

POSSIBLE RADIATION HAZARDS ARISING FROM THE USE OF RADIOACTIVE DETECTORS IN GAS CHROMATOGRAPHY

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INTRODUCTION

Radioactive detectors for use in gas chromatography were first described by LOVELOCK¹; these detectors consist essentially of an ionisation chamber containing a source of radiation in the form of a radioactive foil. Commonly used sources of radiation are 10 to 20 mC of strontium-90 or promethium-147, 200 mC of tritium, and 100 μ C radium-226 or radium-D.

The hazards which may arise from handling radioactive materials fall into two categories; namely, external radiation, that is radiation originating from sources outside the body, and internal radiation, which results from the entry of radioactive material into the body. In the case of external radiation, the magnitude of the hazard depends on the nature of the radiation (whether α -, β -, or γ -rays), on the isotope concerned and its activity, on the distance from the source, on the presence of shielding and on the time of exposure. Some exposure to external radiation is almost inevitable whenever radioactive materials are used, but with proper precautions this should be very slight in the use under consideration. In the case of internal radiation, the magnitude of the hazard depends not only on such physical aspects as radioactive half life and the nature and quantity of the radiations emitted, but also on the uptake and localisation of the element in question in the body, and on the method and rate of its elimination from the body. In the use of radioactive materials in gas chromatography, the internal hazard can be almost entirely eliminated if proper attention is paid to laboratory technique, cleanliness and good ventilation.

In general, the radioactive detectors in gas chromatography are handled by persons who would not otherwise be concerned with radioactive materials and it is therefore desirable, unless there are very strong reasons to the contrary, not to have to classify them as radiation workers. This means that the annual dose received by the whole body and individual organs (except the thyroid gland) from both external and internal radiation should not exceed 1.5 rem, the corresponding dose to the skin and the thyroid gland being 3 rems². The question of a higher figure for the hands and forearms, feet and ankles is at present under review and an annual maximum permissible dose of 7.5 rems may be agreed.

CONSIDERATION OF THE POSSIBLE HAZARDS

The various possibilities of external and internal hazard are considered separately below. Internal hazards will only arise in the event of the liberation of radioactive

material, which may occur as a result of (a) mechanical damage to the foil during assembly and cleaning, (b) emission of radioactive gas such as radon (from ^{226}Ra) and tritium, (c) chemical attack of the foil by the vapour under investigation, and (d) the effect of heat.

External radiation

In the case of tritium and promethium-147 foils the detector body itself is sufficient to absorb all the primary β radiation. The same may, in general, be true of Ra-D foils but, if the apparatus is constructed entirely of glass, some additional shielding may be necessary to stop the more energetic β particles. However, in stopping β -particles bremsstrahlung* is produced and, with the exception of the β -radiation from tritium, shielding is usually necessary against it. For the ^{90}Sr and ^{226}Ra sources in current use, external shielding must be provided which is sufficiently thick to reduce to acceptable levels the β -radiation and any associated bremsstrahlung, as well as the γ -radiation in the case of ^{226}Ra . The protection of β -ray sources by various materials is discussed by HAYBITTLE³, and WYARD⁴ gives a formula for calculating the dose rate due to bremsstrahlung. Although lead is very often used as a shielding material, some other material such as copper should be used if it is intended to use the gas chromatography apparatus at temperatures in excess of 250° on account of the low melting point of lead (327°).

As an example of the importance of bremsstrahlung, one detector containing a 20 mC ^{90}Sr source was submitted for test here and found to give a dose rate due to bremsstrahlung of about 100 mrad/h at its surface despite the fact that the body of this particular detector was constructed of brass about 1 cm thick and was shielded with 1 cm lead. The dose rate at an accessible point can be reduced to an acceptable level by enclosing the detector in a screen of suitable dimensions; a screen placed 20 cm from the surface of the assembled detector would limit the dose rate to 0.75 mrad/h, which would permit continuous handling, but handling the shielded detector without its screen would be limited to about one and a half hours per week for a person not classified as a radiation worker (assuming 7.5 rems/year is accepted as the limit for the hands). This is in accordance with I.C.R.P. concepts; in the United Kingdom the Factory Sealed Sources Regulations 1961⁵ may impose more severe limitations if persons are not "classified workers".

So far only handling and protection of the assembled detector have been discussed but, in certain instances, operators may wish to build or clean their own detector. In these circumstances the use of forceps is necessary in order to reduce the very high radiation dose which would otherwise be received by the hands in close proximity to the unshielded active area of the radioactive source. Some radiations, namely the α -rays from ^{226}Ra and Ra-D, as well as the β -rays from tritium are so readily absorbed that they do not penetrate to the sensitive parts of the skin and hence are considered to produce no external radiation hazard. More energetic β -rays do penetrate deeper, and the dose rate at the surface of the skin due to β -radiation can be roughly estimated if we assume that at a distance of 10 cm from an unfiltered point source of 1 μC , of ^{226}Ra and daughters, Ra-D and daughters, $^{90}\text{Sr} + ^{90}\text{Y}$, and ^{147}Pm , the dose rate will be approximately 25, 9, 15, and 2.5 mrad/h, respectively.

