CHROMATOGRAPHIC SEPARATION AND PURIFICATION OF XENON-133

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SUMMARY

A process has been developed for the separation of Xe-133 from a fission product gas mixture, consisting in collection of fission noble gases with a charcoal cold trap and purification and dispensation of xenon by chromatographic separation using activated charcoal as adsorbent. Impurities such as hydrogen, oxygen, oxides of nitrogen and krypton are almost completely removed from the xenon product. Analyses of the fission gas components were performed by gas chromatography using Porapak Q, Spherocarb and molecular sieves as adsorbents. The purity and yield of the product are satisfactory for domestic requirements in nuclear medical applications.

INTRODUCTION

Radioactive krypton and xenon are normally emitted with the off-gas during the dissolution of irradiated uranium. Rare gases can be separated from gas mixtures by physical means[1], *e.g.*, preferential adsorption on solids, absorption in liquids, low-temperature distillation and several differential diffusion processes[2,3]. Usually, krypton and xenon are recovered together in most processes and they are separated by distillation, selective adsorption or gas chromatography.

The rare gas isotopes most useful in nuclear medicine and industry are ^{133}Xe and [85]Kr. The fission yields for thermal neutron bombardment of [235]U are 6.8% for ^{133}Xe and 0.29% for [85]Kr[4]. As [85]Kr decays primarily by beta-emission associated with gamma rays only to the extent of 0.4% of its decay, this isotope is of limited use for *in vivo* measurements[5]. [133]Xe decays with a half-life of 5.25 days by emitting a beta-particle accompanied by 81 keV gamma radiation[6]. Currently, ^{133}Xe is the most commonly used radioactive gas isotope in nuclear medicine for imaging in lung ventilation studies[7–9], in organ blood flow measurements[5,10,11] and in the determination of tissue lipid and lipid-free fractions[12,13].

A method for the collection and concentration of rare gases has been established in this study. Activated carbon has previously been demonstrated to be successful for the chromatographic separation of rare gases at various temperatures[14–17]. In this work, a procedure for the pre-treatment and chromatographic separation of krypton and xenon at room temperature and atmospheric pressure was established[18]. The dispensation of the xenon product can be performed by using a gas diffusion device.

EXPERIMENTAL

Collection of rare gases

The system design for the collection of rare gases from the fission product gas mixture source is shown in Fig. 1. The charcoal trap is connected to the fission product gas system by using a bypass loop and a four-way ball-valve.
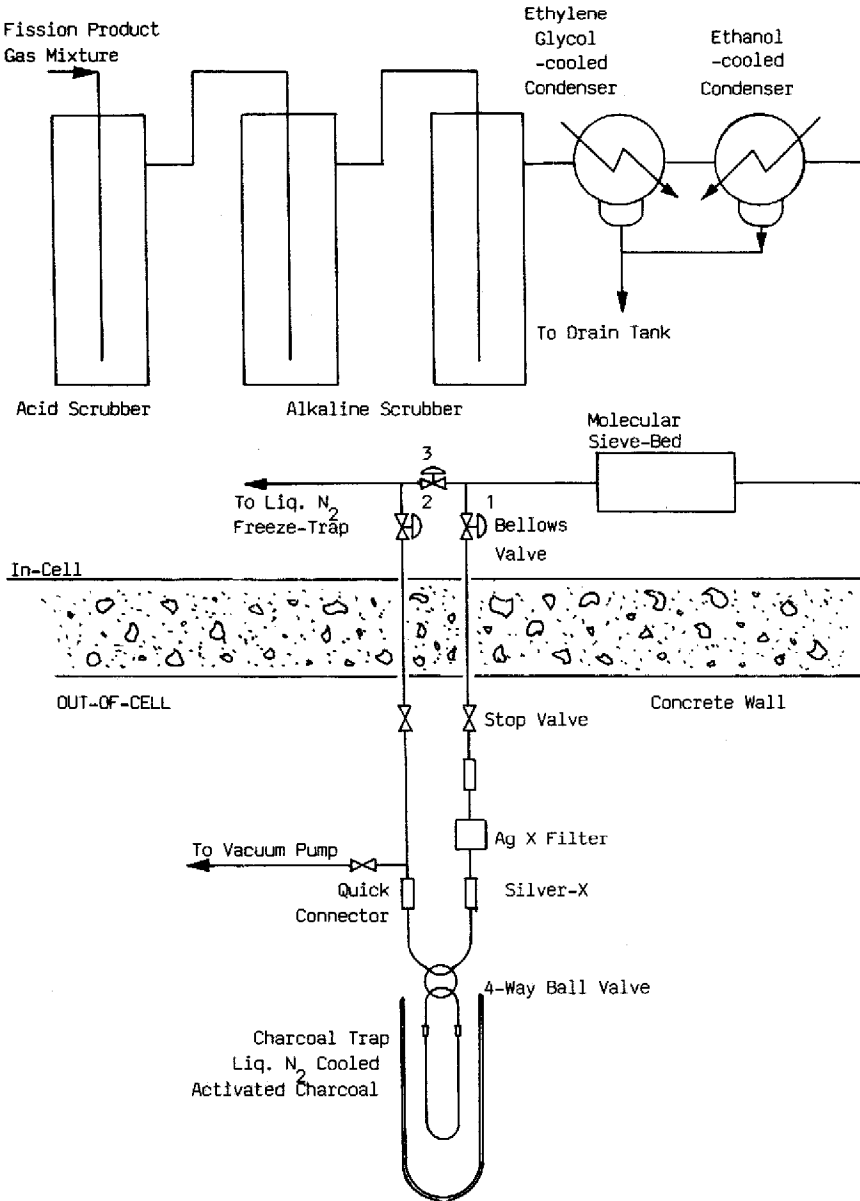

Fig. 1. Rare gas collection from fission product gas mixtures using a charcoal trap.

