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BY NEUTRON ACTIVATION ANALYSIS.
APPLICATION TO HAIR SAMPLES**

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Netherlands Energy Research Foundation

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Netherlands Energy Research Foundation ECN

P.O. Box 1

1755 ZG Petten (NH)

The Netherlands

Telephone (0)2246 - 6262

Telex 57211

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ABSTRACT

- A fast rabbit system for instrumental activation analysis with reactor neutrons is described.
Its use in the determination of selenium in hair is discussed.
- A survey is given of the correction factors which are inherent to the use of short-lived radionuclides.
- An alternative to INAA is NAA based on the separation of arsenic, selenium and antimony by hydride evaporation and adsorption to active carbon.
- Data for some Standard Reference Materials are given.
- This work was done under research contract 2440/RI/RB with the IAEA.

1. INTRODUCTION

- The multi-element analysis of hair samples by instrumental neutron activation analysis (INAA) was the subject of an earlier investigation, undertaken in co-operation with the IAEA [1].

The determinations are based on radionuclides with $T_{1/2} > 3$ minutes. Tentative experiments on the possible application of shorter lived radionuclides indicated that Se and Ag may be determined by way of ^{77m}Se , $T_{1/2} = 17.5$ s and ^{110}Ag , $T_{1/2} = 24.6$ s, if a reliable and fast pneumatic rabbit system is available. The apparatus should meet the following requirements:

- a high thermal neutron flux of $4 \cdot 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$;
- reproducible irradiation times down to 0.1 s;
- constant and short transport times;
- automatic separation of shuttle and sample capsule;
- automatic mounting in the counting position and start of counting;
- multi-sample processing with a sample stock and an automatic administration of sample codes and irradiation and counting conditions;
- magnetic tape storage of γ -ray spectra for off-line processing.

During the period of the present IAEA-contract, this device was realized and tested. A summary of the features and the routine-handling is given in this report.

- Application of short-lived radionuclides inevitably implies an appreciable decrease of sample count-rate over the measuring period. This is often accompanied by high initial total dead-time fractions. For the resulting systematic bias a correction procedure has to be available which fits into the routine analysis. This text gives a survey of the formulae by way of which the correction is applied.
- Some important elements are outside the scope of INAA or at least not determinable in all hair samples. A prominent example is As. Consequently, the possibilities of As-determination by NAA including radiochemical separation were investigated. Mineralization with $\text{Mg}(\text{NO}_3)_2$ and evaporation as the hydride was

chosen to this end.

As it is possible to determine Sb and Se in the same way, these elements were studied too.

- The developed techniques were applied to the ECN in-house hair test material COOG which was also used in the previous study.

2. THE FAST RABBIT SYSTEM FASY IN THE HFR AT PETTEN

2.1. General

- A survey of the state of the art in pneumatic fast rabbit systems is presented in ref. [2]. Applications divide into the determination of short half-lives, delayed neutron counting and INAA. For the last category, a return time of ≥ 0.1 s seems to be sufficient. Essential features are a constant background and capsule-blank, a variable but reproducible time schedule and automatic starting of the counting apparatus at the end of the preset decay-time.
- The present facility is located in a horizontal beam tube (HB-10) of the HFR 45 MW materials testing reactor at Petten, The Netherlands. Figure 1 gives a general view while figure 2 is a schematic view of the conveying system. The apparatus is equipped with an "Ada 2000" computer, a 35 cm³ coaxial Ge(Li) detector in a 4" lead shield lined with 1.5 mm Cd and Cu, and a 4000-channel analyzer with 7-tracks magnetic tape output.

The thermal neutron flux at the irradiation position is
 $4 \times 10^{13} \text{ cm}^{-2} \cdot \text{s}^{-1}$.

2.2. Features of the system

- The conveying time from the end of the irradiation until the arrival in the counting position varies from 150 to 500 ms. This return time depends on pressure setting, total mass of the shuttle and the number of shots made with the same shuttle. Thus it is advisable to use a shuttle only once.
- The shuttle and sample capsule used are shown in figure 3. It permits the separation of shuttle and capsule during their return from the irradiation position. The capsule is held by three notches only, which give way when the shuttle is stopped suddenly on its way back. To prevent the shuttle from oscillating during the

deceleration, it is stopped by an air buffer. The adjustment of the slowing down has to be done in a series of careful and time-consuming preliminary experiments. For the routine use in the measurements mentioned in this report, the return time was found to be ≤ 0.3 s.

