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THE UTILIZATION OF PROMETHIUM-147 AS AN IONIZATION SOURCE IN ELECTRON-CAPTURE DETECTORS

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SUMMARY

An electron-capture detector which utilizes promethium-147 as the ionization source has been studied for its use in pesticide analysis. A method has been found to electroplate promethium-147 on gold foils which can be heated to 400° without apreciable loss of activity. The properties of the foil as an ionization source are comparable to those of nickel-63. The detector has been used to analyze pesticides in aqueous media in the range 0.1–100 p.p.b.*.

INTRODUCTION

Electron-capture detectors require for high-temperature gas chromatography a stable ionization source which will not volatilize under normal operating conditions. At present, the only source available which is used extensively is ^{63}Ni. In this work, ^{147}Pm was considered as an alternative source and a technique was developed which permits its electrodeposition on to gold or platinum foils. ^{147}Pm has the advantage of lower cost, since the cost of a 10-mCi foil is one-sixth that of a comparable ^{63}Ni foil[1]. Several foils were studied at temperatures up to 400° without any appreciable loss of radioactive material being observed. A detector was constructed for this source and used extensively for the analysis of pesticide residues in water at the level of 0.1–100 p.p.b. The detector was used in either the d.c. or the pulse-voltage mode of operation and was found to possess the characteristic properties of electron-capture detectors[2,3].

EXPERIMENTAL

The chromatograph used was a Hewlett-Packard 5750 provided with flame ionization and tritium detectors. The promethium detector was mounted in the position normally occupied by the tritium detector. Three glass columns, 6 ft. long, 6 mm

* Throughout the paper the British (10^9)billion is meant.

O.D. and 2 mm I.D., were used. They were packed with 3% Dow-Corning 200, 3% NE-60, and 3% OV-1 on Chromosorb W AW, HMDCS, having a mesh size of 80–100.

Nitrogen and a 9:1 mixture of argon and methane were used as carrier gases in the d.c. mode and pulsed mode of operation, respectively. The carrier gases were purified by passage through a molecular sieve (5 Å) which was regenerated every 3–4 days. The electronic apparatus was composed of an EH model 132A pulse generator and the pulses were measured using a 180 A Hewlett-Packard 50 MHz oscilloscope. The current was measured with a Keithley 417K electrometer provided with a stable current-suppression generator. The decreases in base current were recorded with a Hewlett-Packard model 7100B strip-chart recorder capable of accepting d.c. signals from 1 mV to 100 V. The recorder was fitted with a disc integrator.

Pesticide residues analyses were performed utilizing standard techniques[4]. Identification of sample components was carried out by comparing the retention times with known standards in three different columns. Standard solutions were prepared from pesticides obtained from the Polyscience Corporation (nanograde standards) and the U.S. Federal Drug Administration.

Detector construction

The detector housing consisted of two stainless-steel sections and a high-voltage 931-U connector mounted in a massive aluminium heating block provided with a thermocouple for detector temperature measurements and a 100-W cartridge heater. The detector and aluminium block were fitted in a metal box packed with glass wool. The negatively pulsed and d.c. potentials were applied to the body of the detector, which required that the detector be electrically isolated from the chromatograph. This was achieved by using 2 cm long, 1/8 in. O.D. glass tubing as a transfer line between the column exit and the detector entrance. All necessary tubing connections were minimized in size so as to obtain a minimum of dead volume. The detailed construction of the detector is shown in Fig. 1.

Foil preparation

The ionization foil consists of 8 mCi of ^{147}Pm deposited on a gold foil measuring 21 × 33 mm. The electrodeposition method employed in the present work is based on the results first reported by PARKER AND FALK[5], and later applied to the rare-earth elements[6].

