*Journal of Chromatography*, 90 (1974) 113–118
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CHROM. 7169

# CONTAMINATION PROBLEMS WITH $^{63}$Ni ELECTRON CAPTURE DETECTORS

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(Received September 6th, 1973)

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## SUMMARY

A study was performed on two $^{63}$Ni electron capture detectors operating in d.c. mode. Several parameters have been examined. It appeared that the temperature difference between the detector and the column is important. Scavenger gas temperature and detector isolation are not less important. Furthermore the detector polarization switch must always be off when no chromatogram is being run. These modifications help to keep the detector sensitivity much longer, with a consequent reduced number of washings.

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## INTRODUCTION

In gas chromatography, the electron capture detectors (ECDs) using tritium foil, commonly used in the analyses of organochlorine residues, are of the greatest sensitivity. However, they must be used at relatively low temperature which causes serious problems of contamination. Different ways of overcoming these problems, as already mentioned[1], have been used: (1) The pulse mode; (2) the use of $^{63}$Ni as a radioactive source allowing use of higher temperature, and electron capture detection using a rare gas discharge to produce electrons.

The first method has its limitations, since it needs argon and methane, both relatively expensive gases. Moreover, these gases cannot be used when an ECD is coupled in series with a flame ionization or a flame photometric detector.

The use of $^{63}$Ni, although allowing much higher temperatures, is also faced with some problems. In view of the low activity of $^{63}$Ni, it has been necessary to substitute the plane-parallel geometry of Lovelock and Lipsky[2] for the cylindric configuration of the argon detector. This increases the area of the radioactive cell and consequently makes the detector as sensitive or even more sensitive than the tritium detector (Fig. 1). To decrease further the degree of contamination of this $^{63}$Ni detector, we have tried a few modifications that we wish to report here.

## MATERIALS AND APPARATUS

Our experiments were run on a Microtek 220 equipped with two $^{63}$Ni (10 mCi) ECDs in a d.c. mode. Three types of columns were used: (A) Dexsil 300-GC (15%) on Gas-Chrom Q (80–100 mesh); (B) SE-30 (4%) plus QF-1 (6%) on Chromosorb W

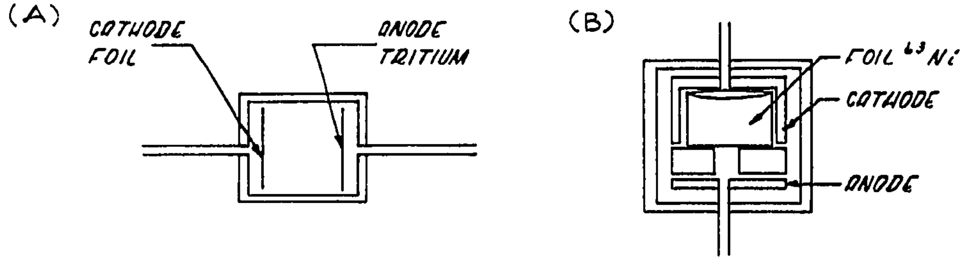

Fig. 1. Geometrical types of electron capture detectors. (A) Parallel-plane configuration; (B) cylindric configuration (*cf.* Microtek operation manual[3]).

(80–100 mesh); (C) diethylene glycol succinate (DEGS) (2%) plus phosphoric acid (0.5%) on Chromosorb W (80–100 mesh). This latter column has been recently proposed by Uyeta *et al.*[4]. The size of the columns was 6×0.25 in. I.D.. The oven temperature was set at 265° for column A and 185° for columns B and C, while the detector was kept at 295° for column A and at 285° for columns B and C. An attenuation of $16 \cdot 10^2$ was used throughout. Solutions of organochlorine standards were chromatographed as well as water and food extracts.

## METHODS

### *Problems of operation*

The two ECDs operating in d.c. mode were used to analyse pesticides in several food products. Under the conditions prevailing before the below-mentioned modifications, it was necessary to run frequent clean-ups, *i.e.* once every two, three or four weeks.

The need for a clean-up was indicated by the following symptoms: (a) after the detector has been switched on at the beginning of the day, a baseline is obtained which first shows a rapid decrease of sensitivity followed by a gradual return to a plateau (Fig. 2). That reduction of sensitivity was directly related to the degree of contamination; (b) when injecting a sample or a standard, the chromatogram illustrated in Fig. 3 was obtained. The sensitivity showed an immediate increase but decreased in the same way as in the case of symptom a.

Moreover, in order to maintain good sensitivity with increasing number of analyses, we had to adjust the polarizing voltage up to a maximum level, after which the sensitivity decreases, indicating the necessity for a clean-up.

Using a Dexsil column, stable up to 450–500°, at a low bleeding temperature (265°) has not reduced the necessity of frequent clean-ups. In the meantime, we have noted that one detector, even if heavily contaminated, could clean itself when kept at its operating temperature for three months without polarization, purge or carrier gas.

