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## A COMPARATIVE STUDY OF THE $^{147}\text{Pm}$ AND $^{63}\text{Ni}$ ELECTRON CAPTURE DETECTORS UNDER IDENTICAL GEOMETRICAL CONDITIONS

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### SUMMARY

A detector that is capable of housing either an 8 mCi  $^{147}\text{Pm}$  or a 15 mCi  $^{63}\text{Ni}$  ionization source was used to compare the electron capture properties of these ionization sources under identical detector geometry. The background current due to the  $^{63}\text{Ni}$  source was 2.4 times greater than that obtained for the  $^{147}\text{Pm}$  source. Both detectors showed similar linear ranges and electronic absorption coefficients. The  $^{63}\text{Ni}$  detector was 1.2-1.9 times more sensitive than the  $^{147}\text{Pm}$  detector. This difference is small and is due only to the difference in background current. The  $^{147}\text{Pm}$  detector showed smaller losses in background current than the  $^{63}\text{Ni}$  detector when chromatographing samples that easily contaminate the foils.

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### INTRODUCTION

Recently, LUBKOWITZ AND PARKER<sup>1</sup> have reported the design and construction of an electron capture detector that utilizes  $^{147}\text{Pm}$  as the ionization source. It was shown that  $^{147}\text{Pm}$  is an adequate alternative to  $^{63}\text{Ni}$  as an ionization source. Although the work showed that the detector can be used routinely in pesticide residue analyses, no comparisons were made of the performance of the  $^{147}\text{Pm}$  detector with that of the  $^{63}\text{Ni}$  detector. The purpose of the present work is to compare the  $^{63}\text{Ni}$  and  $^{147}\text{Pm}$  detectors under identical geometrical conditions, *i.e.*, using detectors that are capable of housing a  $^{147}\text{Pm}$  as well as a  $^{63}\text{Ni}$  ionization source. Differences due to detector geometry are thus obviated. The comparisons are made in terms of the magnitude of the background current, linearity, electron absorption coefficients, minimum detectable concentrations and loss of background current with use.

### EXPERIMENTAL

The chromatograph used was a Pye Unicam 104, originally equipped with an alkali flame ionization detector and a  $^{63}\text{Ni}$  electron capture detector. The instrument was modified so that the column outlet entered directly into the designed detector. The detector was placed adjacent to the lateral wall of the column oven.

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The detectors designed have a cylindrical geometry<sup>1</sup>. The <sup>147</sup>Pm ionization source contained 8 mCi and was prepared by using an electrolytic cell that has been previously described<sup>1</sup>. The <sup>63</sup>Ni source contained about 15 mCi and was obtained from the New England Nuclear Corporation.

For all studies, a glass column, 3 ft. long, 6 mm O.D. and 4 mm I.D., was used. The column was packed with 3% OV-1 on Chromosorb W, AW-HMDCS, having a mesh size of 80-100. A 9:1 mixture of argon and methane was used as the carrier gas and the detector was operated only with pulsed voltage. The carrier gas was purified by passage through molecular sieve 5A, which was regenerated weekly.

The pulse generator used was a Model EH 132A and the pulses were measured with a 180A Hewlett-Packard 50 MHz oscilloscope. The current was measured with a Keithley 417K electrometer provided with a stable current-suppression generator. The decreases in background current were recorded with a Hewlett-Packard Model 7100 B strip-chart recorder capable of recording the changes in base current directly in amperes since the electrometer is directly calibrated in amperes.

Standard solutions were prepared from pesticides obtained from the Poly-science Corporation (nanograde standards) and from the U.S. Federal Drug Administration.