* Bremsstrahlung is a form of secondary electro-magnetic radiation which is produced during the absorption of β -rays.

For example, 100 μC ^{226}Ra will give a β -ray dose rate of approximately 2.5 rad/h and 20 mC ^{90}Sr a β -ray dose rate of approximately 300 rad/h when handled with forceps 10 cm long. In addition to the β -radiation, there will also be a γ dose of approximately 9 mrad/h in the case of the ^{226}Ra source. As will be seen from the above figures, the handling of unshielded sources will, with the exception of tritium sources lead to dose rates far in excess of that which can be accepted continuously by persons not classified as radiation workers and should therefore be restricted to the persons classified as radiation workers and the appropriate handling techniques for such sources must be used.

Internal radiation

(a) *Mechanical damage.* The tritium sources consist of a copper strip covered with a thin evaporated layer of titanium in which the tritium is absorbed; the other sources consist of silver or gold foil strips in which the isotope is firmly bonded. In the case of the ^{226}Ra and Ra-D foils, the isotope is completely enclosed by the gold foil except at the cut ends of the strip. On either side of the active area there is an inactive area, 2.5 to 7.5 mm wide, depending on the source, which may be used for handling the source or for fixing it in the detector. In order that the α -radiation may penetrate the foil, the front face of the foil has a very thin "window" 4 to 5 μ in thickness. The ^{147}Pm foils are similar except that there are no active ends, and the isotope is completely enclosed within the foil. In the case of ^{90}Sr , the isotope is completely enclosed but the thickness of the active face is 50 μ .

To prevent mechanical damage to the extremely fragile "window" over the active area the sources should only be manipulated by their inactive edges and again the use of forceps is indicated.

In cases where it is necessary to clean the detector it is recommended that the detector be flushed out with a non-corrosive solvent which is suitable for the deposit to be dissolved. If the source has suffered any mechanical damage or damage due to chemical action, the wash liquor will be radioactive and it is advisable that workers should wear rubber gloves when handling the wash liquor and should decontaminate the apparatus used after completion of the washing. The liquor itself should be regarded as radioactive waste and treated accordingly with respect to disposal. Under no circumstances should the foils be swabbed, or damage will result.

(b) *Emission of radioactive gas.* Experiments to determine the leakage of radon from radium-226 sources were carried out at the Radiological Protection Service (R.P.S.) with a foil containing 100 μC radium and have shown that about 10^{-4} μC of radon escape from the foil each minute when the apparatus is operating at a temperature of 200°. There was also evidence that when the foil was cut into two pieces the rate of emission increased possibly because the length of cut edge was increased.

Assuming that the source is in a room of 1000 ft.³ having three air changes per hour, the concentration of radon in air would then be about 10^{-10} $\mu\text{C}/\text{cm}^3$. This is 30 times less than the value, $3 \cdot 10^{-9}$ $\mu\text{C}/\text{cm}^3$, recommended by the International Commission on Radiological Protection for uncontrolled areas, assuming a 40 hour week. Under conditions of a fairly large room and normal ventilation the leakage rate of radon does not present a hazard, but where space is restricted and ventilation poor it is advisable to lead the outlet of the column outside the building or into a fume extractor.

Data appertaining to leakage from tritium sources can be obtained on application to the Radiochemical Centre⁶ who state that molecular tritium is slowly evolved from a 200–300 mC source at room temperature to the extent of 5 $\mu\text{C}/\text{day}$. There is a further reduction in activity of about 40 $\mu\text{C}/\text{day}$ as a result of radioactive decay. The leakage rate has been found to increase with elevation of temperature; for example, it increases ten fold between 200° and 250°, 1 % of the tritium in the source being lost in 24 hours at 250°. It would therefore be advisable to limit the use of these sources to a maximum temperature of 200° and to lead the effluent gas outside the building or into a fume extractor. In any event, the ventilation of the room in which the detector is used should be sufficient to ensure that the average concentration of tritium in the form of tritium oxide does not exceed the maximum permissible level of $5 \cdot 10^{-7} \mu\text{C}/\text{cm}^3$ for non-occupational exposure for a 40 hour week or $2 \cdot 10^{-4} \mu\text{C}/\text{cm}^3$ of molecular tritium (T_2 or HT)².

(c) *Chemical attack.* It is difficult to predict what the effect of chemical attack on these foils will be. The tritium sources are reported⁶ as being affected by acidic and basic vapours to varying degrees dependent on temperature. The strontium foils, by virtue of their sealed ends and of their thicker "window", will be less subject to attack than the ¹⁴⁷Pm, Ra-D and ²²⁶Ra foils, with their thinner "windows", but the ultimate effect of chemical corrosion on the "window" will be the same. The Ra-D and ²²⁶Ra foils are also more vulnerable to chemical attack owing to their open ends.