- The irradiation position is placed close to the end of the beam tube. In order to reduce gamma heating the irradiation position is surrounded by a lead shield of ≈ 3 cm with a cooling spiral through which a constant water flow is maintained (figure 4). A photocell detects the shuttle outside the beam-tube and serves for irradiation timing.
- The measuring position is surrounded by a lead cell. The transport system (figure 2) enters the cell through one of the 10 holes in the roof of the cell. This gives the possibility of varying the sample detector distances (figure 5).
The internal dimensions are $(800)^3 \text{ mm}^3$ at a lead thickness of 4", lined at the inner side with 1.5 mm sheets of copper and cadmium. A 35 cm^3 coaxial Ge(Li) crystal serves as detector. It is connected to a 4000 channel analyzer with 7-tracks magnetic tape output.
The magnetic tape is transported to the central CYBER computer of ECN and processed according to the procedure described in ref. [3].
- The loading mechanism is placed on top of the lead cell (figure 6). It is equipped with an automatically operating pneumatic control valve.
- Electronic control is possible through a "Televideo" Terminal (figure 1). The programme, written in BASIC, is available. It contains automatic control of the main mechanical and electronic failures. Loading mechanism and multi-channel analyzer are started automatically.

2.3. Testing of the system

- The conveying system was subjected to rigorous out-of-core tests to determine its reliability and to measure the fluctuations in irradiation and return time.

Results are collected in table I. It can be seen that there is no apparent influence of the sample-mass.

2.4. Standardisation

- Standards should be of the same size and shape as the samples to eliminate geometry differences during irradiation and counting. Either aqueous solutions or very pure active carbon, loaded with a known amount of certain elements, may be used.
- Alternatively the standard solutions may be evaporated to dryness. Measurements on 50 μ l aliquots of a ^{133}Ba and a ^{60}Co -solution, mounted in eight different positions through the shuttle, revealed no systematic influence and resulted in the following relative standard deviations:

81 keV	^{133}Ba	4.5 %
356	"	2.3 %
1116	"	2.4 %
1173.2	^{60}Co	1.1 %
1332.5	"	1.0 %

The observed differences are probably due to the (varying) influence of the compton-background in the peak-area determination.

3. DEAD TIME CORRECTION IN THE MEASUREMENT OF SHORT LIVED RADIONUCLIDES

3.1. Formulation of the residual influence of total dead time

- Counting is done in the life-time mode. The measurement is stopped when the total life time becomes equal to the preset counting-time. A residual correction is needed when the radionuclide involved decays appreciably during measurement.

The approach followed here is based on earlier work reported elsewhere [4-6].

- It appears that the residual influence of dead time for countings in the life-time mode can be written as a factor f_{τ} , defined by equation (1).

$$f_{\tau} = \frac{(1 - D_0) \cdot \lambda \cdot T'_m}{[1 - \exp(-\lambda T'_m)]} \int_0^{T'_m} \frac{\exp(-\lambda t)}{(1 - D_0) + D_0 \exp(-\lambda' t)} \cdot dt \quad \dots(1)$$

The meaning of the symbols is:

D_0 = total dead-time fraction at the beginning of the measurement

λ = decay constant radionuclide of interest [s^{-1}]

λ' = average apparent decay constant over the (measured portion of the) γ -ray spectrum [s^{-1}]

T_m = preset counting time [s]

T'_m = extended counting time in the life-time mode [s]

t = time [s]

The value of λ' may be obtained from the variation of the total dead-time fraction over the measuring period:

$$\lambda' = \frac{1}{T'_m} \cdot \ln \frac{1 - D_T}{D_T} \cdot \frac{D_0}{1 - D_0} \quad \dots(2)$$

where D_0 is the D-value at the beginning and D_T that at the end of the (life-time mode) measurement.

From the experimental D versus t curves it may be deduced whether a single λ' is sufficient to describe the decay of the sample during measurement [6], as supposed in the derivations of equations (1) and

(2). In any case, λ' may be translated into an average (matrix) half life $(T_{1/2})' = (\ln 2)/\lambda'$.

Table II gives f_{τ} as a function of $(T_{1/2})'$ for the radionuclide ^{77m}Se , $T_{1/2} = (17.8 \pm 0.3)$ s, at a preset counting-time of 60 s and D_0 values 0.02 - 0.3. The integral in expression (1) has to be solved numerically. A programme for a PDP-11, written in CLASS, serves this purpose.

- The value of f_{τ} increases with the allowed decay time. Thus it is possible to estimate the optimal counting conditions by considering the product $f_{\tau} \cdot e^{-\lambda t}$ as a function of $t =$ decay time. However, the statistical error in the net number of counts is also governed by the Compton background and its decay.