## RESULTS AND DISCUSSION

### *Effect of detector geometry*

Two detectors with different volumes were constructed so as to obtain reasonable values of the background current for both the <sup>63</sup>Ni and <sup>147</sup>Pm ionization sources. The detectors had volumes of 6.12 and 2.47 cm<sup>3</sup>. It must be considered that the distances travelled by the majority of the  $\beta$ -particles, in a 9:1 gaseous mixture of argon-methane, are 19.7 and 5.41 cm for the  $\beta$ -particles of <sup>147</sup>Pm and <sup>63</sup>Ni, which have average energies of 0.062 and 0.017 MeV, respectively<sup>2</sup>. However, the detectors cannot be constructed with dimensions such that the energy of the  $\beta$ -particle is completely expended in the detector volume, because this would result in a detector with large dead-volumes, so that the separation achieved in the column would be lost in the detector. Furthermore, it is possible that the detector may not function as an electron capture detector but as an ionization cross-section detector or a combination of both<sup>3</sup>. The currents were measured at the saturation region, where the current is independent of voltage, at a pulse interval of 100  $\mu$ sec. The detector temperature was kept constant throughout at 250°, since this temperature was considered to be satisfactory for numerous sample analyses and the <sup>63</sup>Ni foil was not drastically affected by residual sample and column contamination. The results obtained are shown in Table I. As expected, the current is always higher, regardless of source, in the detector with the larger volume. This is to be expected because a larger ionization volume is present. Also, the <sup>63</sup>Ni source yields a background current which is 2.4 times greater than that obtained with <sup>147</sup>Pm source. The activity deposited on the <sup>63</sup>Ni foil is about twice that of the <sup>147</sup>Pm ionization source. No measurable difference in peak widths could be observed between chromatograms obtained with the two detectors. The larger detector was therefore used for the comparison of the two ionization sources. It is important

TABLE I

EFFECT OF THE DETECTOR VOLUME ON THE CURRENT-VOLTAGE CURVES

Detector volume (cm <sup>3</sup> )	Ionization source	Saturation <sup>a</sup> current (A)
6.12	<sup>63</sup> Ni	8.8 × 10 <sup>-9</sup>
6.12	<sup>147</sup> Pm	3.7 × 10 <sup>-9</sup>
2.47	<sup>63</sup> Ni	5.6 × 10 <sup>-9</sup>
2.47	<sup>147</sup> Pm	2.1 × 10 <sup>-9</sup>

<sup>a</sup> Obtained at a pulse amplitude of 20 V and a pulse period of 100 μsec. Detector temperature 250°.

to choose that detector geometry which yields a higher ionization current with both sources, as the minimum detectable concentration is inversely proportional to the magnitude of the background current.

*Linearity studies*

The electron capture detectors are notorious for their limited linear range. Attempts are therefore presently being made to electronically linearize the response of the electron capture detector<sup>4,5</sup>. From the practical aspect of routine pesticide residue analyses, it is important to know the linear range of the detector for a particular component being analyzed. Furthermore, it is also important to know the detector response for samples that contain the minimum detectable concentration. Although in this region the response function may be linear, it frequently occurs that the response function does not pass through the origin, probably owing to sample-column interactions. A knowledge of the linear range will permit the selection of an appropriate method of quantitation of the detector response. The linear range was measured for both ionization sources by injecting solutions containing increasing concentrations of lindane, heptachlor, aldrin, dieldrin and *p,p'*-DDT. The concentration of the solutions injected was varied from that required to obtain peak heights equal to 1.0 cm (signal-to-noise ratio of 3) up to that concentration at which the detector no longer responds linearly. The ratio of the amounts in nanograms required to produce these two conditions is the linear range. The results are shown in Table II. The linear range is slightly higher for the <sup>63</sup>Ni source,

TABLE II

LINEAR RANGE OBTAINED WITH <sup>63</sup>Ni AND <sup>147</sup>Pm IONIZATION SOURCES

Compound	Linear range	
	<sup>63</sup> Ni	<sup>147</sup> Pm
Lindane	100	83
Heptachlor	134	121
Aldrin	150	130
Dieldrin	147	116
<i>p,p'</i> -DDT	115	91

as this source produces a background current that is 2.4 times greater than that produced by the  $^{147}\text{Pm}$  ionization source.

