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## IRON-55 AS AN AUGER ELECTRON EMITTER

### NOVEL SOURCE FOR GAS CHROMATOGRAPHY DETECTORS

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#### SUMMARY

In order to avoid non-linear response in the pulse feedback method of electron capture detection, an ionising source is required giving low noise with small operating currents. The advantages of iron-55 as an Auger electron emitter over conventional sources in this application are reported.

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#### INTRODUCTION

Ever since the invention by Deal *et al.*<sup>1</sup> of the ionisation cross-section detector, gas chromatographers have found sources of ionising radiation to be a most convenient and stable means of rendering a gas conducting. The signal relating to the concentration of solute from an ionised gas can be transduced in many ways, but almost all of the different detectors so used are simple diodes. In these devices the base ion current and its fluctuations are directly related to the strength and the nature of the ionising source. It is usually assumed that the fluctuations of the signal (noise), which set a limit to the smallest signal which can be seen, are a consequence of the statistical nature of radioactive decay. This assumption has led to the general use of  $\beta$ -emitting nuclides as radiation sources on the grounds that  $\alpha$ -emitting sources are too "noisy", and  $\gamma$ -emitting sources would cause radiological exposure problems at the strength required to give reasonable ion currents. Tritium and nickel-63 are the nuclides most frequently employed.

This paper reports the use of a novel ionising source, namely iron-55, as an Auger electron emitter. This provides a high signal-to-noise ratio at a considerably lower ion current than is usually employed in gas chromatography (GC), and is at the same time a stable and a conveniently applied radiation source.

#### PHYSICAL BASIS

The production of ion pairs by ionising particles is complete within  $10^{-12}$  sec,

so that in terms of the pass band of a typical GC amplifier (d.c. to 1 Hz) the process is instantaneous. The drift velocity of electrons to the anode of a typical detector is about 1 cm/ $\mu$ sec with commonly used polarising potentials (10–100 V) and with the carrier gases hydrogen, helium, nitrogen, argon and methane. In these circumstances, the time taken for the package of electrons produced by each ionising event to reach the anode is about 1  $\mu$ sec. The current flowing at the detector anode is therefore made up of a series of random pulses. The variation in this current is a function of the square root of the number of ionising particles ( $N$ ) emitted in a chosen interval, in accordance with the statistics of nuclear decay, and the number of ion pairs ( $A$ ) generated by each ionising particle. Low noise for a given current is favoured by making  $N$  as large and  $A$  as small as possible.

From this it follows that  $\alpha$ -emitting sources, which produce more than  $10^5$  ion pairs per event will for a given current be very much noisier than  $\beta$  sources, which produce say 100 ion pairs per event, and these in turn will be noisier than  $\gamma$  emitters, which in a typical detector produce perhaps only one ion pair per ionising event. On the other hand, the source strength required for a given current will go in exactly the opposite order, so that for a typical detector current in the range 1–10 nA activities of the order of 10  $\mu$ Ci of  $\alpha$ , 10 mCi of  $\beta$  and 1 Ci of  $\gamma$  would be required.

In general, these predictions are confirmed by practice, but the calculation of expected noise levels of chromatography detectors is subject to considerable uncertainty owing to the effects of an unknown amount of self-absorption in the sources used on values of  $N$  and  $A$ .

#### A NEW LOW-NOISE SOURCE

With the pulse feedback method of electron capture detection high ionisation currents cause non-linear response to increasing sample concentration where strongly electron-absorbing compounds are involved<sup>2</sup>. A low ion-current low-noise source is therefore needed in this application. Considerations of radiological safety and practicability rule out the use of  $\gamma$  emitters, and so the availability of low-energy electron sources was reviewed.