An 8-mCi solution of ^{147}Pm in 0.5 *N* HCl was obtained from the New England Nuclear Co., having a specific activity of 0.9 Ci/mg and a total solids content of less than 1 mg. Following conversion to the nitrate form, 50 μg of uranium nitrate were added and the entire solution was evaporated to dryness. The promethium–uranium residue was dissolved in 100 μl of distilled water and added to 15 ml of isopropanol. For the purpose of the deposition, an electrodeposition cell of the type shown in Fig. 2 was used, consisting of a self-sealing Teflon barrel and a brass cathode block. A rotating platinum anode should be used and a cathode–anode distance of 30 mm maintained. An applied potential of 400 V at 1.0–1.5 mA for a period of 60 min is sufficient to ensure quantitative deposition. It is important that the electrodeposition current should not exceed the above value as this would result in a non-adhesive, powdery deposit owing to excessive gas evolution at the cathode (foil surface). The uranium nitrate was used as a carrier for the promethium, ensuring quantitative deposition.

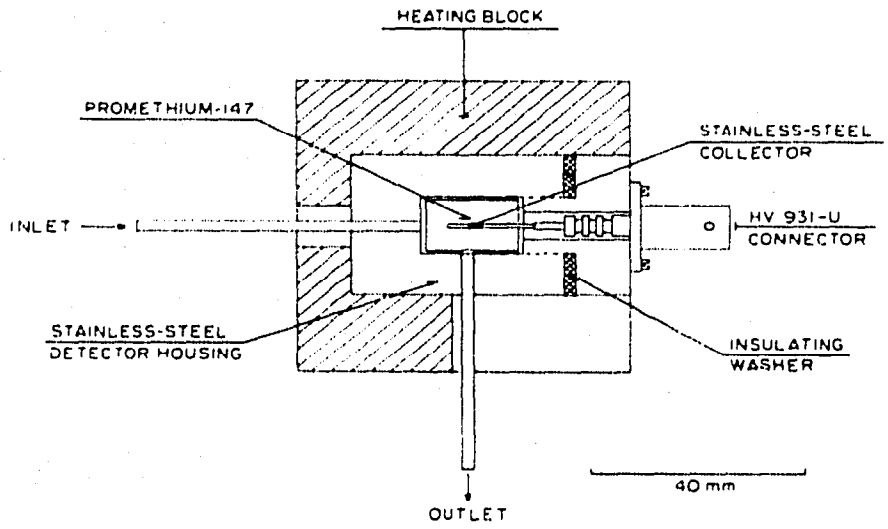

Fig. 1. Schematic diagram of the construction of the detector.

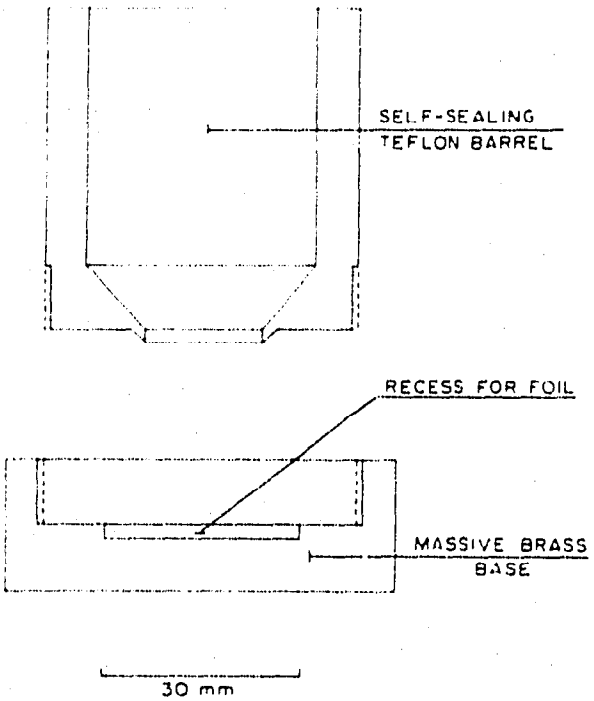

Fig. 2. Schematic diagram of the self-sealing electrodeposition cell.