The linear range depends on the magnitude of the background current. In the linearity studies, the detector was operated with a pulse width of  $1\ \mu\text{sec}$  and a pulse interval of  $100\ \mu\text{sec}$ . The linear range values obtained are of the expected magnitude. The noise current value for the  $^{147}\text{Pm}$  ionization source is about  $2 \times 10^{-12}\ \text{A}$ . If it is considered that a peak is detected when the reduction in the background current is equal to twice the noise level, and if the detector response is considered to be linear within a 10% reduction of background current, *i.e.*,  $3.7 \times 10^{-10}$ , then the linear range is about 100.

A typical response curve obtained with the  $^{147}\text{Pm}$  ionization source is shown in Fig. 1. It can be seen that the  $^{147}\text{Pm}$  ionization source yields the typical response curves obtained with the  $^{63}\text{Ni}$  detectors, which show a linear and a non-linear response region<sup>3</sup>. If the concentration of the component yields a reduction in the background current greater than the background current produced by the ionization source, then the detector response is independent of the concentration of the component in the sample.

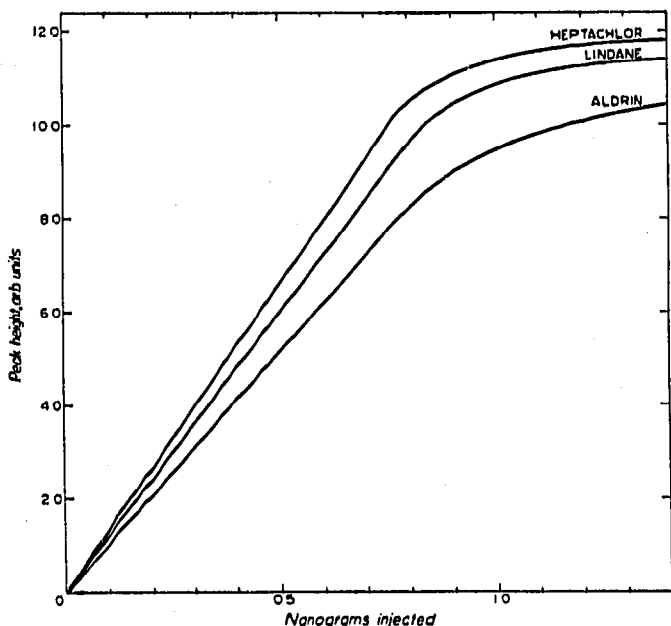


Fig. 1. Linear range of the  $^{147}\text{Pm}$  electron capture detector. Pulse width,  $1\ \mu\text{sec}$ ; pulse interval,  $100\ \mu\text{sec}$ ; column temperature,  $170^\circ$ ; carrier gas flow-rate,  $45\ \text{ml/min}$ .

#### Sensitivity comparison

There are two important factors which affect the response of the electron capture detector: the variation of the pulse interval, and the detector temperature. The latter has been fixed, as it is a variable that is fixed under analytical conditions which are determined by column temperature, type of sample and prior cleanup of the sample. As previously explained, this temperature was maintained at  $250^\circ$ .

The optimum parameters in the pulsed-voltage operation mode were determined with both ionization sources for lindane, heptachlor, aldrin, endrin and *p,p'*-DDT.