### *Modifications made to the instrument*

As a first corrective measure, we have replaced the Dexsil 300-GC by an already known column, 4% SE-30–6% QF-1, and used a lower temperature: 185°.

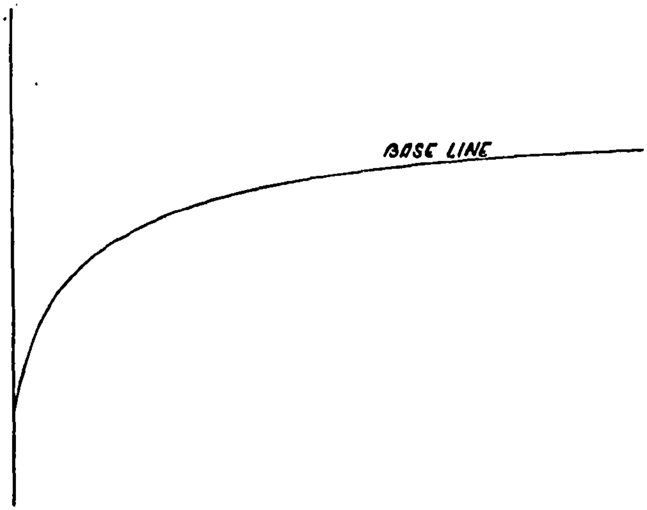

Fig. 2. Drifting of the baseline following polarization of a contaminated ECD.

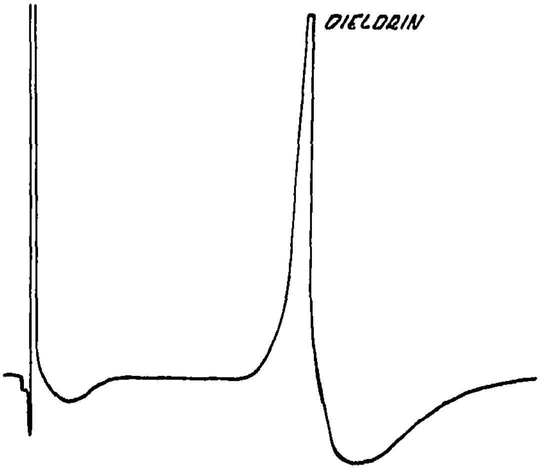

Fig. 3. Sample peak obtained by a contaminated ECD.

Even if the QF-1 phase has a non-negligible bleeding at that temperature compared to Dexsil, the frequency of decontamination was reduced by a factor of two or three.

The second detector was used with the column of 2% DEGS–0.5% phosphoric acid at 185°. Due to the considerable bleeding, the sensitivity of that detector was lowered somewhat, but there was no comtamination, even after several months of use. It then follows that the temperature difference between the column and the ECD must be larger than the one used with the flame ionization detector in order to avoid the problems of contamination.

As a second means of improving the instrument, we introduced some insulating material between the detector and the supporting plate which also serves as the heating unit of the inlets. This plate was normally at 50 or 60° below the temperature of the detector when used with the second and third columns. By the addition of the insulating material, the temperature of the detector was markedly increased.

As a further step we added two more spirals to the gas line around the ECD in order to increase the temperature of the scavenger gas.

As a last measure, we stopped the polarization of the ECD during the nights, week-ends and when possible between analyses.

## RESULTS

During a period of one year, we cleaned the ECD connected to the DEGS column only once, due to an accidental contamination. The second ECD was used for seven months with the afore-mentioned modifications. About 400 samples went through this detector during that time without major signs of contamination (Fig. 4).

