldrin in the same ECD after careful cleaning.

What has been said above all applies to the common, constant-voltage operational mode of a d.c. ECD. Now, we have very recently described[9] constant-current operation of a d.c. ECD and shown that it, too, can result in an increase in linear range. Somewhat surprisingly, however, when constant-current operation is used in conjunction with a dopant, the latter provides no further beneficial effects. In that mode, neither the response nor the linearity of the ECD is changed to any significant extent.

It is not clear at this moment why doping improves ECD performance under "dirty" conditions, but does not bring any significant improvement when the ECD is very clean or when it is operated in constant-current mode. A few speculations, however, may be in order.

Aside from the increase in initial ionization, dopants could be expected to play a number of roles. They can serve as hydrogen donors for product radicals, can mediate energy transfer, and will influence the mobility of electrons and other charged species. In d.c. operation, the question whether the speed of electrons is a linear function of the field gradient and, if so, within what limits, could play an important role in considerations of linearity[9]. Dopants could be expected to change these limits. Thus they may influence the residence times, hence reaction rates, of charged species. (The fact that constant-current operation was not influenced in any significant fashion by the presence of dopants, may however indicate that a linear correlation does indeed exist between electron velocity and field gradient.)

Another item of speculation involves the positive ions; a species often conveniently forgotten in electron-capture theory. Plasma chromatography[10] and API–atmospheric pressure ionization–mass spectrometry[11] have given us valuable information on cations likely to be present in an ECD.

There are, in essence, four groups of species that need to be considered. In a scrupulously clean ECD, in the absence of a peak, such species as N_4^+ may occur. In the presence of some contaminants like oxygen, water or ammonia, various hydrated species of the proton, the ammonium ion or the nitric oxide cation do appear. Additionally, and often unavoidably, there is column bleed. Most of these species would be expected to form positive ions. Finally, there is the analyte itself. Even though its major reaction is electron capture, many typical electron-capturing analytes give positive ions to some extent as well. Furthermore, the fragmentation products of the analyte (after electron attachment and/or neutralization) would be even more prone to accept positive charge.

Cations thus originating from the analyte itself must be highly concentration-dependent. Considering the rapidity of charge-exchange reactions, the composition of the positive ions in the ECD must change drastically when a peak comes through. On this occasion, one could imagine innumerable reaction sequences leading to a (continuously changing) minimum free energy state of the system.

Now, regardless of one's view of ECD mechanism, it is clear that neutralization of positive ions must occur in the gas phase to an appreciable extent during passage of a large peak. But the positive ions, as we have seen, then change in composition in response to the nature and the concentration of analyte passing through. Consequently, the neutralization rates must change with the amount of analyte injected and this could be expected to lead to non-linearity in the calibration curve.

To improve linearity in d.c. operation, one can therefore imagine two approaches. First, to eliminate column bleed or carrier gas contamination. Here one would be left with only the positive species of the carrier in the baseline state. And, within limits, cations from the analyte should increase in concentration as the amount injected is increased; so the linearity of the calibration curve ought not to be seriously impeded.

Second, to introduce a dopant that, by its sheer amount, would provide, directly or indirectly, the vast majority of cations in the system. If the nature of the cations remains the same during passage of a peak, the same neutralization reactions should occur throughout the event. Such may have been the case in this study.

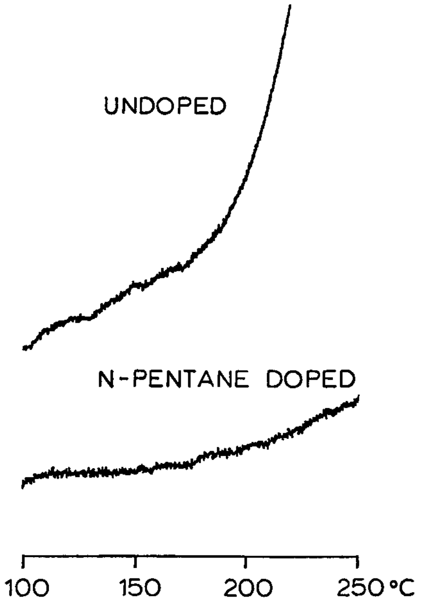

Fig. 3. Baseline stability during temperature programming. Column: 3% OV-101 on Carbowax 20M-modified Chromosorb W (45–60 mesh). Programming rate: 7.5°/min.

It is interesting to note that a dopant of this sort would be expected to counteract column bleed or, more precisely expressed, diminish its influence. The overwhelming presence of a dopant should thus alleviate the normally drastic effects of temperature programming on the baseline of a d.c. ECD.

While we do not consider this to be an overly important effect in practical terms, it is interesting that it does indeed occur, as shown in Fig. 3. Whether we are really observing an effect of the positive ion composition, however, is a question still open to discussion.

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