Off-gas pre-treatment. The in-cell off-gas system provides pre-treatment of the incoming gas stream. Prior trapping of water vapour and other gases such as the oxides of nitrogen and carbon is essential in order to prevent saturation of the adsorber or to avoid plugging of the cold trap. Radioactive iodine is separated by passing off-gases to acid and alkaline scrubbers in sequence. Nitrogen dioxide and carbon dioxide are also trapped in the alkaline scrubbers. Water vapour can be removed by condensation of the off-gas stream and by adsorption on a molecular sieve bed. It was found that the pre-treated inlet gas stream had a dew point below $-78°C$, and trace amounts of radioactive organic iodine had to be separated.

Rare gas collection. The rare gas collection system located out of the cell consists of an inlet–outlet gas line, a silver halide filter and a charcoal trap. Residual organic iodine compounds can be separated by chemisorption using silver zeolite.

The charcoal trap was made from a U-shaped piece of copper tubing; activated charcoal was held in the trap with glass-wool and stainless-steel screens. The copper tube filled with charcoal was accommodated in a Dewar flask. During operation, the liquid nitrogen level was maintained at about 2 in. below the top of the flask, which was covered with two pieces of half-moon Polylon plate. The collection efficiency of the trap was found to be essentially 100% for both xenon and krypton at gas flow-rates below 3 l/min. This trap was also used for the recovery of chromatographically purified xenon.

Principle of chromatographic separation of krypton and xenon

Because the activity of ^{85}Kr (39.5 mCi) is low, application of the chromatographic process with activated charcoal is limited to the purification of ^{133}Xe only. The process sequence is illustrated in Fig. 2, and consists of the following steps.

(1) Adsorption of He–Kr–Xe mixture at room temperature and atmospheric pressure up to the first breakthrough. During this step, the outflowing gas is free of krypton and xenon and is vented to waste.

(2) The adsorption phase is continued. The outflowing gas contains krypton at the same concentration as that in feed gas ($C = C_F$) and is vented to waste.

(3) After the adsorption phase, the adsorber is flushed with helium at room temperature and atmospheric pressure until the krypton concentration in outflowing gas has fallen to $0.001 C_F$. During this flushing step, no significant xenon breakthrough takes place.

(4) Xenon is then desorbed by flushing the adsorber with heated (60°C) helium under atmospheric pressure. The released xenon is collected and concentrated in a liquid nitrogen-cooled charcoal trap.

(5) When xenon desorption is completed, the inlet and outlet valves of the adsorber are closed to keep the adsorbent dry.

The process is based on the concept that the co-adsorbed krypton is more easily desorbed than xenon during the flushing step. This makes it possible to carry out the adsorption–desorption process at normal pressures and temperatures (preferably at room temperature). Sufficient separation of krypton from xenon can be achieved by appropriate control of the adsorption and desorption operation.

Equipment and procedure

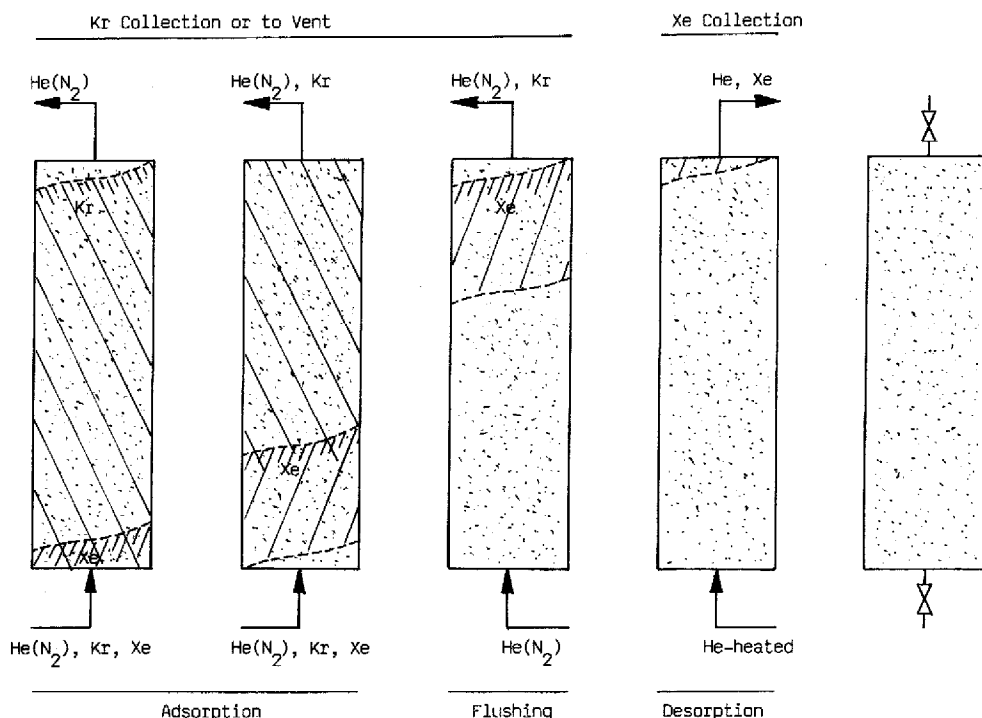A simplified scheme of the experimental equipment is shown in Fig. 3. The

Fig. 2. Basic principle of separation of krypton and xenon by adsorption and desorption.

apparatus makes it possible to adjust various operating parameters such as the gas flow-rate, pressure, carrier gas, temperature, adsorber length, particle size of adsorbent and rare gas concentrations. The flow-rate was controlled by needle valves. Temperature was measured by means of thermocouples and indication controllers. The adsorbers used, 50–100 cm in length and 2 cm I.D., were filled with activated charcoal and preheated with heating tape for 2 h at 60°C under a nitrogen sweep and a negative pressure of 100 Torr.