3.2. The combination of the correction for dead time and pile-up losses

- When a Ge(Li) detector is used, the effect of pile-up has to be considered. It may be measured with an electronic pulser. It can be asked now whether the corrections for pile-up and residual dead-time losses may be combined.
- The pile-up losses are due to spurious coincidences in the pre-amplifier. They can be described by a (formal) dead time τ' , per pulse which may change over the measuring period due to variations in the γ -ray spectrum. If then τ is the dead time in the ADC one arrives at the formalism given in table III. The calculation of f (equation 3), the loss factor which includes pile-up phenomena, implies knowledge of τ'/τ . This ratio follows from the application of equation (4) to pulser-peak losses in γ -ray spectra of long-lived radionuclides, recorded with the same measuring chain. Usually it is around 0.2 - 0.3.
- The separate corrections for pile-up and residual dead-time losses, using equations (1) and (4), may be combined to the simultaneous correction by way of equation (3). For τ'/τ -values up to 0.5, the results differ less than 0.5% while for $\tau'/\tau \leq 1$ the final systematic bias is 1% or less.

3.2. Experiments

- The experimentally determined variation of the total dead-time fraction D with time is given in table IV, together with the corresponding $(T_{\frac{1}{2}})'$ -values, for some relevant matrices.

- The $(T_{\frac{1}{2}})'$ of hair increases rapidly with the decay-time, approximately according to

$$(T_{\frac{1}{2}})' = 120 \cdot \exp(-3.2 \times 10^{-3} \cdot t) \dots \dots (6^a)$$

For nail one arrives at

$$(T_{\frac{1}{2}})' = 150 \cdot \exp(-2.2 \times 10^{-3} \cdot t) \dots \dots (6^b)$$

For granite, coal and fly-ash the value of $(T_{\frac{1}{2}})'$ does not differ significantly from the half-life of ^{28}Al : $T_{\frac{1}{2}} = 135$ s. In rainwater there exists an initial contribution from ^{19}O , $T_{\frac{1}{2}} = 27.1$ s.

- The ratio τ'/τ was measured as 0.29 ± 0.03 (σ) for a series of sediment samples with a measuring chain consisting of:

- "Harshaw" 60 cm³ flat coaxial Ge(Li) detector.
- "Harshaw-NB 21" preamplifier.
- "Ortec Type 471" spectroscopy amplifier.
- "Elscint HV-N-1A" HV (2500 V) power supply
- "BNC model DB-2" random pulse-generator (500 c.s⁻¹)
- "Didac 4000" channel analyzer.

- The γ -ray spectrum of hair after a short irradiation in the fast rabbit system is given in figure 7. Figure 8 gives the blank γ -spectrum.

The following radionuclides may be assayed quantitatively. The order is that of decreasing specific count-rate.

^{77m}Se	162 keV	6×10^4 c. μg^{-1}	at an irradiation-time of 30 s,
^{110}Ag	658	6×10^4	a decay-time of 5 s and a counting-
^{177m}Yb	104	2×10^4	time of 40 s.
^{52}V	1434	3×10^4	
^{56}Mn	847	$1 \cdot 10^4$	
^{66}Cu	1039	1.5×10^2	
^{51}Ti	320	1×10^2	
^{128}I	441	1×10^2	

4. THE DETERMINATION OF ARSENIC, ANTIMONY AND SELENIUM IN DRY
BIOLOGICAL MATERIAL

4.1. General [7, 8]

- Rapid and sensitive procedures for the determination of As, Sb and Se may be based on reactor neutron activation and open mineralization with a saturated $\text{Mg}(\text{NO}_3)_2$ -solution, followed by hydride evaporation and adsorption to active carbon. This adsorber is then counted for the γ -rays of ^{76}As , ($T_{1/2} = 26.4 \text{ h}$); ^{122}Sb , ($T_{1/2} = 2.7\text{d}$) and ^{75}Se , ($T_{1/2} = 120 \text{ d}$).
- It is necessary to determine Se separately. Both the long half-life of ^{75}Se and the necessity to reduce possibly present hexavalent Se to the four-state press for this.
- The limits of determination are of the order of 10 ng for all three elements.

4.2. The determination of arsenic and antimony

4.2.1. Reagents and apparatus

- | | |
|--|--|
| - NaBH_4 p.a. | - Hydride generation apparatus with |
| KI p.a. | a septum for NaBH_4 injection |
| α -ascorbic acid p.a. | (see figure 10) |
| HCl, "Suprapur" or "p.a." | - Heating plate |
| $\text{Mg}(\text{NO}_3)_2$ p.a. saturated solution | - Muffle furnace (min.: 500 °C) |
| Pressurizer He as carrier gas | |

4.2.2. Tracer experiments

- Tracer experiments with ^{74}As and ^{124}Sb were carried out to check the recovery of As and Sb from the $\text{Mg}(\text{NO}_3)_2$ mineralization and the recovery of the hydride generation. Both steps gave quantitative yields within the experimental error. Previous experiments with H_2SO_4 - HNO_3 in a teflon-lined pressure decomposition vessel resulted in incomplete hydride generation with variable recoveries of 70 - 90%, probably due to incomplete destruction.

