Nickel-63 Foil in a Standard Concentric Cell for Electron-Capture Detection

A. W. AHREN[1] AND W. F. PHILLIPS

Concentric design electron-capture detectors were converted, using ^{63}Ni, for operation at 300° C. in pesticide residue analyses, and the characteristics and reliability were evaluated. During 2 years of continuous operation with normal maintenance, there have been no indications of "dirty" detectors and no change in sensitivity.

The theory and modes of operation of electron-capture gas chromatography have been reported by Lovelock and Lipsky (1960), Lovelock (1961a, 1961b, 1963), Clark (1964), Dimick and Hartman (1964), Gaston (1964), and Peters and Schmit (1964). These references should be studied for an understanding of the electron-capture detection and the effect of various gas chromatographic parameters.

Many early users of electron-capture gas chromatography were unable to achieve high instrument performance. Residue analysts were plagued with instrument down time for a variety of reasons: "dirty" detectors, "noisy" detectors, and unstable response. For example, because of the temperature limitation of tritium foils (220° C. maximum), frequent cleaning and restandardization have been necessary.

The purpose of this work was to develop a system capable of long-term continuous operation with high reliability. Because the properties of ^{63}Ni appeared to offer desirable characteristics for electron-capture detection, early in 1965 the authors inquired of the U.S. Radium Corp. about the availability of this isotope for use in a high temperature cell. This article reports the operating characteristics of two concentric design detectors fitted with ^{63}Ni foils at different radioactive levels. Yauger, Addison, and Stevens (1965) reported the use of ^{63}Ni for electron-capture gas chromatography using a pin-cup concentric design (0.8 cc.) detector, operated at 300° C.

This work was conducted using a Barber-Colman Model 10 dual column gas chromatograph originally equipped with high temperature A4146 ^{226}Ra beta ionization detectors and 50-mv. recorders. After several years of operation at high temperature and low and high voltage, these detectors were reconditioned and converted to ^{63}Ni by the U.S. Radium Corp. The physical form of this isotope is pure ^{63}Ni electroplated to a stainless steel foil. This first detector was fitted with a foil containing 13.5 mc. of ^{63}Ni. Three months later a second detector was fitted with a 20-mc. ^{63}Ni foil. After more than 1 year of continuous operation at 300° C., there has been no significant change in standing current and no radioactive leakage detected.

Residue Laboratory, Campbell Soup Co., Camden, N.J.

[1] Present address, Campbell Institute for Food Research, Camden, N.J.

The major advantages of high temperature detector operation (400° C. maximum for ^{63}Ni) are that it reduces the possibility of contamination of the source from sample impurities and from "bleeding" of the liquid phases from columns. The detectors during this period had to be flushed once or twice with solvent and the temperature lowered semiannually to comply with AEC wipe-test requirements. Aside from that they have been in continuous operation.

Figure 1 is a diagram of the Barber-Colman A4146 detector. The volume of the detector chamber is approximately 4.8 cc. The detector when heated to 310° C. gave a standing current to 4.1×10^{-9} ampere with 13.5 mc. of ^{63}Ni and 7.6×10^{-9} ampere for 20 mc. of ^{63}Ni with purified nitrogen passing through the system and with no voltage applied. There are several carrier gases suitable for use in both modes; however, nitrogen was employed for the d.c. operation and a 5% methane in argon mixture for the pulsed mode.

Figure 2 shows the current-voltage curves for the two detectors. The curve labeled "detector 2" represents the detector with the lower activity level. The current reaches a maximum or saturation point at an applied