The operating procedure for a typical run consists of three steps: (1) adsorption, (2) flushing and (3) desorption. For the adsorption step, a flow of dry helium or nitrogen containing a known concentration of admixed krypton or xenon was passed through a charcoal bed at room temperature and under atmospheric pressure. The outlet gas samples were taken with small vacuum bulbs at sufficient intervals to give effluent concentration–time curves. Gas sampling was carried out at constant flow-rates and samples were analysed by gas chromatography[19]. An HP Model 5840 A gas chromatograph (Hewlett-Packard) equipped with a thermal conductivity detector was used. Porapak-Q, Spherocarb and molecular sieve columns were examined for the analysis of the different components involved such as krypton, xenon, hydrogen, nitrogen, oxygen, methane, carbon dioxide, nitrogen dioxide and dinitrogen oxide. The rare gas concentration at the outlet was compared with that at the inlet.

For the flushing step, a flow of helium or nitrogen was passed through the

charcoal bed and the procedure followed was the same as for adsorption. For the desorption step, the charcoal bed was flushed with heated helium or nitrogen under atmospheric pressure and the desorbed gas was sampled in order to measure the xenon concentrations with the gas chromatograph. The chromatographically purified xenon was recovered by using the same charcoal trap as for rare gas collection.

RESULTS AND DISCUSSION

Information on the penetration of rare gases through the charcoal bed is needed in order to specify appropriate desorption conditions for the separation and recovery of the krypton and xenon fractions. In a series of experiments, the effects of flow-rate, carrier gas, temperature, length of charcoal bed, particle size of adsorbent and concentration on rare gas penetration were examined by measuring the shapes and positions of the krypton and xenon breakthrough curves.

Adsorption of krypton and xenon
The effect of nitrogen carrier gas at flow-rates in the range 250–750 ml/min on the breakthrough of krypton and xenon was studied, as shown in Table I. The results indicate that krypton and xenon are separated under the experimental conditions. Decreasing the flow-rate increases the separation efficiency, but consequently also lengthens the separation time. When helium was used as the carrier gas, the same krypton breakthrough curve was observed, but the residence time of xenon was 5.3 min longer. It was also found that krypton and xenon did not affect each other's separation behaviour in the studied concentration range. This is consistent with the results reported by Eshaya and Kalinowski[20].

The effect of temperature on the breakthrough of krypton and xenon was studied at 17 and 28°C with a helium flow-rate of 250 ml/min. The results (Table II) indicate that an increase in temperature reduces the residence time by 32 min for xenon. The Antoine equation[21] for gas adsorption is

$$K_d = \exp[A + B/(C + T)] \tag{1}$$

TABLE I

EFFECT OF CARRIER GAS FLOW-RATE ON THE BREAKTHROUGH OF KRYPTON AND XENON

Charcoal bed, 100 cm × 2 cm I.D.; activated charcoal, 8–14 mesh, 125 g; temperature, 16 ± 1°C; krypton flow-rate, 5 ml/min; xenon flow-rate, 5 ml/min.

Carrier gas	Flow-rate (ml/min)	Column head pressure (kg)	Breakthrough time at C/C_F = 0.5 (min)*	
			Krypton	Xenon
Nitrogen	750	0.7 ± 0.03	6.8	85.8
Nitrogen	500	0.32 ± 0.02	9.1	92.9
Nitrogen	250	0.13 ± 0.01	15.3	133.8
Helium	250	0.05 ± 0.01	15.3	139.1