RESULTS AND DISCUSSION

The utilization of ^{147}Pm as an ionization source has been previously suggested by LOVELOCK[7]. It was also considered as an acceptable radiation source by SHOEMAKE *et al.*[8]. However, ^{147}Pm and ^{85}Kr were never used because of technical difficulties encountered in the preparation of these isotopes as a source adaptable to a detector

cell design. ^{147}Pm is otherwise a logical choice since it is considerably cheaper than ^{63}Ni, has a higher specific activity and is the isotope having the next higher β^- energy after ^{63}Ni. Moreover, ^{147}Pm can be considered as essentially a β^- emitting isotope of 0.223 MeV since its gamma emission of 0.121 MeV occurs with only a 0.004 % abundance[9]. The 8-mCi source placed in the detector housing showed no measurable exposure ($\leq$ 0.01 m rem/h) at the surface of the detector when employing a standard radiation monitoring instrument. This is in agreement with backscattering studies performed in this laboratory using a 10-mCi source of ^{147}Pm and aluminium foils having a thickness of 10 mg/cm^2. The half-life of ^{147}Pm is 2.66 years. Thus the foil will probably need replacement in about 3 years. However, in electron-capture detectors, the rate at which the current decreases as a result of sample and column contamination is much larger than the rate at which current decreases as a result of decay. The relative low cost of the ^{147}Pm foil permits replacement of the foil at 2-year intervals.

The foil was installed in the detector, and current and noise measurements were carried out using d.c. and pulsed potentials with nitrogen, and the 9:1 mixture of argon and methane. The potential was selected so that in the d.c. mode the detector would operate in the recombination region of the current–potential curve and in the saturation region for pulsed potential operation[10]. A comparison with previously reported results is shown in Table I. The measurements for ^3H, ^{63}Ni and ^{147}Pm were made under gas-chromatographic conditions, that is by utilizing a well conditioned column (3 % OV-1) at 190° and with the detectors operated at 220°, 255° and 250°, respectively. It can be observed that the ^{147}Pm detector has a favourable signal-to-noise ratio in both the pulsed and d.c. mode when compared with other detector sources. This is an important consideration since the minimum detectable concentration is directly proportional to the noise and inversely proportional to the background current. Thus this ratio must be optimized, although it is not the only criterion. The minimum detectable concentration is also a function of the electronic absorption coefficient.

TABLE I

CHARACTERISTICS OF RADIATION SOURCES FOR ELECTRON-CAPTURE DETECTORS

Source	*Activity (mCi)*	*Maximum[a] operating temperature (°C)*	*Carrier gas*	*Operational current (A)*		*Signal-to-noise[b] ratio*	
				D.c. potential	*Pulsed potential*	*D.c. potential*	*Pulsed potential*
^3H	250	225	Ar–10% CH_4	[c]	1.3×10^{-8}	–	0.5×10^3
^{63}Ni	8.5	350	N_2	1.3×10^{-9}	[d]	1.1×10^3	–
^{99}Tc	0.3	500	Ar – 5% CH_4	2.0×10^{-11}	2.7×10^{-11}	2.1×10	1.0×10^2
^{226}Ra	0.05	500	Ar – 5% CH_4	1.14×10^{-8}	8.0×10^{-9}	3.2×10^3	3.6×10^3
^{241}Am	10	500	Ar – 5% CH_4	3.6×10^{-8}	8.0×10^{-9}	7.5×10^3	1.4×10^3
^{147}Pm	8	400	Ar–10% CH_4	–	3.2×10^{-9}	–	1.7×10^3
			N_2	2.8×10^{-9}	–	2.0×10^3	

[a] Maximum temperature for safe operation of the ionization source.
[b] Measurements made with a band pass of 0 to 1 cycle per second.
[c] Measurements made with an instrument designed for use with pulsed potential only.
[d] Measurements made with an instrument designed for use with d.c. potential only.