The choice of  $\beta$  emitters has not usefully increased since the review in 1965 by Shoemake *et al.*<sup>3</sup>. However, electrons are produced by processes other than  $\beta$  decay, notably in extra-nuclear re-adjustments which follow radioactive decay by orbital electron capture. The initial vacancy created by orbital electron capture (usually in the K shell) is most frequently filled by an electron from the next highest shell (L), the process of re-adjustment then proceeding through successively higher shells. Following each electron transition, the difference in binding energy between the shells may be emitted as a characteristic X-ray, or may be expended in an internal photoelectric process in which an orbital electron is emitted. The emitted electron is known as an Auger electron. The fraction of vacancies in a given shell the filling of which is accompanied by X-ray emission is called the fluorescence yield, and the fraction which involves an Auger process is the Auger yield. Auger yields increase markedly (and fluorescence yields decrease correspondingly) with decreasing atomic number of the nuclide concerned, varying from about 50 to 95% between atomic numbers 30 and 15. Electron capture nuclides falling in this region, whose spectra are not complicated by undesirable radiations (positrons, gammas), are given in Table I.

TABLE I  
ELECTRON CAPTURE NUCLIDES

<i>Nuclide</i>	<i>Half-life</i>
Argon-37	35 days
Calcium-41	$1.1 \times 10^5$ years
Vanadium-49	330 days
Manganese-53	$2 \times 10^6$ years
Iron-55	2.6 years
Nickel-59	$8 \times 10^4$ years

Of the above nuclides only iron-55 fulfils the necessary practical criteria, namely, satisfactory half-life and specific activity, and ready availability in a form suitable for source preparation. The Auger yield is about 75%, and shows a multiplicity of lines between 5.387 and 5.640 KeV (ref. 4). The electron energies being less than the  $\beta$  energies of tritium (maximum 18.6 KeV) and nickel-63 (maximum 67 KeV), a more favourable value for  $A$ , the number of ions generated by each ionising particle, is to be expected.

#### SOURCE PREPARATION

Iron-55 is available at specific activities up to about 40 Ci/g, and so sources containing 1–2 mCi/cm<sup>2</sup> are sufficiently thin to allow reasonably efficient emission of Auger electrons, whose range is of the order of 50  $\mu$ g/cm<sup>2</sup>. A method of preparation<sup>5</sup> has been devised to give sources which are stable towards moisture, and towards heat at temperatures up to and beyond those to which GC detectors are normally subjected. Sources heated for 48 h at temperatures up to 400° showed no detectable loss in standing current when checked afterwards at ambient temperature. Above 400° diffusion of the iron-55 into the backing foil leads to progressive reduction in electron emission efficiency and standing current.

#### SOURCE EVALUATION

Table II shows the observed noise levels of a number of ionising sources. The conditions of measurement were: 21°; ambient pressure; nitrogen carrier gas; flow-

TABLE II  
COMPARISON OF VARIOUS IONISING SOURCES

Abbreviations:  $I_s$  = d.c. saturation current;  $I_{op}$  = operating current.

<i>Nuclide</i>	<i>mCi</i>	$I_s$ (nA)	$I_{op}$ (nA)	<i>Noise</i> (pA)	<i>Signal (pA)</i>		<i>S/N ratio</i>	
					<i>F-II</i>	<i>CCl<sub>4</sub></i>	<i>F-II</i>	<i>CCl<sub>4</sub></i>
H-3	500	30	15	3	132	30	44	10
Am-241	0.015	16	7	30	110	35	3.7	1
Ni-63	15	9	5.3	1.5	80	19	54	13
Ni-63	0.5	0.48	0.34	0.4	10	2.8	25	7
Fe-55	5	0.5	0.3	0.1	6.4	1.7	64	17

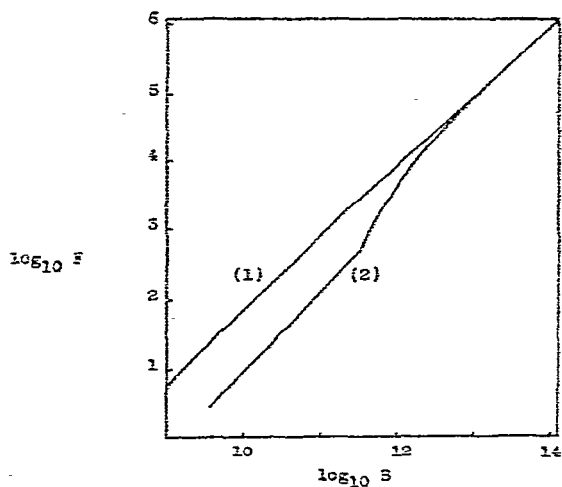


Fig. 1. Variation of pulse frequency ( $F$ ; Hz) with rate of sample input ( $B$ ; molecules/sec) for: (1) 0.5 nA and (2) 10 nA.