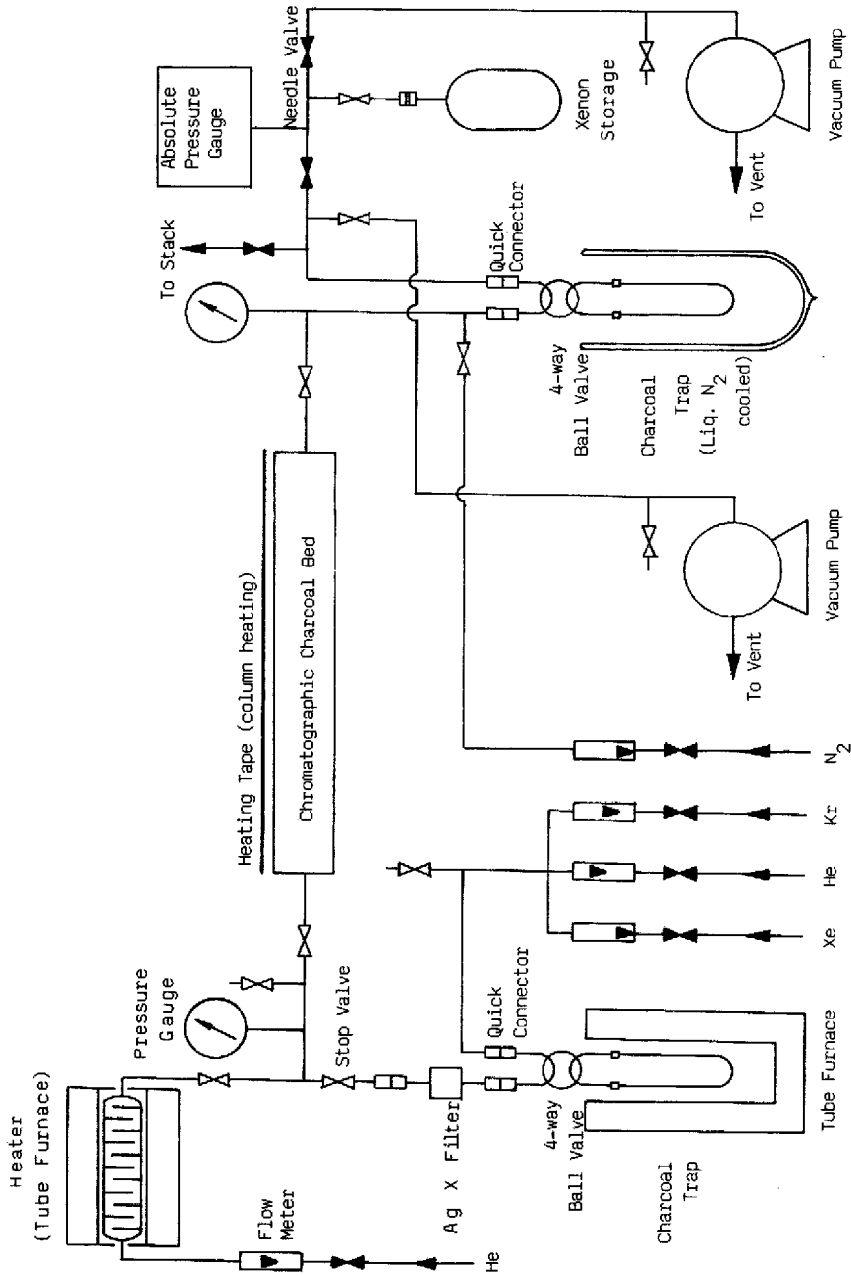* C = concentration; C_F = inlet concentration.

Fig. 3. Experimental equipment for the study of the chromatographic separation of krypton and xenon.

where K_d is the dynamic adsorption coefficient (cm^3/g), A, B and C are constants and T is temperature (°C). The adsorption behaviour of rare gases on activated charcoal can be described in terms of the number of theoretical plates[22], which leads to the conclusion that the predicted breakthrough curves converge to an integral Gaussian distribution equation. The theoretical results show that the mean residence time of the adsorbate gas in an adsorbent bed is given by

$$t_m = \left(\frac{N-1}{N}\right) \cdot \frac{K_d M}{F} \qquad (2)$$

where t_m is the mean residence time (min), N the number of theoretical plates, M the mass of the adsorbent (g) and F the flow-rate of the gas containing the adsorbate (cm^3/min). When the number of theoretical plates is large, eqn. 2 reduces to

$$t_m = \frac{K_d M}{F} \qquad (3)$$

Substituting eqn. 1 into eqn. 3, we obtain

$$\frac{t_m}{t'_m} = \frac{\exp[A + B/(C + T)]}{\exp[A + B/(C + T')]} \qquad (4)$$

which is the working equation used for calculating the breakthrough times for rare gases on activated charcoal. Using eqn. 4, the calculated breakthrough times (at $C/C_F = 0.5$) for krypton and xenon are as shown in Table II. The deviations of the calculated data from the experimental results are possibly due to the different charcoal adsorbents and experimental equipment used[21].

The effect of the bed length on the adsorption of krypton and xenon was investigated. The results show that a 50% reduction in the bed length causes a 50% decrease in the residence times of krypton and xenon. Activated charcoal was used as the adsorbent in this study because it has substantially better adsorption properties than molecular sieves and silica gel. The ratio of the bed diameter to mean particle

TABLE II

EFFECT OF TEMPERATURE ON THE BREAKTHROUGH OF KRYPTON AND XENON

Charcoal bed, 100 cm × 2 cm I.D.; activated charcoal, 8–14 mesh, 125 g; helium flow-rate, 250 ml/min; krypton flow-rate, 5 ml/min; xenon flow-rate, 5 ml/min; column head pressure, 0.05 ± 0.01 kg.

Parameter	Breakthrough time at $C/C_F = 0.5^*$			
	Krypton		Xenon	
Ambient temperature (°C)	17	28	17	28
Experimental result (min)	15	12	139	107
Calculated result (min)	16	11	160	93

* C = concentration; C_F = inlet concentration.

diameter, $20/1.5 = 13$, was sufficient to reduce wall effects to a negligible level. Wall effects might become important if larger charcoal granules were used in the bed. The effect of the particle size of the charcoal on the breakthrough curves was examined at room temperature (*ca.* 29°C) with 8–14, 14–18, 18–25 and 25–50 mesh charcoal. No significant effect was observed in the four experimental runs. The xenon breakthrough time at $C/C_F = 0.5$ was nearly constant. Nevertheless, it was found that the use of higher than 50 mesh charcoal granules would increase the column head pressure.

As the adsorption capacity of a rare gas is reduced in the presence of water vapour on the charcoal bed[2], the use of untreated activated charcoal containing about 10% (w/w) of adsorbed water led to a decrease in the residence time from 59 to 35 min for xenon. Therefore, it is necessary to remove moisture, carbon dioxide and other condensable materials from the activated charcoal before it is used as an adsorbent. The charcoal bed was heated at 60°C and swept with nitrogen gas at 1 l/min under a negative pressure of 100 Torr to remove the undesirable materials.