An 80 μC Ra-D foil was tested by the author by passing a number of corrosive vapours through the detector containing it. Various temperature conditions and rates of gas flow were used. The effluent gas was passed into a vapour trap instead of being allowed to discharge into the air as usual and the foil itself was washed with ether after each run. The amount of activity found in the trap and the washings was found to depend to a marked degree upon the temperature of the device and the previous treatment of the foil. When hydrogen chloride was used it was found that no damage to the Ra-D foil occurred at temperatures below 100° but that damage occurred above this temperature.

Once damage had occurred to the foil, up to $10^{-4} \mu\text{C}/\text{h}$ of Ra-D and daughters were identified in the vapour trap when the chromatograph was run with organic substances unlikely to give corrosive breakdown products. However, up to ten times as much Ra-D and daughters were found in the trap when further samples of compounds having breakdown products such as hydrogen chloride, chlorine and thionyl chloride were introduced into the chromatography column. Assuming that the effluent gas discharges into a 1000 ft.³ room having three air changes per hour the concentration of Ra-D in the atmosphere would be about $10^{-12} \mu\text{C}/\text{cm}^3$ when the apparatus is used for non-corrosive vapours and up to $10^{-11} \mu\text{C}/\text{cm}^3$ in the case of corrosive vapours. These are respectively one tenth and equal to the maximum concentration in air which is recommended by the I.C.R.P. for non-classified workers, assuming a 40 hour week. However damage once started is progressive, and the amount of damage depends on the concentration of the breakdown products in the carrier gas and also on the presence of water vapour which aggravates the damage. In exceptional cases the compound under investigation can itself produce a volatile compound with the radioactive material in the foil, in which case the activity in the effluent gas would certainly exceed the quantities stated above. For example, the R.P.S. was asked to examine a number of organic phosphohalogen compounds one of

which, phenyl-dichlorophosphine, removed as much as $0.02 \mu\text{C}$ of Ra-D from the source when a single sample was introduced into the chromatography column. If this $0.02 \mu\text{C}$ of Ra-D had been allowed to enter a 1000 ft.^3 laboratory it would have produced an average concentration of twenty times the maximum permissible level.

(d) *Effect of heat.* The effect of heat on tritium and ^{226}Ra sources and the production of radioactive gas has already been referred to.

In the case of the α -emitting foils it is known that, if the temperature is allowed to rise above 450° , damage to the "window" occurs with resulting leakage of activity⁷. There is also some evidence to suggest that, over prolonged periods of heating, damage may occur below this temperature. Tests on sources up to temperatures of 250° appear to result in little or no damage to the source as will be seen below, but it would seem that breakdown of the foil takes place progressively in the temperature range 250 – 450° . No tests were carried out on ^{147}Pm foils but it would be expected that their behaviour would be similar to other foils.

Tests were carried out at the R.P.S. on a detector containing a $20 \text{ mC } ^{90}\text{Sr}$ source. The temperature was maintained at 200° and argon was continuously passed through the detector for about a month. The effluent gas from the detector was passed into a trap and contents of the trap were assayed daily for ^{90}Sr . Amounts of the order of $10^{-6} \mu\text{C/day}$ were detected; this is, of course, very small in comparison with the 20 mC of ^{90}Sr actually enclosed within the foil and, if escaping into a well-ventilated room, would give air concentrations well below the maximum permissible concentration for non-classified workers of $3 \cdot 10^{-11} \mu\text{C/cm}^3$.

CONCLUSIONS

Provided that this extremely useful type of detector is treated with due regard to the fact that it contains radioactive material, there is very little hazard involved. Handling of the sources should be kept to a minimum for the reasons mentioned above, and overheating of the detectors should be avoided; the temperature should preferably be below 250° . As a safety measure, it would be advisable to pass the effluent gas from the apparatus into a fume cupboard, in order to minimise the hazard which would arise as a result of overheating or chemical attack. It is possible to avoid some of these problems by enclosing the foil in, for example, a thin glass envelope. This would protect the foil from chemical attack and would contain any isotope released as a result of overheating. This form of protection, however, is only suitable in the case of fairly energetic β -emitters such as ^{90}Sr and would, of course, exclude those with insufficient energy to penetrate the glass. It must not be forgotten, however, that external shielding of the detector as a whole is still necessary.

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SUMMARY

The hazards which may arise due to the use of radioactive foils in the gas chromatography detectors are reviewed; they are external radiation, effect of mechanical damage, emission of radioactive gases, the effect of chemical attack and the effect of heat. Overheating of the foils is the principle source of danger to the majority of users, but the other hazards particularly effect those persons who build or service their own apparatus.

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