Temperature effects

After preparation, the source was placed in a sealed container which had entrance and exit tubes. The container was placed in the heating block which was heated to 400° in a muffle furnace. The source was continuously flushed with helium which was bubbled into a 5 % sodium hydroxide solution. After one week, the solution was evaporated and counted in a proportional counter. Absolute activity measurements showed that the detector lost less than 30 pCi per day.

The current–potential curves were measured at different temperatures under pulsed and d.c. potential conditions so as to determine the optimal operational voltages of the detector. This is an important consideration since these conditions determine whether the detector operates, in the case of d.c. potential, in the recombination region of the current–potential curve, while in the case of pulsed potential the measurements define the saturation region where the response of the detector is independent of the applied potential. The current–potential curves are shown as a function of temperature in Figs. 3 and 4 for the d.c. mode and the pulsed potential mode, respectively. The use of a d.c. potential at 200° yields a saturation current of 3.8×10^{-9} A and an operational current in the recombination region of 2.8×10^{-9} A. A similar study was made with a pulsed potential. At 250°, a saturation current of 3.2×10^{-9} A was obtained. This temperature was considered to be optimum since, after numerous injections of pesticide residues, the current did not decrease appreciably for a period of four months. It is interesting to notice the shape of the current–potential curves as the temperature is increased. In all instances, a reduction of current is observed as the temperature is increased. When applying a d.c. potential, the current–potential curve is shifted to a lower potential but a new saturation current value is obtained. This phenomenon is contrary to the results obtained by DEVAUX AND GUIOCHON[3] who used d.c. conditions and observed the shift of the current–potential curve to a lower potential, and it was also observed that the saturation current value was independent of temperature. It is possible that at the higher temperature, the fraction of electron recombination is larger and thus causes a decrease in current. At present, further experiments are being carried out to determine the reasons for this effect. It is interesting to note that the reduction of the background current as the temperature increases

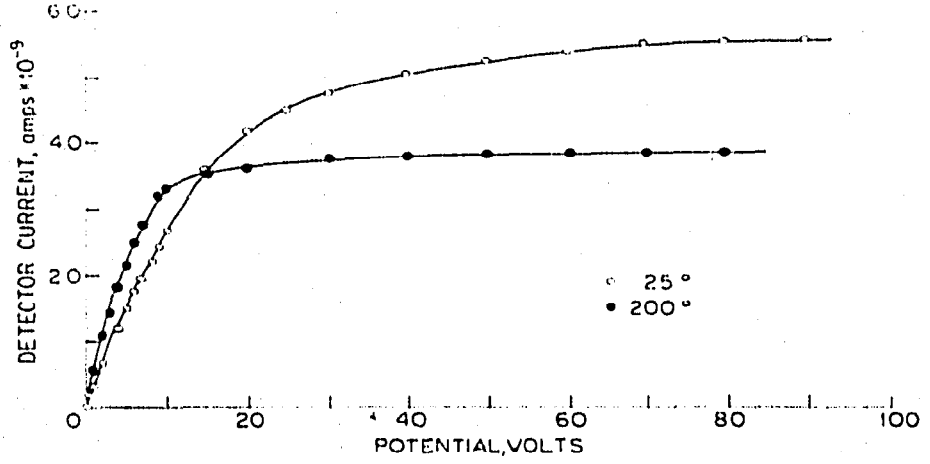

Fig. 3. Current–potential curve obtained at 25° and 200° with the application of d.c. potential. Carrier gas, nitrogen; flow rate, 55 ml/min; column, 3% OV-1.

has also been observed by SCOLNICK[11]. The current obtained at these temperatures was found to be satisfactory for operation and the 8-mCi source was considered to be adequate for operation.