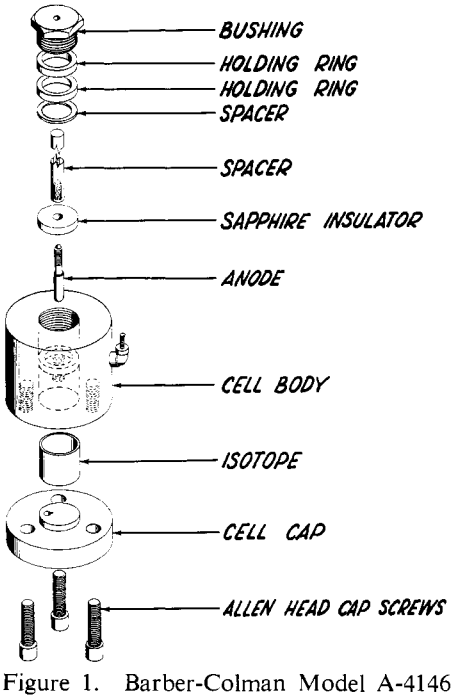

Figure 1. Barber-Colman Model A-4146 detector

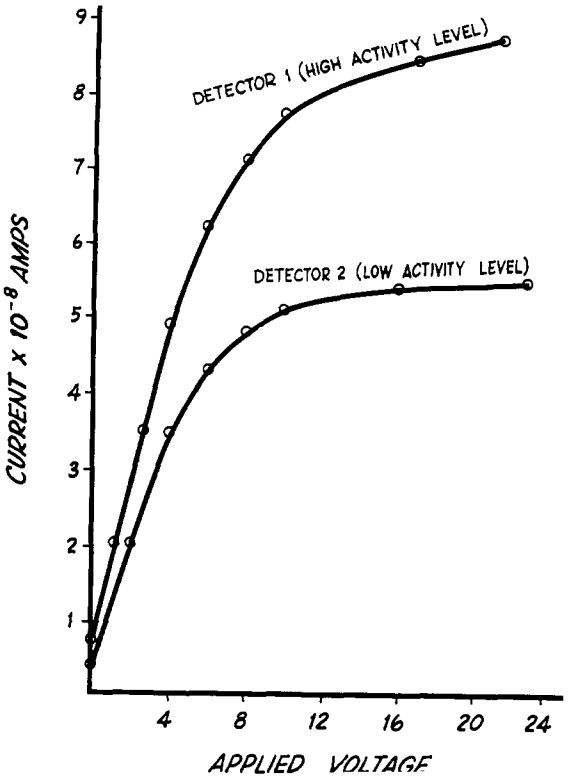

Figure 2. Current *vs.* applied voltage

voltage of 8 to 9 volts. The curve labeled "detector 1" represents the detector with the higher activity level and also appears to reach a saturation current at 8 to 9 volts, but the plateau is not as sharp.

Figure 3 shows the relationship between applied voltage and detector sensitivity for lindane and heptachlor in detector 2. Approximately the same applied potential (8 to 9 volts) required to attain saturation current also gave maximum detector response for the two compounds. In detector 1, however, maximum detector response shown in Figure 4 for lindane and heptachlor was at 4 volts, while the apparent saturation current occurred at an applied potential of 8 to 9 volts. Applied potentials of 4 volts in detector 1 and 8 volts in detector 2 were used for normal operation and gave good quantitative results.