As antimony (V) is reduced more slowly by NaBH_4 than antimony (III) a reduction with KI and L-ascorbic acid is required to convert all forms of arsenic present in the sample to the trivalent state. Grains of active carbon are used for collection of the hydrides. With a segmented adsorber the collection efficiency was checked and 1 gram of carbon proved to be quite sufficient.

4.2.3. Procedure

4.2.3.1. Sample preparation and irradiation

- Approximately 300 mg of sample is dried according to NBS specifications or in a freeze-dryer, transferred to a polythene capsule and weighted.
- Standards of As and Sb are prepared by pipetting 50 μl aliquots of standard solutions (As : $200 \mu\text{g}\cdot\text{ml}^{-1}$, Sb : $200 \mu\text{g}\cdot\text{ml}^{-1}$) on pure active carbon (home-made quality) in vials as used for the samples.
- Thin iron rings are used as flux monitors and mounted on top of every individual vial.
- Samples and standards are irradiated for 2 hours in a rotating facility at a thermal neutron flux of $2.10^{12} \text{ cm}^{-2}\cdot\text{s}^{-1}$.

4.2.3.2. Mineralization of samples

After cooling for ≈ 12 hours the samples are transferred to 100 ml beakers, to which 5 ml of saturated $\text{Mg}(\text{NO}_3)_2$ solution is added. Care should be taken to immerse the samples completely.

- The beakers are placed on a hot plate and the solutions evaporated to dryness by heating slowly to $\approx 200^\circ\text{C}$. Then an extra 5 ml of saturated $\text{Mg}(\text{NO}_3)_2$ solution is added so as to immerse incompletely mineralized parts of the sample. The beakers are placed on the hot plate and again heated to $\approx 200^\circ\text{C}$.
- When the samples are dry, the beakers are heated in a muffle oven to $\approx 450^\circ\text{C}$ for 30 minutes. A white residue is obtained.
- This residue is dissolved in 30 ml 6N HCl.
- The total procedure takes ≈ 4 hours per 20 samples if 5 hydride generators are used simultaneously.

4.2.2.3. Hydride generation

- The solution is transferred to the hydride generation vessel, which is closed. A stream of He is passed through the solution at a rate of $1 \text{ l} \cdot \text{min}^{-1}$ to carry the hydrides formed to the carbon absorber.
- Through the septum 2 ml 0.2 M KI-10%(w/v) L-ascorbic acid is added. Then 5 ml of 15% NaBH_4 is introduced.
- After 2 minutes a second injection of NaBH_4 follows. After a total reaction time of 4 minutes the He-flow is stopped and the carbon adsorber transferred to a testtube for counting.

4.2.2.4. Counting

- Samples and standards are counted on a Ge(Li) detector coupled to a multichannel analyzer. The spectra are recorded on tape and processed by a computer program, which accounts for partial overlap of photo-peaks, corrects for pulse-pile up by a pulser, for decay and sample weights.
- The thin iron rings are measured in a 3 x 3 inch NaI detector coupled to a 400-channel analyzer. The 1292 keV photopeak area is normalized against previously determined count rates for this ^{59}Fe peak. The specific count rates for the 559 keV peak of ^{76}As ($T_{1/2} = 26.4 \text{ h}$) and the 564 keV peak of ^{122}Sb ($T_{1/2} = 2.68 \text{ d}$) at the end of a 2-hours irradiation at $2.10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ are 3800 cpm per $\mu\text{g As}$ and 1650 cpm per $\mu\text{g Sb}$ respectively.

4.2.4. Results

- The data obtained for the IAEA and NBS (Standard) Reference Materials (table V) are in good agreement with earlier literature data [7].

4.3. Determination of selenium

4.3.1. The reduction of Se^{VI}

- The mineralization of the sample is identical to that applied for the determination of As and Sb.
Then however, it is mandatory to reduce the hexavalent element to the

tetravalent state. This should be done in an oxygen free atmosphere to eliminate the risk of re-oxidation.