The variation of the detector response as a function of the pulse interval was determined by injecting a mixture containing 0.2–0.4 ng/ $\mu\text{l}$  of the above compounds into the chromatographic system equipped alternately with the  $^{147}\text{Pm}$  and  $^{63}\text{Ni}$  ionization sources. The response obtained for each compound was within the linear response region of the detector. The results are shown in Figs. 2 and 3,

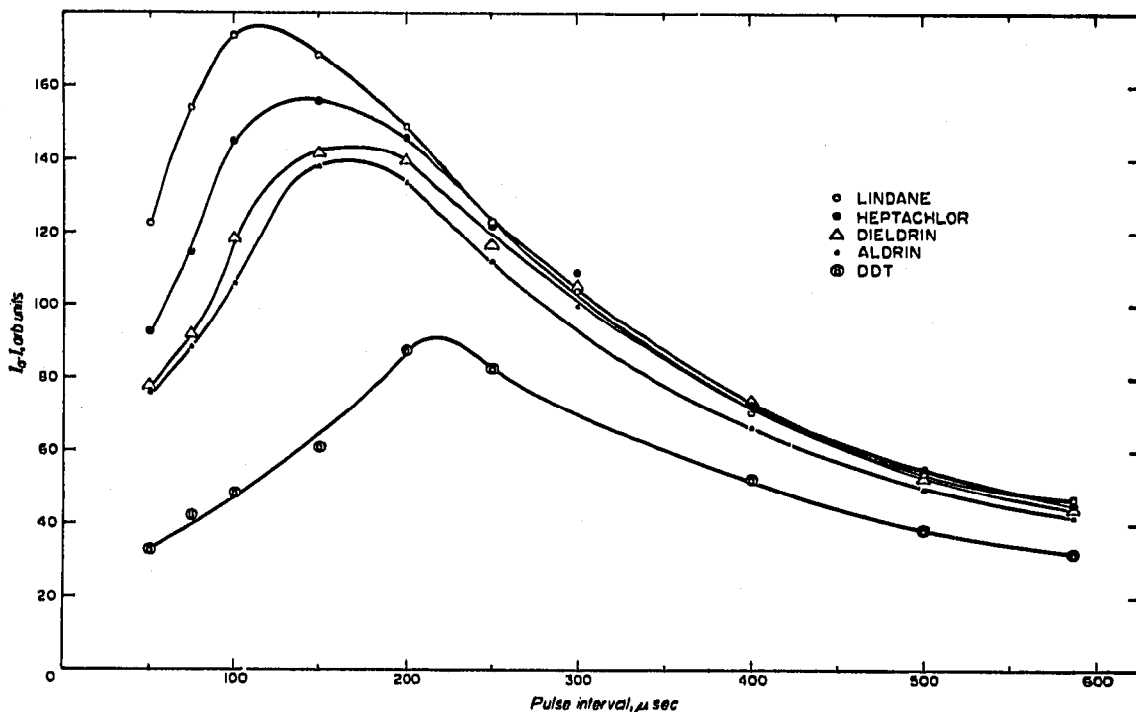


Fig. 2. Variation of the detector response as a function of the pulse interval obtained with the  $^{147}\text{Pm}$  ionization source. Pulse width, 1  $\mu\text{sec}$ ; column temperature, 163°; carrier gas flow-rate, 30 ml/min. One arbitrary unit of  $I_0 - I = 0.42 \times 10^{-10}$  A.

which show the reduction in the background current at selected pulse intervals for both the  $^{147}\text{Pm}$  and  $^{63}\text{Ni}$  ionization sources. The optimum pulse interval for the compounds studied varied from 125 to 212  $\mu\text{sec}$  in both detectors using both ionization sources. It is also important to note that the pulse interval at which optimum response is obtained with the  $^{147}\text{Pm}$  ionization source does not differ by more than 15  $\mu\text{sec}$  from that required to yield the maximum response utilizing the  $^{63}\text{Ni}$  ionization source. Hence the geometrical factor is important in comparing different detectors having different geometries and ionization sources. DEVEAUX AND GUIOCHON<sup>6</sup> have shown that the pulse interval at which optimum response is obtained with  $^3\text{H}$  and  $^{63}\text{Ni}$  ionization sources placed in different geometries may vary by a factor of 3.