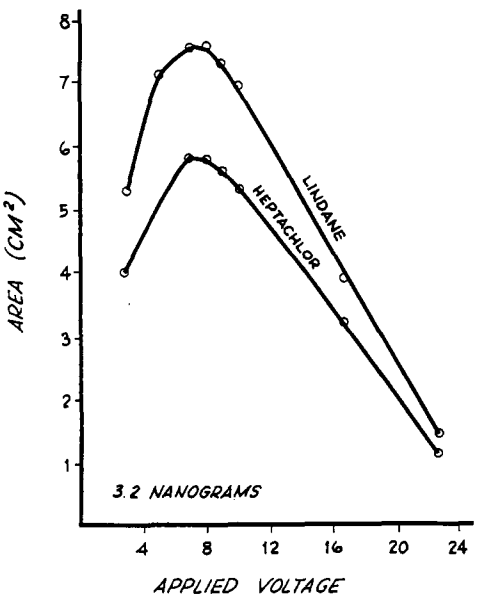

Figure 3. Applied voltage *vs.* detector sensitivity, detector 2

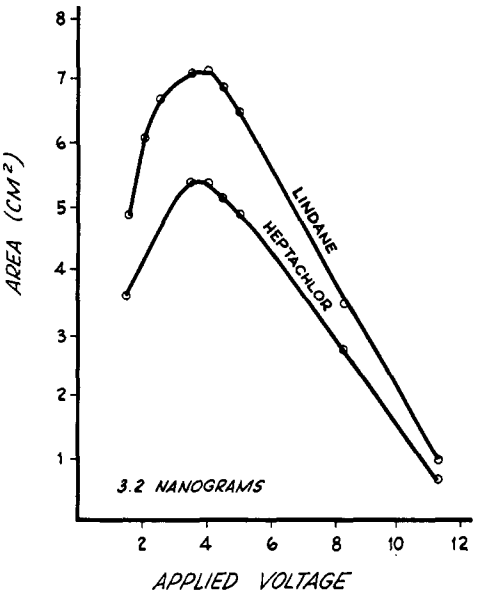

Figure 4. Applied voltage *vs.* detector sensitivity, detector 1

The linear range for the two detectors was investigated for chlorine-containing pesticides and is plotted on a log-log scale in Figure 5. Both detectors were stable and have good linearity over the range 1×10^{-10} to 1×10^{-8} gram. The absolute linear range for both detectors therefore is 1×10^{-2} gram and was the same in the pulsed mode.

Calibration curves are necessary over the linear range and unknowns must contain amounts within that range.

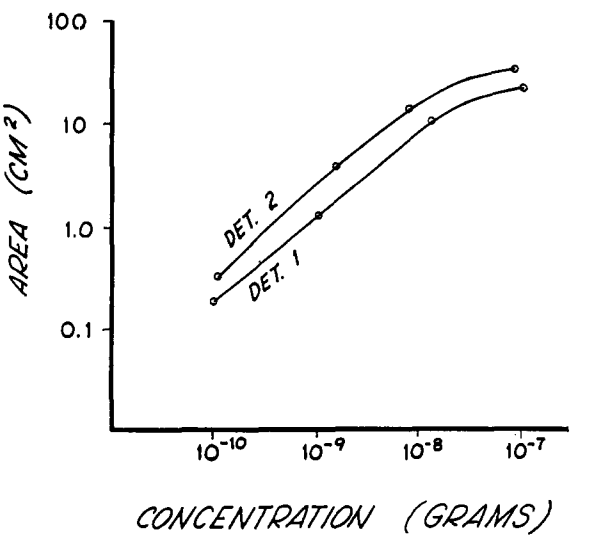

Figure 5. Linear ranges for both detectors

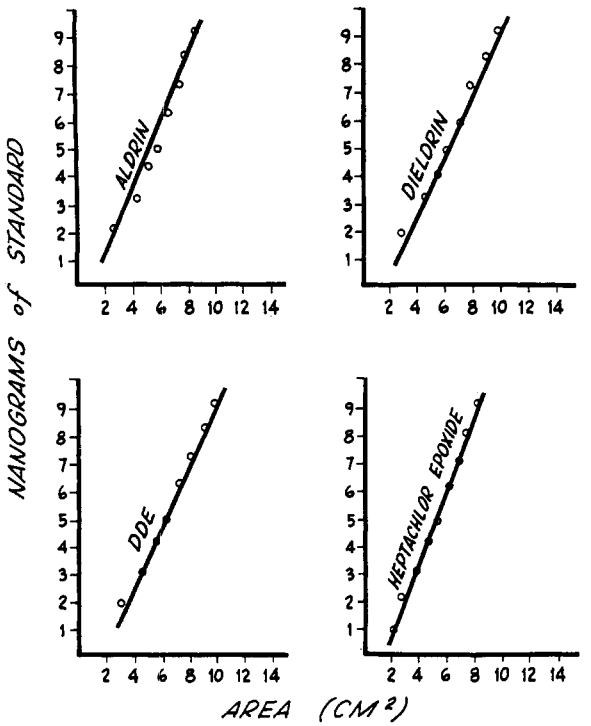

Figure 6. Calibration curves for detector 1

Figure 6 exemplifies calibration curves for four compounds in detector 1. Both detectors have given reliable and reproducible quantitative results when operated in the d.c. mode.

Both detectors give about 60% scale deflection for 100 picograms of lindane at maximum sensitivity. The signal to noise ratio for 100 picograms of lindane in detector 1 was 52 to 1 and 60 to 1 for 110 picograms of lindane in detector 2. Operation at maximum sensitivity is limited to small volume injections (1 to 2 μl.)