- A convenient procedure is the refluxing of the solution, obtained by dissolving the white MgO-residue from the muffle oven heating (cf. section 4.2.3.2.) in as small as possible an amount of 6N HCl, with 20 ± 5 ml 7N HCl in a round bottom flask under a He-atmosphere for ≥ 30 minutes. The added HCl should have been deaerated with He. It is essential to allow the resulting solution to cool down to room temperature before starting the hydride volatilization. The (cooled) solution is transferred to the evaporation vessel and the round-bottom is rinsed with 10 ml 7N deaerated HCl. The vessel should then be deaerated with He-gas for 15 minutes at a flow-rate of 2 l.m^{-1} .

4.3.2. Standardization, irradiation and γ -ray energy

- Standards are prepared by pipetting 10-50 μl aliquots of a standard solution of Se ($50 \mu\text{g.ml}^{-1}$) on pure (home-made) active carbon.
- Irradiation takes 6-12 h at $2.10^{12} \text{ cm}^{-2}\text{s}^{-1}$ in the low flux rotating facility.
- The γ -ray energies of 121.1; 136.0; 264.6 or 279.6 keV are used in case of counting with a flat coaxial Ge(Li) detector. If a well-type crystal is used, the 401 keV (sum-)peak can be applied too. The latter option has been used for the hair analysis.

The specific count-rates are, for an irradiation of 12 h at $\sim 3.10^{12} \text{ cm}^{-2}\text{s}^{-1}$ and counting with a 90 cm^3 well-type Ge(Li) detector.

121.1 keV	3.85×10^3	$\text{c.}\mu\text{g}^{-1}.\text{h}^{-1}$
136.0	1.25×10^4	
264.6	3.7×10^3	
279.6	2.65×10^3	
401.0	3.0×10^3	

Figure 9 gives the γ -ray spectrum of the Se counting-aliquot obtained from a hair sample.

- The standard deviation due to peak-area determination features the predicted shape [9].

The determination on Standard Rocks by the hydride technique (cf. ref. 8) may be used here as the spectra of the separated counting-
aliquots are independent of the original matrix.

One finds $\sim 1.5\%$ at $1 \mu\text{g.g}^{-1}$, $\sim 5\%$ at 50 ng.g^{-1} ; $\sim 10\%$ at 35 ng.g^{-1} , $\sim 35\%$ at 10 ng.g^{-1} and $\sim 70\%$ at 4 ng.g^{-1} .

4.3.3. Results

- Data for some (Standard) Reference Materials are given in table VI.
If possible, Se was determined by INAA too. These results are given for comparison.

5. THE ANALYSIS OF HAIR

5.1. Sample material

The developed techniques were applied to the in-house test material "COOG" discussed in our previous report [1].

The material was sampled and cleaned according to IAEA regulations.

5.2. Use of the fast rabbit system

The determination of Se in hair by way of ^{77m}Se , $T_{1/2} = 17.8$ s, was tested for routine applications. Conditions are:

irradiation-time: 30 s	or	30 s	Aliquot-mass: 30-50 mg
decay-time : 5 s		5 s	
measuring-time : 20 s		40 s	

Results are given in table VII, together with those for 10-50 mg aliquots of some other biological materials and some SRM's.

5.3. Application of the hydride technique

- The elements As, Sb and Se were determined using the following radio-nuclides and γ -ray energies:

^{76}As	$T_{1/2} = 26.4$ h	559.2 and 657.0 keV
^{112}Sb	2.7 d	564.0 keV
^{75}Se	120 d	121.0; 136.0; 279.6 and 401.0 keV.

Results are summarized in table VIII. Aliquots masses are = 200 mg.

It should be noted that the count-rate under the 657.0 keV peak of ^{76}As is much lower than that under the 559.2 keV.

5.4. Comparison of the two techniques for the determination of selenium

- The inhomogeneity of "COOG" is reflected by the data. The repeated runs on one aliquot give reproducible results. Different portions of the sample tend to feature marked variations.
- For routine purposes INAA with the fast rabbit system is the preferred technique. The hydride separation with its resulting low compton-background is to be reserved for reference purposes.

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Table I. Sending- and return-time of the shuttle in the fast rabbit system at the conditions for routine analysis

<u>Load</u>	<u>Sending-time</u>	<u>Return-time</u>
Empty shuttle and capsule	540 \pm 20 m.s	290 \pm 20 m.s
+ 250 mg	530 \pm 20	290 \pm 20
+ 500 mg	550 \pm 20	290 \pm 10

Quoted uncertainties are standard deviations.

Table II. The loss-factor f as a function of the total dead-time fraction for ^{77m}Se ($T_{1/2} = 17.8$ s) at various average (matrix) half-lives.