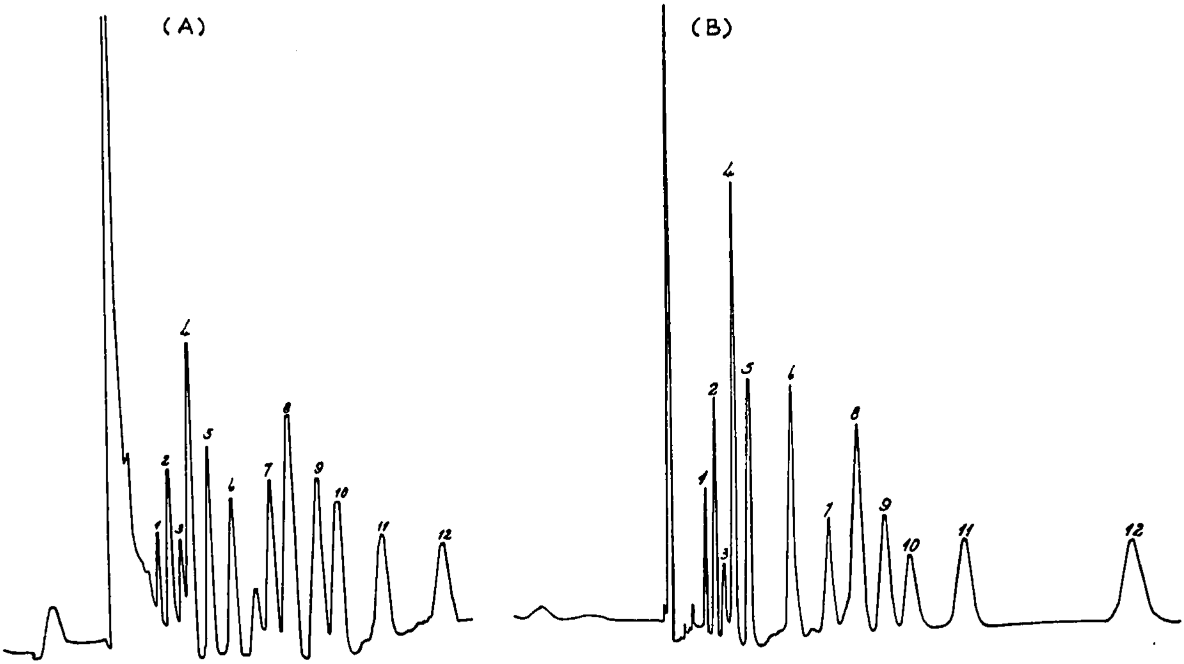

Fig. 4. Degree of contamination as obtained with unmodified (A; after 75 samples) and modified (B; after 400 samples) instrument. Pesticides were eluted in the order indicated. $1=\alpha$-BHC; $2=\gamma$-BHC; $3=\beta$-BHC; 4=Heptachlor; 5=Aldrin; 6=Heptachlor epoxide; 7=DDE; 8=Dieldrin; 9=*o,p*-DDT; 10=TDE; 11=*p,p*-DDT; 12=Methoxychlor.

## DISCUSSION

The contamination of an ECD first leads to an adsorption of materials on electrodes and to a contact potential set up on the cathode[1,5].

Beta particles, when striking the contaminated cathode, cause charges to be set up. These charges are not neutralized by low-energy electrons which flow towards the anode. Subsequently, these adsorbed positive charges, which are in contact with the negatively charged electrode, cause a fall in the polarizing potential as well as in the resulting current. A sample, negatively charged by the capture of electrons, or an electron coming from the ionization when polarization is off, can easily neutralize these adsorbed positive ions and leave the possibility for a normal electric field to develop. This would partly explain the increased sensitivity, soon after polarization has been switched on, and soon after electron absorbing materials have passed through the ECD (symptoms a and b). Thereafter ionization of adsorbed layers would gradually appear, setting up the contact potential.

However, the anode of our ECD does not build up a contact potential, due to an appropriate device. Indeed, a narrow window, about one centimeter long, prevents nearly all $\beta$-particles from reaching the anode and thus ionizing adsorbed materials. Moreover, electrons formed by ionization, being of too weak energy, cannot set up this contact potential on the contamination layers.

Furthermore, another phenomenon comes to strengthen the latter: that is the space charge effect. As suggested by the slow decontamination reported, it seems that there is, in the detector, a very slow and continuous evaporation of adsorbed materials as well as an ionization of these substances. Because these oily substances have poor electron affinity, they have little chance of capturing electrons and when ionized, they migrate slowly towards the cathode as a positively charged cloud. This phenomenon has been called space charge effect[5]. These space charge effects can even be enhanced by an uneven distribution of temperature within the detector. When an electron absorbing substance goes through the detector, there is formation of negative ions. These particles then neutralize positive ions and diminish the space charge effect of the cathode. Soon after the electron adsorbing substance has gone out, the space charge effect is diminished as well as the contact potential. The electric field and ionic current are increased, but they decrease rapidly due to the set up of the contact potential and of the space charge effect, both originating from the contaminating layers and vapors. Furthermore a scavenger gas, if kept at a too low temperature when reaching the ECD, will cause a condensation of contaminating vapors, bringing all sorts of troubles.

Finally, we must be conscious that even polarization enhances contamination. In fact, the cathode attracts clouds of positive ions and this suggests leaving the polarizing voltage off as often as possible between analyses. This will allow contaminating vapors to be evacuated by the gas flow. This corresponds to the non-polarization which improves the pulse mode operation.

Even if $^{63}$Ni ECD is less susceptible than $^{3}$H ECD to contamination, problems still remain when used on direct current, so that a few clean-ups have to be run every year, the frequency depending on the utilization of the instrument. If more clean-ups are necessary the following points have to be examined:

(1) The difference between column and detector temperature.

(2) The presence of a temperature gradient in the detector, due to a poor insulation.

(3) The temperature of the scavenger gas; if this is too low, it can be improved by increasing the number of spirals in the gas line on the detector wall.

(4) The feasibility of stopping the polarization during nights, week-ends and between analyses.

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