Fig. 4 shows the effect of the inlet xenon concentration on the breakthrough curves of xenon. Increasing the xenon concentration from 0.64 to 4.00 vol.% causes a decrease in the residence time from 90 to 50 min. Fig. 4 also indicates that the higher the xenon concentration, the sharper is the breakthrough curve. Broadening effects might be expected to dominate the adsorption at very low concentrations of xenon. Certain concentrations of krypton and xenon were used in these experiments to eliminate the possibility of distortion of the breakthrough curves by a non-linear isotherm.

Removal of krypton by flushing

After the adsorption step, the charcoal bed was flushed with carrier gas at the same flow-rate of 250 ml/min until the krypton concentration in the effluent was reduced to less than 0.1 vol.-% of the initial concentration. Fig. 5 indicates that complete removal of krypton is achieved in 40 min with either nitrogen or helium flushing, while xenon at this point is still maintained in the charcoal bed.
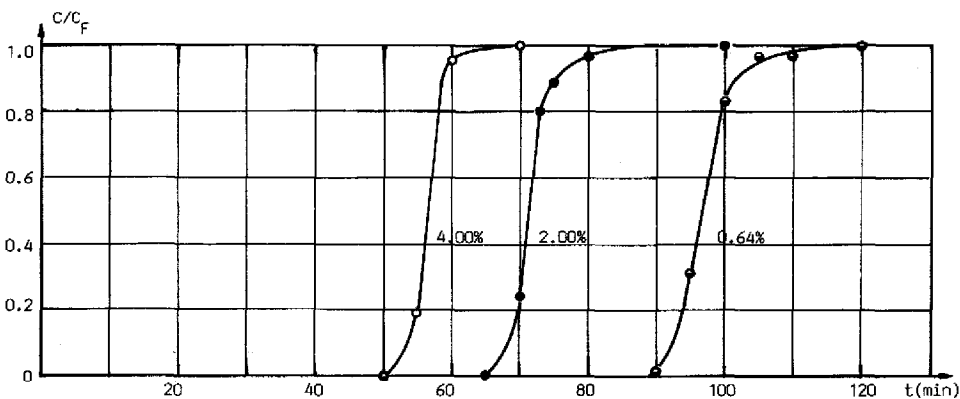

Fig. 4. Effect of xenon concentration on the breakthrough curve at 19 ± 1°C, a helium flow-rate of 250 ml/min and a column bead pressure of 0.05 ± 0.01 kg. C = concentration; C_F = inlet concentration. Charcoal bed, 50 cm × 2 cm I.D.; activated charcoal, 8–14 mesh, 62 g. Xenon flow-rate, ○, 10; ●, 5; and ◐. 1.6 ml/min.
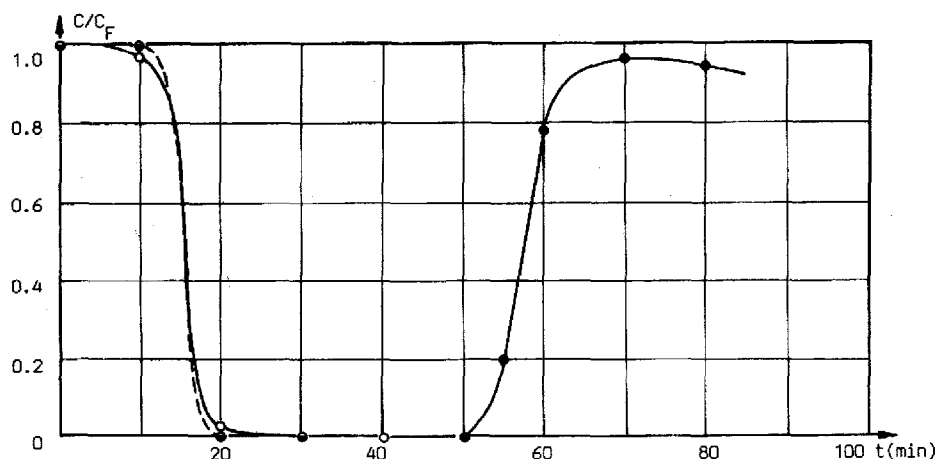
Fig. 5. Variation of krypton and xenon concentrations with time during the flushing step. C = concentration; C_F = inlet concentration. Charcoal bed, 100 cm × 2 cm I.D.; activated charcoal, 8–14 mesh, 125 g; feed gas, helium (250 ml/min) + 2.00% (v/v) krypton + 2.00% (v/v) xenon; adsorption time, 80 min. Temperature, 17°C; helium (nitrogen) flow-rate, 250 ml/min; column head pressure, 0.05 kg (helium) or 0.13 kg (nitrogen). ○, Krypton in helium; ◒, krypton in nitrogen; ●, xenon in helium.

In order to verify the feasibility of the chromatographic separation process, the efficiency of removal of rare gas by flushing in a 50 cm × 2 cm I.D. charcoal bed was examined. Aliquots of xenon and krypton were injected into the liquid nitrogen-cooled charcoal trap, which was then heated at 220°C for 30 min. The released rare gases were then removed with helium carrier gas and fed into the charcoal bed, and the krypton and xenon breakthrough curves were measured. The results in Fig. 6 indicate that a successful separation of krypton and xenon was achieved.