D_o	$(T_{1/2})'$				
	30 s	60 s	120 s	300 s	60 min.
0.020	0.986	0.986	0.985	0.985	0.985
0.040	0.978	0.977	0.976	0.975	0.975
0.060	0.970	0.968	0.966	0.965	0.965
0.080	0.962	0.958	0.956	0.955	0.954
0.100	0.953	0.949	0.946	0.944	0.943
0.120	0.944	0.939	0.936	0.934	0.932
0.140	0.935	0.929	0.925	0.923	0.921
0.160	0.926	0.918	0.914	0.911	0.909
0.180	0.916	0.908	0.903	0.900	0.898
0.200	0.907	0.897	0.891	0.888	0.885
0.220	0.897	0.886	0.879	0.875	0.873
0.240	0.886	0.874	0.867	0.862	0.860
0.260	0.876	0.862	0.854	0.849	0.846
0.280	0.865	0.850	0.841	0.836	0.832
0.300	0.854	0.838	0.828	0.822	0.818

Table III. Formulation of the loss-factor due to pile-up and dead-time in the measurement of short-lived radionuclides

Loss-factor (f_{τ}) for the photopeak due to ADC dead-time only:

$$f_{\tau} = \frac{(1 - D_0) \cdot \lambda}{[1 - \exp(-T_m)]} \int_0^{T'_m} \frac{\exp(-\lambda t)}{(1 - D_0) + D_0 \exp(-\lambda' t)} dt \dots (1)$$

The average (matrix) decay-constant λ' is obtained from

$$\lambda' = \frac{1}{T'_m} \cdot \ln \frac{1 - D_T}{D_T} \cdot \frac{D_0}{1 - D_0} \dots (2)$$

Including pile-up in the pre-amplifier the loss-factor (f) becomes:

$$f = \frac{\lambda}{\lambda(1 - e^{-T_m})} \int_0^{T'_m} \exp(-\lambda t) \left[1 - \frac{D_0 \cdot \overline{\tau'/\tau} \cdot e^{-\lambda t}}{(1 - D_0) - D_0 \cdot \overline{\tau'/\tau} \cdot e^{-\lambda t}} \right] \left[\frac{(1 - D_0)}{(1 - D_0) + D_0 e^{-\lambda t}} \right] d(\lambda t) \dots (3)$$

The loss-factor for the pulser-peak (f_p) can be written as:

$$f'_p = \frac{1}{\lambda T'_m} \int_0^{T'_m} \left[1 - \frac{D_0 (\overline{\tau'/\tau}) \cdot e^{-\lambda t}}{(1 - D_0) - D_0 (\overline{\tau'/\tau}) \cdot e^{-\lambda t}} \right] \cdot \left[\frac{1 - D_0}{(1 - D_0) + D_0 e^{-\lambda t}} \right] d(\lambda t) \dots (4)$$

For measurements on long-lived radionuclides this equation may be reshaped into:

$$\overline{\tau'/\tau} = (1 - f'_p) \cdot T_m \cdot (T'_m - T_m)^{-1} (2 - f'_p)^{-1} \dots (5)$$

The ratio $\overline{\tau'/\tau}$, averaged over the measurement, can thus be determined experimentally.

Symbols:

- D_0 = total dead-time fraction at the beginning of the measurement
- λ = decay constant radionuclide of interest [s^{-1}]
- λ' = average apparent decay constant over the (measured portion of the) γ -ray spectrum [s^{-1}]
- T_m = preset counting time [s]
- T'_m = extended counting time in the life-time mode [s]
- t = time [s]
- τ = dead-time per pulse in the ADC [s]
- τ' = pile-up dead-time in the pre-amplifier [s]

Table IV. Variation of the total dead-time fraction, D, and the apparent (matrix) half-life, $(T_{1/2})'$, for various matrices after a short irradiation.

All times in seconds

<u>Matrix and mass</u>	<u>Irradiation-time</u>	<u>Decay-time</u>	<u>D</u>	<u>$(T_{1/2})'$</u>
Hair 112.5 mg	120	30	0.40	180
		210	0.25	300
		390	0.18	570
		570	0.15	> 2000
		810	0.14	> 2000
		1050	0.13	
Nail 56.1 mg	10	90	0.40	125
		270	0.20	360
		450	0.15	270
		630	0.10	510
		810	0.08	> 800
		990	0.08	
Granite (USGS-G2) 12.8 mg	1	150	0.42	
		270	0.30	
		390	0.18	135 ± 21
		510	0.10	
		630	0.08	
		750	0.04	
Coal 41.3 mg	1	10	0.40	
		130	0.22	
		250	0.13	
		370	0.09	132 ± 45
		490	0.05	
		620	0.03	
		730	0.01	
Fly-ash 12.3 mg	1	60	0.42	
		180	0.30	
		300	0.18	
		420	0.10	141 ± 21
		600	0.05	
		780	0.02	
Rain water 700 mg	120	20	0.40	35
		110	0.10	85
		200	0.05	265
		290	0.05	
		380	0.04	