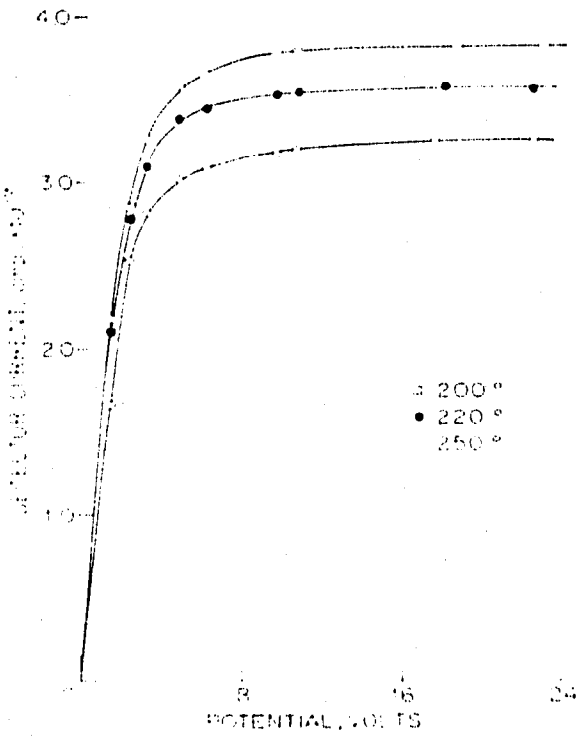

Fig. 4. Variation of the current–potential curves as a function of temperature utilizing a pulsed potential. Pulse width, 1 μsec; pulse period, 200 μsec; carrier gas, 95% argon–5% methane; flow rate, 55 ml/min; column, 3% OV-1.

Background current as a function of pulse period

Because it is important to verify that the detector operates as an electron-capture detector, a study was made of the current–potential curves for different time periods ranging from 600 to 150 μsec and at a constant pulse width of 1 μsec. The results are shown in Fig. 5 and indicate that the current is proportional to the number of pulses per second applied. The current is thus inversely proportional to the period. As the pulse period is increased, an equilibrium is established between the electrons produced by ionization and the electrons or negative ions which recombine in the same time. Under equilibrium conditions, the number of electrons collected by each pulse is the same. Since it is desirable to operate under equilibrium conditions, this pulse period for equilibrium conditions can be determined from Fig. 5 by plotting, at a selected potential, the current *vs.* the reciprocal of the pulse period. At some value of the reciprocal of the period, which occurs for small periods, the current is no longer inversely proportional to the period and electron production is no longer an equilibrium process. For the detector studied, a value of 200 μsec was obtained from Fig. 5. This value is a good compromise between the equilibrium condition and the value of the base current. As there can be no doubt that the detector has the same characteris-

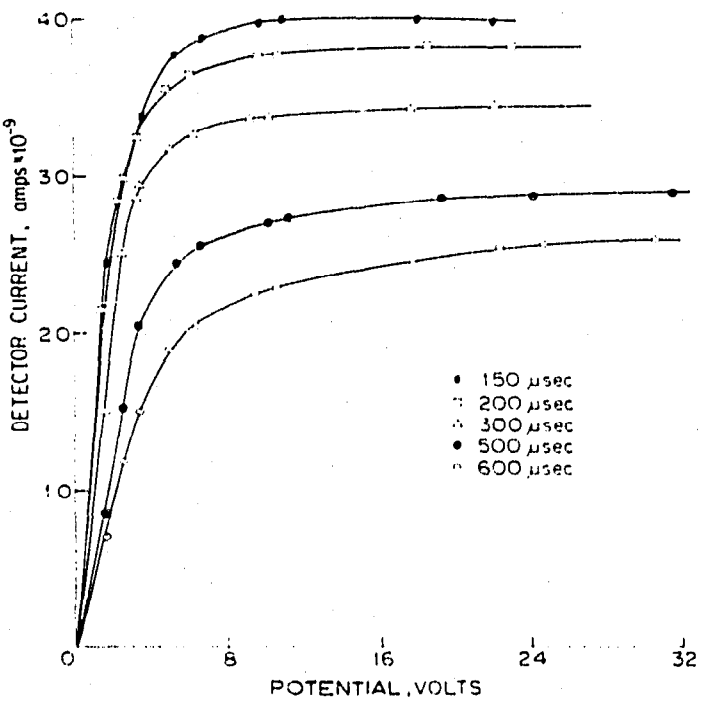

Fig. 5. Current–potential curves as a function of the pulse period. Pulse width, 1 μsec; detector temperature, 240°; carrier gas, 90% argon–10% methane; flow rate, 60 ml/min; column, 3% OV-1.

ties as other conventional electron-capture detectors, it was employed for the study of pesticide residues in aqueous media.