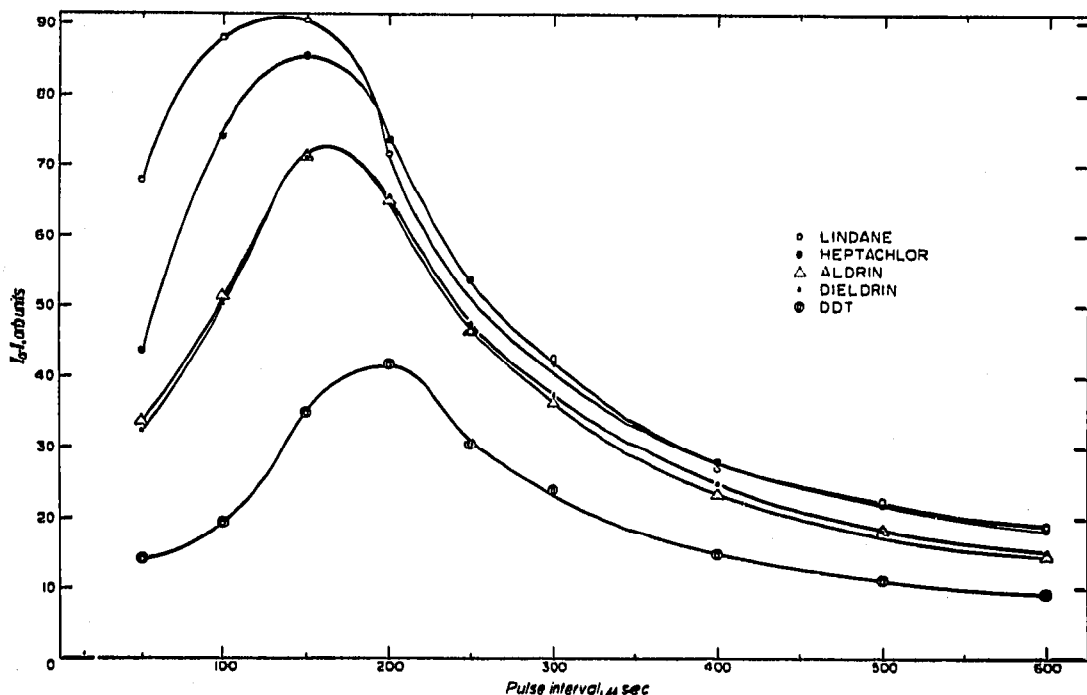


Fig. 3. Variation of the detector response as a function of the pulse interval obtained with the  $^{63}\text{Ni}$  ionization source. Pulse width, 1  $\mu\text{sec}$ ; column temperature, 163  $^{\circ}$ ; carrier gas flow-rate, 30 ml/min. One arbitrary unit of  $I_0 - I = 0.96 \times 10^{-10}$  A.

To compare the sensitivities of both ionization sources within the same detector geometry, the following expression must be evaluated:

$$\frac{C_M(^{147}\text{Pm})}{C_M(^{63}\text{Ni})} \quad (1)$$

where  $C_M$  represents the minimum detectable concentration of the compound in the carrier gas expressed in mole/cm<sup>3</sup>.

The response of the electron capture detector is given by the following expression:

$$C = \frac{I}{k} \ln \left( \frac{I_0}{I} \right) \quad (2)$$

where  $I_0$  is the background current obtained with pure carrier gas and  $I$  is the background current obtained when a compound, having an electron absorption coefficient  $k$ , enters the sensitive volume of the detector at a concentration  $C$  in the carrier gas. Since  $I_0 - I$  represents the peak height, eqn. 2 can be expressed in terms of  $C_M$  by defining that this concentration will yield a peak height  $I_0 - I = 3i$ , where  $i$  is the noise contribution of the current due to the stochastic process of radioactive decay. Substituting for  $I = I_0 - 3i$  in eqn. 2 yields:

$$C_M = \frac{I}{k} \ln \left( \frac{I_0}{I_0 - 3i} \right) \quad (3)$$

Eqn. 3 cannot be evaluated directly since  $I_0 \gg 3i$ , but it can be approximated by a series expansion to yield the expression:

$$C_M \approx \frac{I}{k} \cdot \frac{3^i}{I_0} \tag{4}$$

Thus, to evaluate  $C_M$  in eqn. 4, it is necessary to determine the electronic absorption coefficient,  $k$ . The electronic absorption coefficient can be evaluated from eqn. 2 provided that a relationship exists between the concentration of the sample at the maximum peak height and the mass of the compound injected. Such a relationship has been derived by PURNELL<sup>7</sup>:

$$C = \frac{N^{\frac{1}{2}} m}{(2\pi)^{\frac{1}{2}} V_r^0} \tag{5}$$

where  $V_r^0$  is the adjusted retention volume,  $N$  is the number of theoretical plates of the column and  $m$  is the mass of material injected. By obtaining chromatograms for the compounds studied under identical chromatographic conditions and by using the pulse intervals that yield the maximum peak height, eqn. 5 can be evaluated and the electronic absorption coefficients in eqn. 2 can also be evaluated. The minimum detectable concentration,  $C_M$ , can be determined by using eqn. 4 and the electronic absorption coefficient,  $k$ . Finally, eqn. 1, which expresses the ratio of the minimum detectable concentrations, can be evaluated. All of the calculations can be checked experimentally by injecting a compound so that the signal-to-noise ratio is 3. From the chromatogram of this injection, all the variables of eqn. 5 are known. For example, in the case of *p,p'*-DDT, the experimental  $C_M$  value found for the <sup>147</sup>Pm detector was  $15.6 \times 10^{-17}$  mole/cm<sup>3</sup>, which is in good agreement with the value obtained via the electron absorption coefficient, which yielded a  $C_M$  value of  $18.2 \times 10^{-17}$  mole/cm<sup>3</sup>. The  $C_M$  values obtained are shown in Table III. The ratio of the minimum detectable concentrations in the <sup>147</sup>Pm and <sup>63</sup>Ni detectors is also given in Table III. The <sup>63</sup>Ni detector is 1.2-1.9 times more sensitive than the <sup>147</sup>Pm detector.

The noise current obtained for the <sup>147</sup>Pm ionization source was  $1.8 \times 10^{-12}$  A, while the <sup>63</sup>Ni ionization source yielded a value of  $2.0 \times 10^{-12}$  A. Both measurements were made with a band pass of 0 to 1 cycle per second. The electron absorption

TABLE III

ELECTRONIC ABSORPTION COEFFICIENTS AND MINIMUM DETECTABLE CONCENTRATIONS FOR THE <sup>147</sup>Pm AND <sup>63</sup>Ni IONIZATION SOURCES

Compound	Electronic absorption coefficient, $k$ (cm <sup>2</sup> /mole)		Minimum detectable concentration, $C_M$ (mole/cm <sup>3</sup> )		$\frac{C_M (^{147}\text{Pm})}{C_M (^{63}\text{Ni})}$
	<sup>147</sup> Pm	<sup>63</sup> Ni	<sup>147</sup> Pm	<sup>63</sup> Ni	
Lindane	$1.4 \times 10^{15}$	$1.2 \times 10^{15}$	$1.1 \times 10^{-16}$	$5.8 \times 10^{-17}$	1.9
Heptachlor	$2.5 \times 10^{15}$	$2.2 \times 10^{15}$	$5.8 \times 10^{-17}$	$3.1 \times 10^{-17}$	1.9
Aldrin	$1.7 \times 10^{15}$	$1.2 \times 10^{15}$	$8.7 \times 10^{-17}$	$5.7 \times 10^{-17}$	1.5
Dieldrin	$1.9 \times 10^{15}$	$1.0 \times 10^{15}$	$8.2 \times 10^{-17}$	$6.6 \times 10^{-17}$	1.2
<i>p,p'</i> -DDT	$0.80 \times 10^{15}$	$0.55 \times 10^{15}$	$1.8 \times 10^{-16}$	$1.2 \times 10^{-16}$	1.5

coefficients are about the same for both ionization sources, as shown in Table III. Examination of eqn. 4 shows that when both detectors are compared, the term that is significantly different is the background current. The differences in the sensitivity can be accounted for by the difference in the activities of the ionization sources. However, this condition can easily be corrected by increasing the activity on the  $^{147}\text{Pm}$  foil, but it is not necessary because the difference in sensitivities between the two ionization detectors is not large.