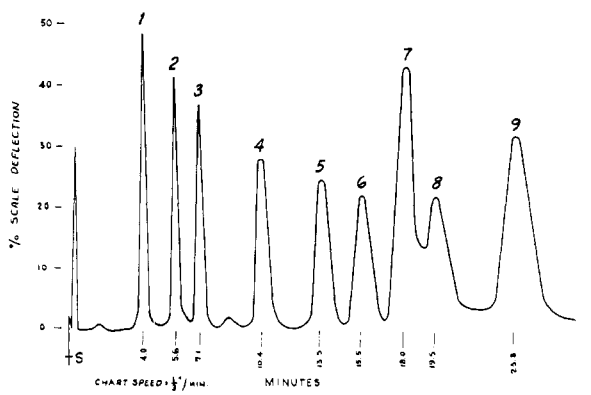

Figure 7. Standard solution of nine pesticides

1. Lindane (3.3 ng.)
2. Heptachlor (3.3 ng.)
3. Aldrin (3.3 ng.)
4. Heptachlor epoxide (3.3 ng.)
5. DDE (3.3 ng.)
6. Dieldrin (3.3 ng.)
7. Endrin (16.5 ng.)
8. TDE (3.3 ng.)
9. *p,p'*-DDT (16.5 ng.)

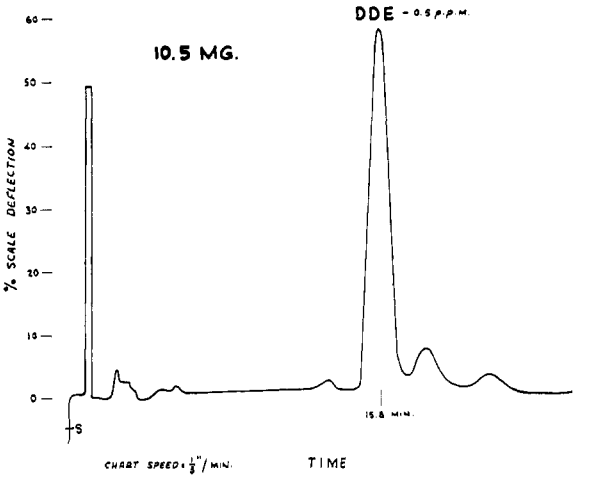

Figure 8. Chromatogram of "cleaned up" carrot sample

because of volume effect on response and relative error when injecting small quantities in a large volume.

Cleaned-up extracts of a wide variety of samples, such as fruits, vegetables, dairy products, poultry products, and soils, have been analyzed successfully utilizing this ^{63}Ni detection system. Figures 7 and 8 show a few typical chromatograms and give a good indication of the stability of the base line.

Chromatographic Conditions Employed for Operation (D.C. Mode)

Radioactive sources, U.S. Radium Foil Lab #204-1A coated with 13 to 20 mc. of ^{63}Ni.

Column temperature, 200° C.

Detector temperature, 310° C.

Injection temperature, 255° C.

Carrier gas, nitrogen.

Gas flow rate, 50 ml. per minute.

Voltage, 4 volts d.c. and 8 volts.

Gain, 100 (1×10^{-6} ampere full scale).

Attenuation, 16×.

Balance current, 60.

Column, 5 feet, 1/4-inch i.d. borosilicate glass.

Column packing, 10% QF—5% SE-30 on 80- to 100-mesh Gas Chrom Q.

Sensitivity, 78% scale deflection for 3 ng. of lindane.

Operation in the pulsed mode was somewhat restricted owing to the limitations of the equipment available. The Tektronix equipment used provided square pulses with a pulse interval range of 100 to 200 microseconds, amplitude of 0 to 50 volts, and a minimum pulse width of 10 microseconds. Changes in amplitude above 20 volts did not increase detector sensitivity. Figure 9 shows that both lindane and heptachlor in detector 2 gave maximum response at a pulse interval of 160 microseconds with a pulse width of 10 microseconds and an amplitude of 50 volts.