Table V. Results for NBS- and IAEA biological reference materials

SRM/RM	As		Sb	
	This work	Literature	This work	Literature
Orchard leaves SRM 1571	9.76 ± 0.17	10*, 9.94, 9.68	2.90 ± 0.09	2.9*
Bovine liver SRM 1577	0.046 ± 0.002	(0.055)*, 0.046, 0.053, 0.08	0.005 ± 0.002	0.015
Spinach SRM 1570	0.147 ± 0.001	0.150*, 0.120	0.038 ± 0.003	(0.040)*, 0.027
Tomato leaves SRM 1573	0.225 ± 0.003	0.27*, 0.26	0.030 ± 0.001	0.040
Pine needles SRM 1575	0.181 ± 0.003	0.21*, 0.20	0.185 ± 0.003	(0.200)*, 0.180
Wheat flour V2/1-74	0.020 ± 0.001	0.24**, 0.035, 0.013	0.005 ± 0.002	0.008
Animal muscle H4-13	0.005 ± 0.001	0.0074**, 0.0051	<0.002	<0.02
Animal bone A3-74	1.039 ± 0.010	-	0.170 ± 0.005	-
Animal blood A2-74	0.198 ± 0.005	0.212	0.045 ± 0.002	0.045
Fish solubles A6-75	15.80 ± 0.30	14.5**, 17	0.154 ± 0.006	0.072
Bowen's kale	0.098 ± 0.004	0.101, 0.111, 0.14	0.039 ± 0.001	0.070

Table VI. Results for the determination of selenium by the hydride technique and by INAA in some (Standard) Reference Materials.

All data in $\mu\text{g.g}^{-1}$.

<u>Material</u>	<u>Issued by</u>	<u>Certified value</u>	<u>INAA</u>	<u>This work Hydride</u>
SRM-1566 Oyster tissue	NBS	-	1.77±0.05	1.64±0.06
SRM-1577 Bovine liver	NBS	1.1±0.1	0.90±0.06	1.02±0.03
SRM-1577 Spinach	NBS	-	-	0.10±0.01
SRM-1573 Tomato leaves	NBS	-	-	0.09±0.01
SRM-1575 Pine needles	NBS	-	-	0.07±0.01
H-4 Animal muscle	IAEA	-	-	0.29±0.03
MA-A-1 Copepod homogenate	IAEA	3.4±0.5	2.35±0.15	2.85±0.15
MA-A-2 Fish homogenate	IAEA	1.7±0.3	0.75±0.06	1.05±0.15
Standard Kale	H.J.M. Bowen (Univ.of Reading)	-	0.14 (see ref.[10])	0.13±0.01

Table VII. Results for Se in the in-house test material "COOG"
and two Standard Materials by INAA on the
162 keV γ -line of ^{77m}Se .

Specific count-rates:

First run : $(4.52 \pm 0.25) \cdot 10^4$ μg^{-1}
Second run: $(6.78 \pm 0.40) \cdot 10^4$

Material	Aliquot number	Aliquot mass in mg	$\mu\text{g Se.g}^{-1}$	
			First run	Second run
Hair				
	1	54.4	4.1	-
	2	41.3	4.2	4.2
	3	33.3	4.2	4.2
	4	26.6	2.5	3.9
	5	61.7	3.3	2.8
	6	63.5	-	4.2
	7	47.0	-	3.4
Bovine liver SRM 1577				
	1	19.3	1.0	-
	2	11.6	-	1.2
Animal muscle SM IAEA H4-13				
	1	32.4	0.25	-
	2	55.0	-	0.30
Home-made pure active carbon				
	1	118.0	0.09	-
	2	151.4	-	0.07

The standard deviations due to counting-statistics and compton subtraction are:

Hair : 2-4 %

Bovine liver : 10-15 %

Animal muscle : 25-30 %

Active carbon : 20-25 %.