#### *Loss of background current with use*

It is expected that the  $^{147}\text{Pm}$  ionization source should be less affected by column and sample contamination than the  $^{63}\text{Ni}$  source, since the  $\beta$ -energy of  $^{147}\text{Pm}$  is about three times greater than that of  $^{63}\text{Ni}$ . This is true when the  $^{63}\text{Ni}$  and  $^3\text{H}$  detectors are compared. Several injections of different types of extracts were made so as to compare the loss in current of the  $^{147}\text{Pm}$  and  $^{63}\text{Ni}$  ionization detectors. The results are shown in Table IV. The loss in background current is expressed as a percentage by measuring the current prior to the initial and after the final injection of a particular series of injections of the same sample. The  $^{63}\text{Ni}$  is affected by injections of samples that easily contaminate the foil, such as crop samples with no cleanup and fatty residue extracts. However, the  $^{147}\text{Pm}$  ionization is hardly affected by any of the samples studied. The current of the  $^{63}\text{Ni}$  detector could be restored only by washing the foil with alcoholic KOH solution.

TABLE IV  
COMPARATIVE LOSS OF BACKGROUND CURRENT WITH USE

Type of sample <sup>a</sup>	Amount injected (ng)	No. of injections	Loss in background current (%)	
			$^{147}\text{Pm}$	$^{63}\text{Ni}$
Water extract	7	10	—	0.1
Standard solution of aldrin	20	10	0.2	12
Tomato extract with aldrin	2	15	1.6	18.6
Milk extract containing lindane	0.2	10	3.2	26.2

<sup>a</sup> Cleanup performed only on milk samples.

#### CONCLUSIONS

The comparison of the  $^{147}\text{Pm}$  and  $^{63}\text{Ni}$  ionization sources under identical geometrical conditions reveals that the properties of the  $^{147}\text{Pm}$  electron capture detector are very similar to those of the  $^{63}\text{Ni}$  electron capture detector. The linear range and the minimum detectable concentrations indicated a slightly better performance for the  $^{63}\text{Ni}$  electron capture detector. However, the differences are due only to the fact that the  $^{63}\text{Ni}$  ionization source yields a background current 2.4 times greater than that of the  $^{147}\text{Pm}$  ionization source. This difference is due



to the fact that  $^{63}\text{Ni}$  ionization source contained 15 mCi compared with 8 mCi for the  $^{147}\text{Pm}$  source. Ideally, the comparison should be made by using ionization sources that yield the same background current. This is difficult, as it is not possible to predict *a priori* the activity required for each ionization source to give the same background current for a chosen detector geometry. Even under the conditions of this study, the difference in the sensitivities is small and the  $^{147}\text{Pm}$  ionization detector is capable of analyzing samples in the region of 0.1–100 ng/g (ref. 1). A greater advantage is that the  $^{147}\text{Pm}$  foil is less affected by the nature of the sample, owing to its greater  $\beta$ -particle energy. This study confirmed that  $^{63}\text{Ni}$  ionization sources can be replaced with  $^{147}\text{Pm}$  ionization sources while retaining properties similar to those of the  $^{63}\text{Ni}$  electron capture detector but with two added advantages: the cost of the  $^{147}\text{Pm}$  source is one-sixth that of the  $^{63}\text{Ni}$  source, and the  $^{147}\text{Pm}$  ionization source is hardly affected by samples that are difficult to elute from the detector at high temperatures.

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