Desorption of xenon

For the study of xenon desorption, a 100 cm × 2 cm I.D. charcoal bed was previously fed with nitrogen (250 ml/min) + xenon (5 ml/min) for 80 min and flushed with nitrogen (250 ml/min) for 40 min at room temperature. The effect of temperature on xenon desorption was examined at a nitrogen flow-rate of 500 ml/min. The results show that the desorption rate increases with the increasing carrier gas temperature. However, desorption at temperatures higher than 250°C is unsafe owing to the fire hazard with activated charcoal beds[23].

The effect of carrier gas flow-rate on desorption at constant temperature (60°C) is shown in Fig. 7. Increasing the nitrogen flow-rate can cause the rapid desorption of xenon and a considerable increase in the column head pressure. With helium flushing for desorption, complete desorption of xenon from the charcoal bed is achieved in 40 min with heated helium at 60°C at a flow-rate of 1000 ml/min. Desorption experiments were also made at various sub-atmospheric pressures with prior evacuation of the adsorber. The experiments showed that xenon was desorbed completely within a relatively short time of 1 h at pressures down to about 100 Torr with nitrogen or helium flushing at 60°C at a flow-rate of 1000 ml/min. However, quantitative collection of the desorbed xenon with a liquid nitrogen-cooled charcoal trap was difficult at this low pressure.
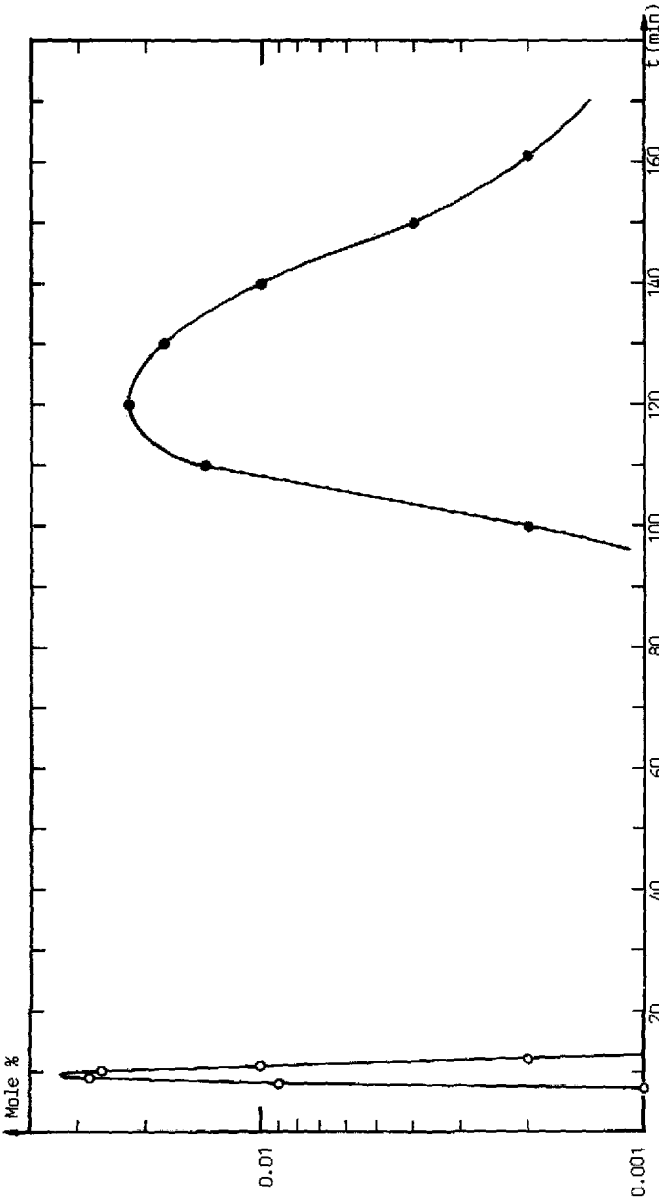
Fig. 6. Variation of krypton and xenon concentrations with flushing time. Feed gas, krypton–xenon–helium mixture from heated charcoal trap. Temperature, 20°C; helium flow-rate, 250 ml/min; column, 50 cm × 2 cm I.D. activated charcoal, 8–14 mesh, 62 g; column head pressure, 0.05 kg. ○, Krypton, 1.2 mg; ●, xenon, 14 mg.
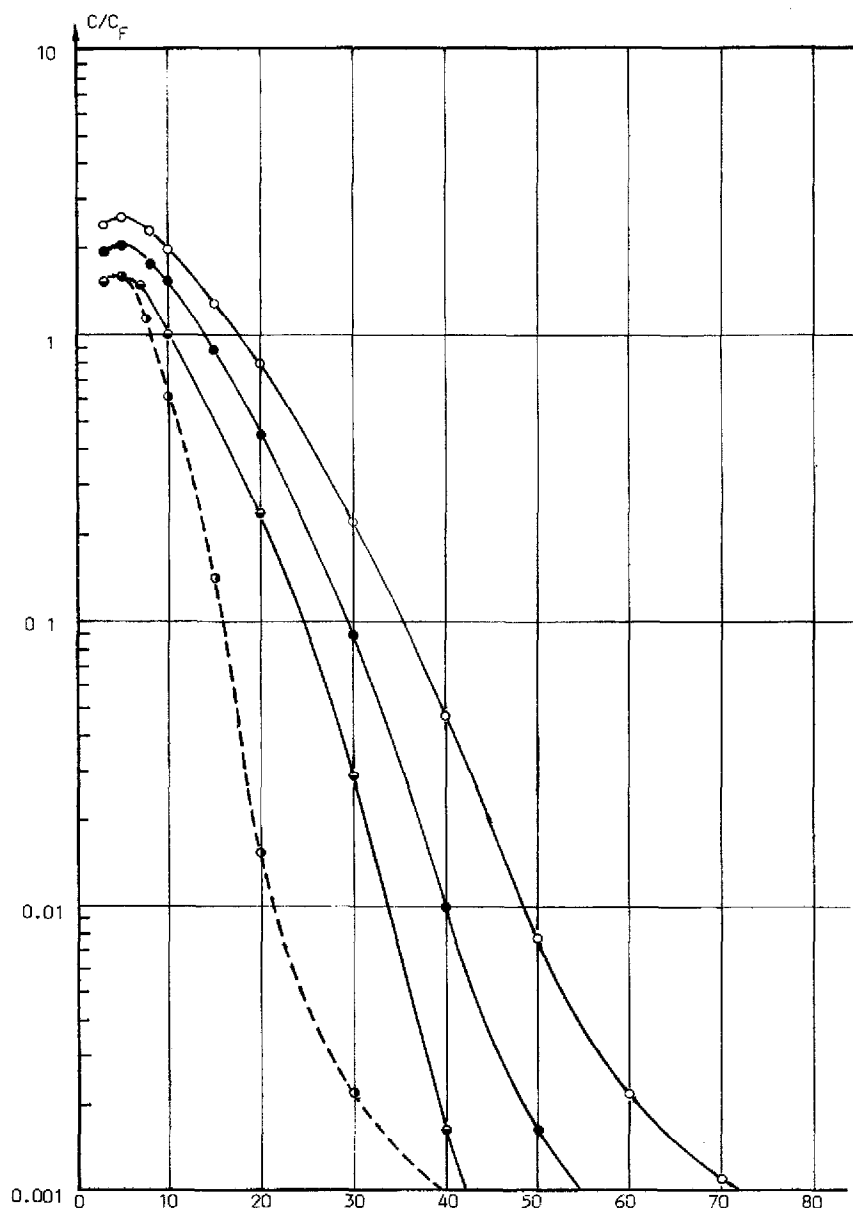
Fig. 7. Xenon concentration *versus* desorption time at different flow-rates. Charcoal bed, 100 cm × 2 cm I.D., activated charcoal, 8–14 mesh, 125 g; adsorption, nitrogen (250 ml/min) + xenon (5 ml/min) for 80 min at room temperature; flushing, nitrogen (250 ml/min) for 40 min at room temperature. Desorption conditions: nitrogen (helium) temperature, 60 ± 1°C; flow-rate and column head pressure, ○, 500 ml/min (nitrogen) and 0.34 ± 0.02 kg; ●, 750 ml/min (nitrogen) and 0.75 ± 0.03 kg; ◓, 940 ml/min (nitrogen) and 1.5 ± 0.05 kg; ◑, 1000 ml/min (helium) and 0.5 ± 0.02 kg.