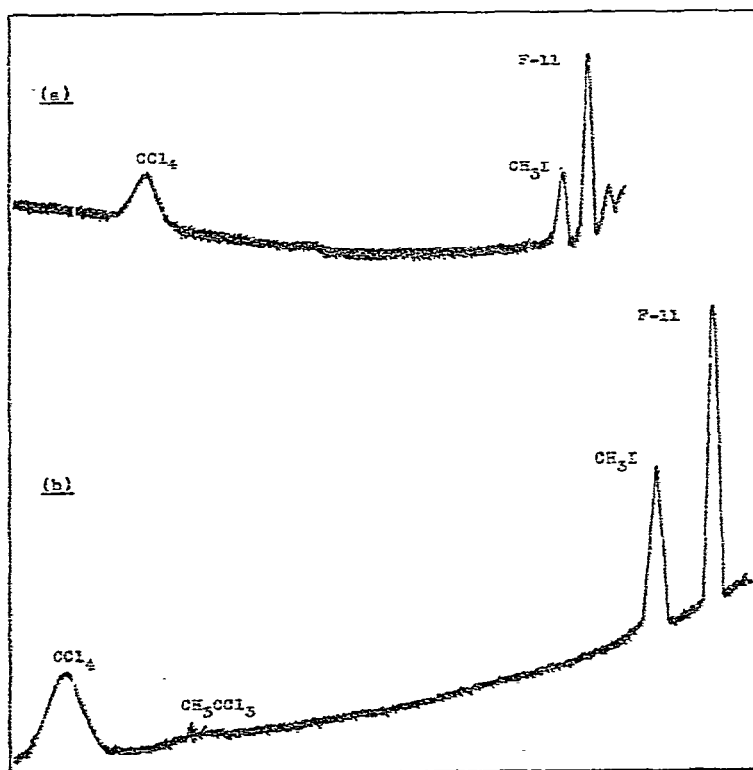


Fig. 2. Analysis of clean air (5-ml sample) for freon 11 (F-11) and carbon tetrachloride. (a) 15-mCi nickel-63 source; (b) 5-mCi iron-55 source.

rate 1 ml/sec. The detector was a simple diode ion-chamber, 1.25 cm long  $\times$  1.25 cm in diameter, with a coaxial anode 1 mm in diameter. Table II shows that there is the expected difference in noise between  $\alpha$  and  $\beta$  sources, and that the lowest noise was associated with the source of lowest electron energy, namely iron-55.

The iron-55 source was compared with a nickel-63 source of the same dimensions and with an activity chosen to provide the same saturation current. The results of this experiment are given in Table II. They indicate that, to attain the given ion current, the strength of the iron-55 source had to be about 10 times that of the nickel-63. They confirm that the associated noise level is greater with the nickel-63 source by a factor close to the square root of 10, which is predicted by theory.

Fig. 1 shows the response expected of an electron capture detector operated in the pulse feedback mode with an ion source giving a current of 0.5 nA and one giving 10 nA when used in the detection of a strongly electron-absorbing material, such as a halogenated pesticide.

Fig. 2 shows a comparison of the noise level of the analysis by electron capture of clean air for freon 11 and carbon tetrachloride present at approximately one part in  $10^{10}$  by volume using: (a) a detector with a 15-mCi nickel-63 source, and (b) identically the same detector with a 5-mCi iron-55 source. This analysis was performed under the more conventional fixed pulse period method of operation.

## CONCLUSION

The connection between low detector noise and low ion density in the chamber has been demonstrated in the work reported above. The introduction of the iron-55 Auger electron source represents a new departure in ionisation sources for GC detectors.

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