The log-log plot in Figure 10 shows the linear range in detector 2 to be 1×10^{-11} to 1×10^{-9} gram. The pulsed mode has the same absolute linear range as the

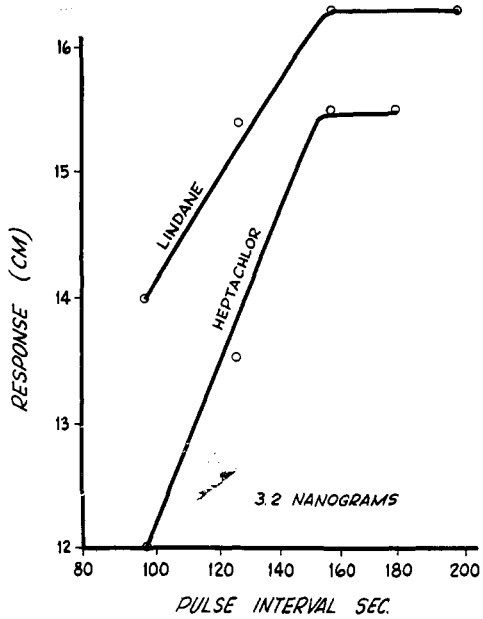

Figure 9. Pulse interval *vs.* detector sensitivity

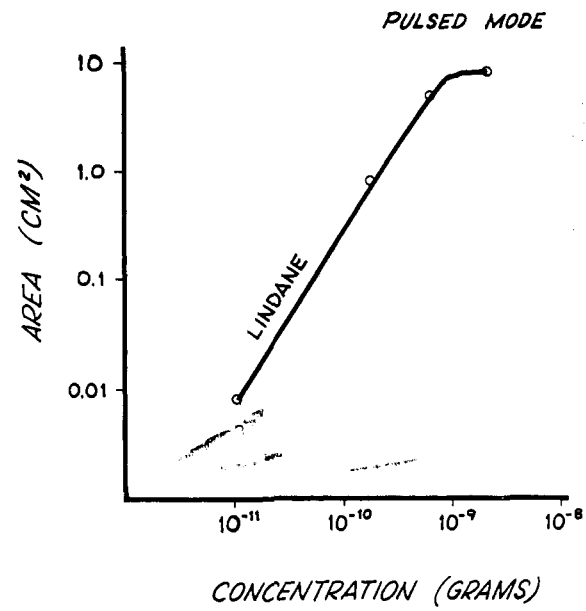

Figure 10. Linear range, detector 2

d.c. mode, but the sensitivity is about 10 times greater. This difference in sensitivity may be attributed in part to the higher electron mobility in the argon–methane carrier gas as compared with nitrogen. Detector 2 when operated in the pulsed mode gave a 40% scale deflection for 13 picograms of lindane at maximum sensitivity.

Theoretically, the pulsed system offers the best electron-capture environment; however, the d.c. mode is preferred because of its simplicity and stability. Although pulsed operation offers higher sensitivity than the d.c. mode, the absolute linear range in both modes is the same and reliable quantitative results can be realized by either mode.

Conclusion

The long-term operating electron-capture characteristics of a standard concentric design ^{63}Ni detector have been presented. This high temperature ^{63}Ni detector provides a continuously operable analytical system of high reliability which requires a minimum of maintenance. The detectors described have been in constant use for more than two years with no difficulty.

Instrument down time has been eliminated since their installation. The only time the detectors were not in operation was because of normal maintenance, such as wipe tests or replacing septums, column packing, and tubes.

Acknowledgment

The authors express appreciation to B. DeRoy, electrical engineer, Campbell Soup Co., for his assistance.

Literature Cited

Clark, S. J., *Residue Rev.* **5,** 32 (1964).
Dimick, K. P., Hartman, H., *Residue Rev.* **4,** 150 (1963).
Gaston, L. K., *Residue Rev.* **5,** 21 (1964).
Lovelock, J. E., *Anal. Chem.* **33,** 162 (1961a).
Lovelock, J. E., *Anal. Chem.* **35,** 474 (1963).
Lovelock, J. E., *Nature* **189,** 729 (1961b).
Lovelock, J. E., Lipsky, S. R., *J. Am. Chem. Soc.* **82,** 431 (1960).
Peters, U. J., Schmit, J. A., *F & M Res. Bull.* **5,** No. 2, 1–9 (August 1964).
Yauger, W. L., Jr., L. M., Stevens, R. K., *J. Assoc. Offic. Agr. Chemists* **49,** 1053 (1966).

Received for review September 26, 1966. Accepted April 3, 1967. Division of Agricultural and Food Chemistry, Pesticide Subdivision, 152nd Meeting, ACS, New York, N.Y., September 1966.