The results of the above laboratory studies make it possible to suggest a process for the separation of krypton and xenon from fission product gases with activated charcoal. Fig. 8 summarizes the overall procedure for the separation and purification of ^{133}Xe from fission product gas mixtures by charcoal adsorption–desorption.

Dispensation of xenon-133 product

Xenon-133 is administered by either inhalation or injection in saline for medical diagnostic applications. In both instances the activity must be apportioned into unit doses (20–30 mCi) which are suitable for patient use[5]. The most practical method of dispensation of ^{133}Xe is to inject it as a gas in sealed glass ampoules. The dispensing system used is shown in Fig. 9. Basically, it consists of storage facilities of known volume (1000 ml, 100 ml), an absolute pressure gauge, a dispenser and a vacuum
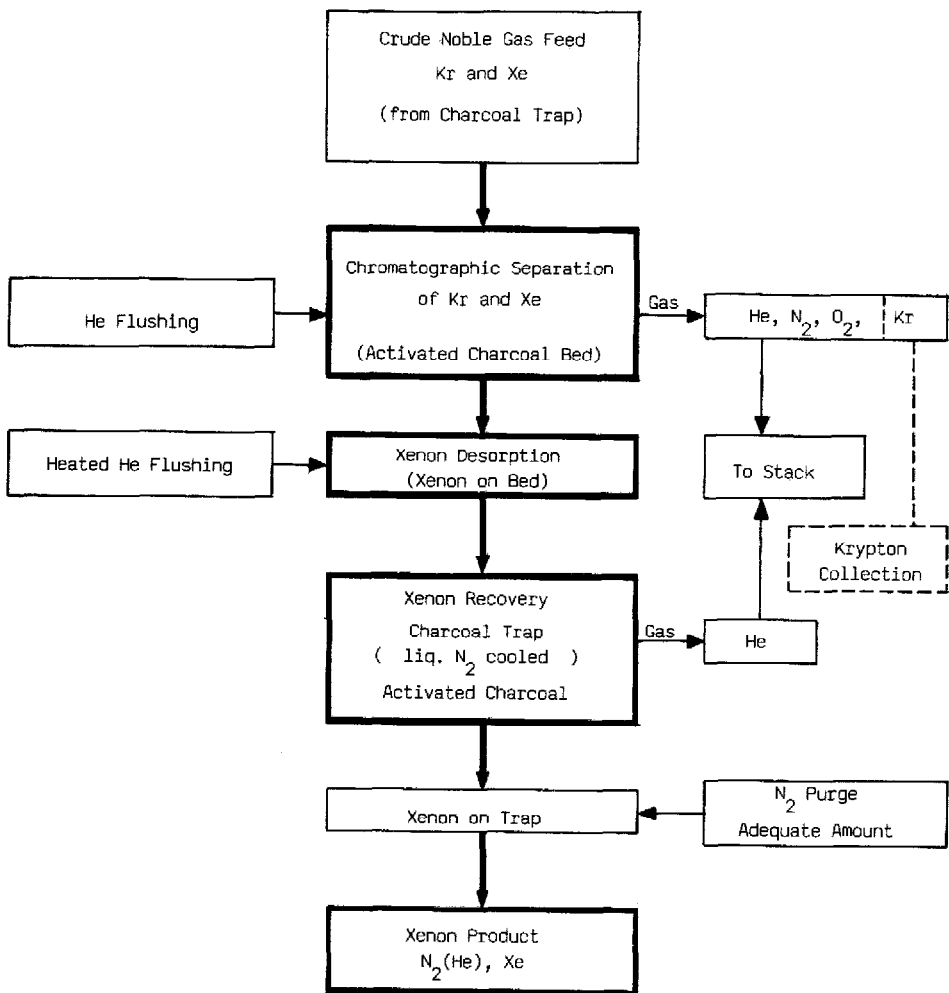