Utilization of the detector for pesticide residue analysis

In order to utilize this detector for pesticide analysis, it was first necessary to measure the linear dynamic range for those components present in the sample. For compounds such as lindane, aldrin, dieldrin, endosulfan and DDT, amounts between 80 and 1300 pg were injected. In all cases, the detector responded linearly and this permitted the analysis of samples containing 1 p.p.b. of these pesticides.

TABLE II

ANALYSIS OF A SYNTHETIC AQUEOUS PESTICIDE MIXTURE UTILIZING THE PROMETHIUM-147 ELECTRON-CAPTURE DETECTOR

Component	*Analytical concentration (p.p.b.)*	*Analyzed concentration (p.p.b.)*	*Recovery (%)*
Endosulfan	2.0	2.7	103
Dieldrin	2.0	2.1	81
DDT	2.3	2.2	96
Aldrin	2.5	2.5	100
Lindane	2.8	2.3	82
Heptachlor	0.8	0.6	75

Once this range had been established, the sample extracts, prior to injection, were diluted so that the detector response would fall within the required range. Standards were injected immediately after the sample and at concentrations that would yield a response equal to the component in the sample. To ensure that the entire analysis was correct, aqueous synthetic samples were prepared with the pesticides to be analyzed. A comparison of the results obtained with the analytical concentrations, at levels between 0.8 and 2.8 p.p.b. are shown in Table II. The results show good agreement and the recovery was in the range 75–103 %. A typical chromatogram obtained with an aqueous sample is shown in Fig. 6. This detector is presently being used routinely in the analysis of pesticides in different media.

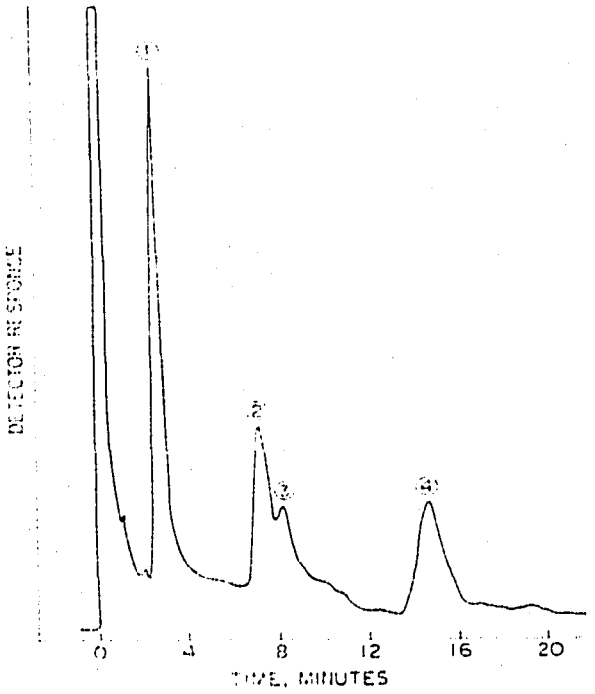

Fig. 6. Chromatogram obtained for the extract of an aqueous sample. Components and amounts injected: 1 = lindane, 0.09 ng; 2 = dieldrin, 0.07 ng; 3 = DDE, 0.10 ng; 4 = DDT, 0.22 ng. Carrier gas, 90% argon 10% methane; flow rate, 67 ml/min; column, 3% NE-60; pulse width, 1 μsec; pulse period, 200 μsec.

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