Fig. 8. Chromatographic separation process for recovery of xenon-133 from trapped rare gases.
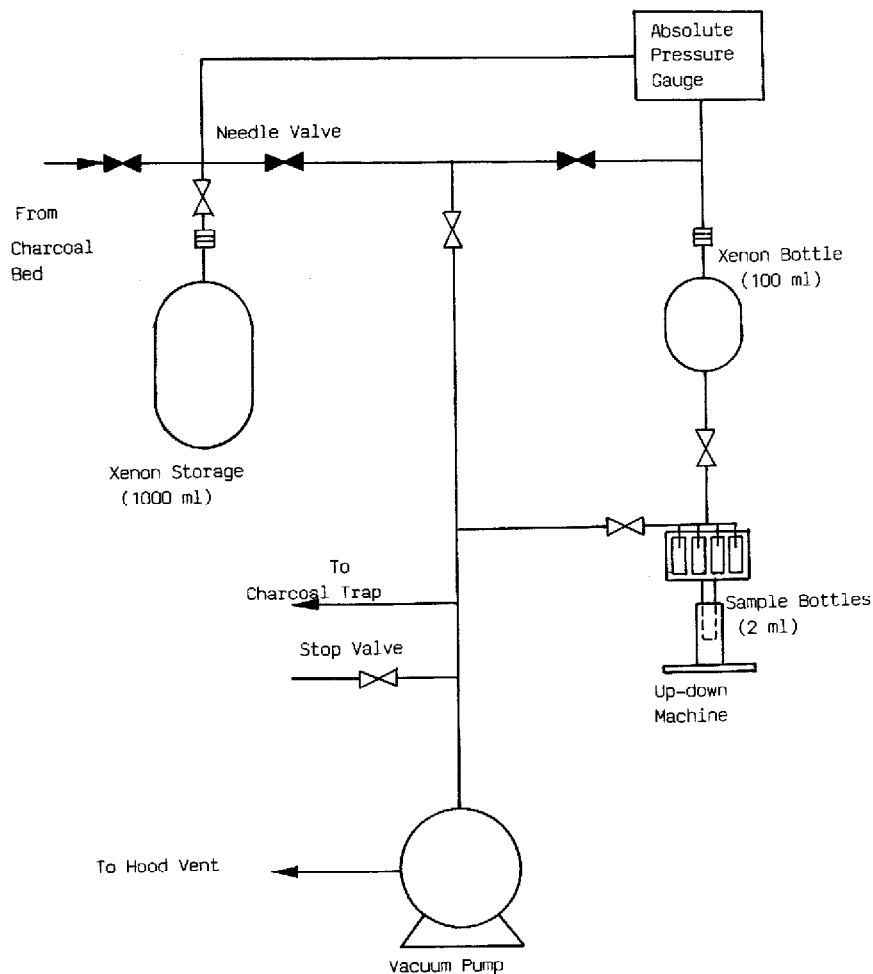
Fig. 9. Xenon-133 dispensing system.

pump. The volume of the sections of the system line is determined from the gas equation $P_1V_1 = P_2V_2$. Dispensation of the ^{133}Xe product is carried out simply by transferring ^{133}Xe quantitatively from the storage bottle to the vacuum bottle upstream to the dispenser. Losses of ^{133}Xe from the dispensing system are inevitable, hence the system should be stored in a well ventilated hood.

CONCLUSION

The charcoal trap of a U-shaped copper tube, filled with activated carbon and cooled in liquid nitrogen, proved very effective for the collection of rare gases. The efficiency of the collection of krypton and xenon is essentially 100% at a flow-rate of helium carrier gas of 3 l/min.

The breakthrough curves (C/C_F vs. t) indicate that the adsorption behaviour of

krypton–xenon–helium mixtures is the same as that of xenon–helium and krypton–helium mixtures in the gas concentration range investigated. From the previous investigation, it is concluded that a 50-cm activated charcoal adsorption column is sufficient for the separation and purification of ^{133}Xe from fission product gases at temperatures below 35°C. This established chromatographic separation process is suitable for the production of ^{133}Xe for medical diagnostic applications in local hospitals.

The advantages of the developed chromatographic separation process are (1) operation at ambient temperature and pressure, (2) cost effective in operation and (3) separation of small amounts of ^{85}Kr and ^{133}Xe to provide a high-purity ^{133}Xe product.

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