Table VIII. Results for As, Sb and Se in the in-house test material "COOG" obtained by the hydride technique

Aliquot No.	Arsenic ₋₁ in ng.g		Antimony in ng.g ⁻¹	Selenium in µg.g ⁻¹			
	559.2 keV	657.0 keV	564.0 keV	121.0 keV	136.0 keV	279.6 keV	401.0 keV
1	67	83	40	-	-	-	-
2	64	65	43	2.4	2.5	2.6	2.3
3	73	67	44	2.0	2.4	2.3	1.8
4	60	55	38	2.0	2.0	1.9	1.9
5	70	64	48	2.7	3.0	2.9	3.6
6	75	70	40	2.5	2.4	2.4	2.1
7	69	89	39	2.6	2.8	2.7	2.9
8	74	78	31	2.3	2.4	2.4	2.3
Average and σ	69 ± 5	71 ± 11	40 ± 5	2.4 ± 0.3	2.5 ± 0.3	2.5 ± 0.3	2.4 ± 0.6

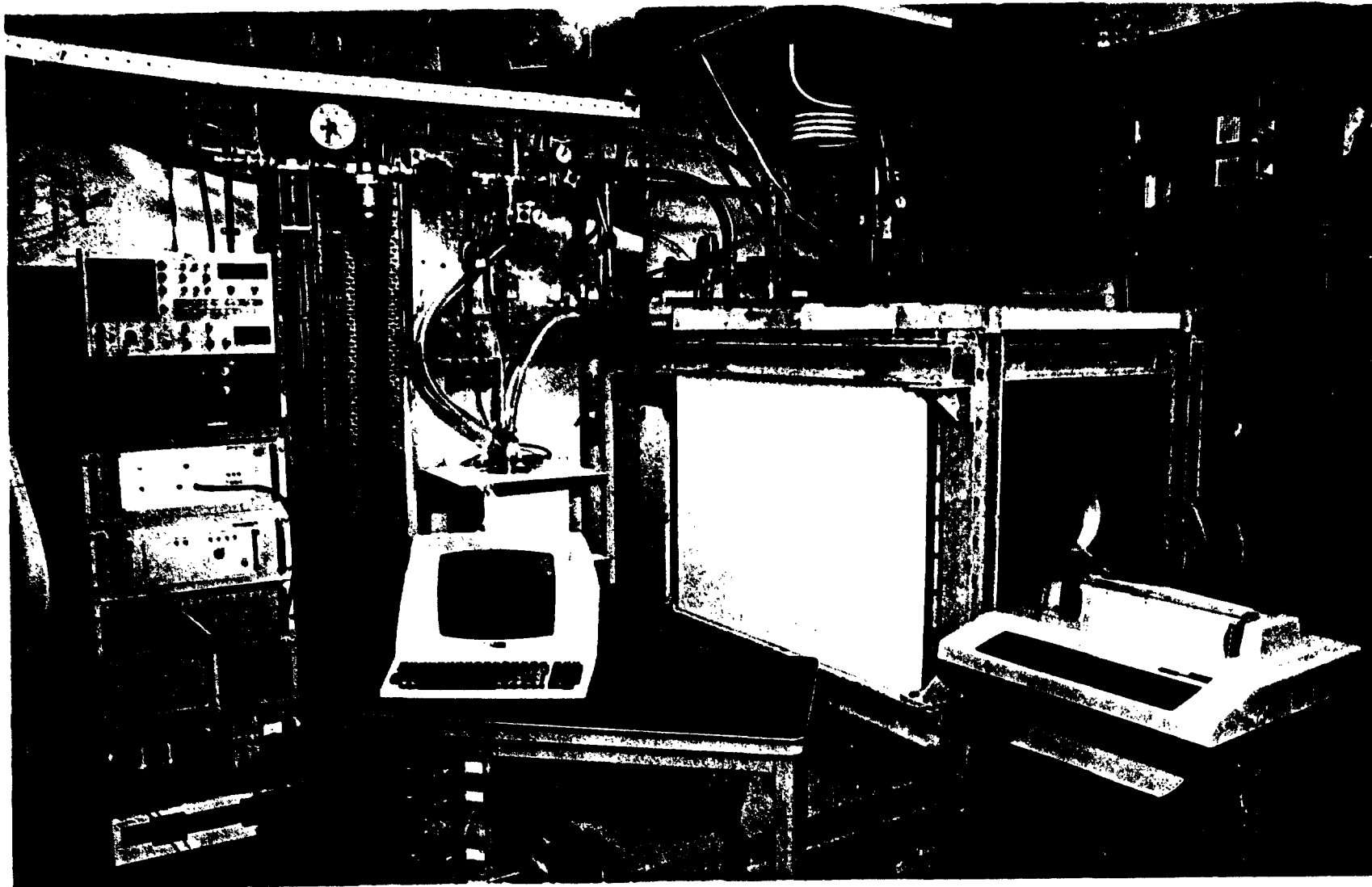
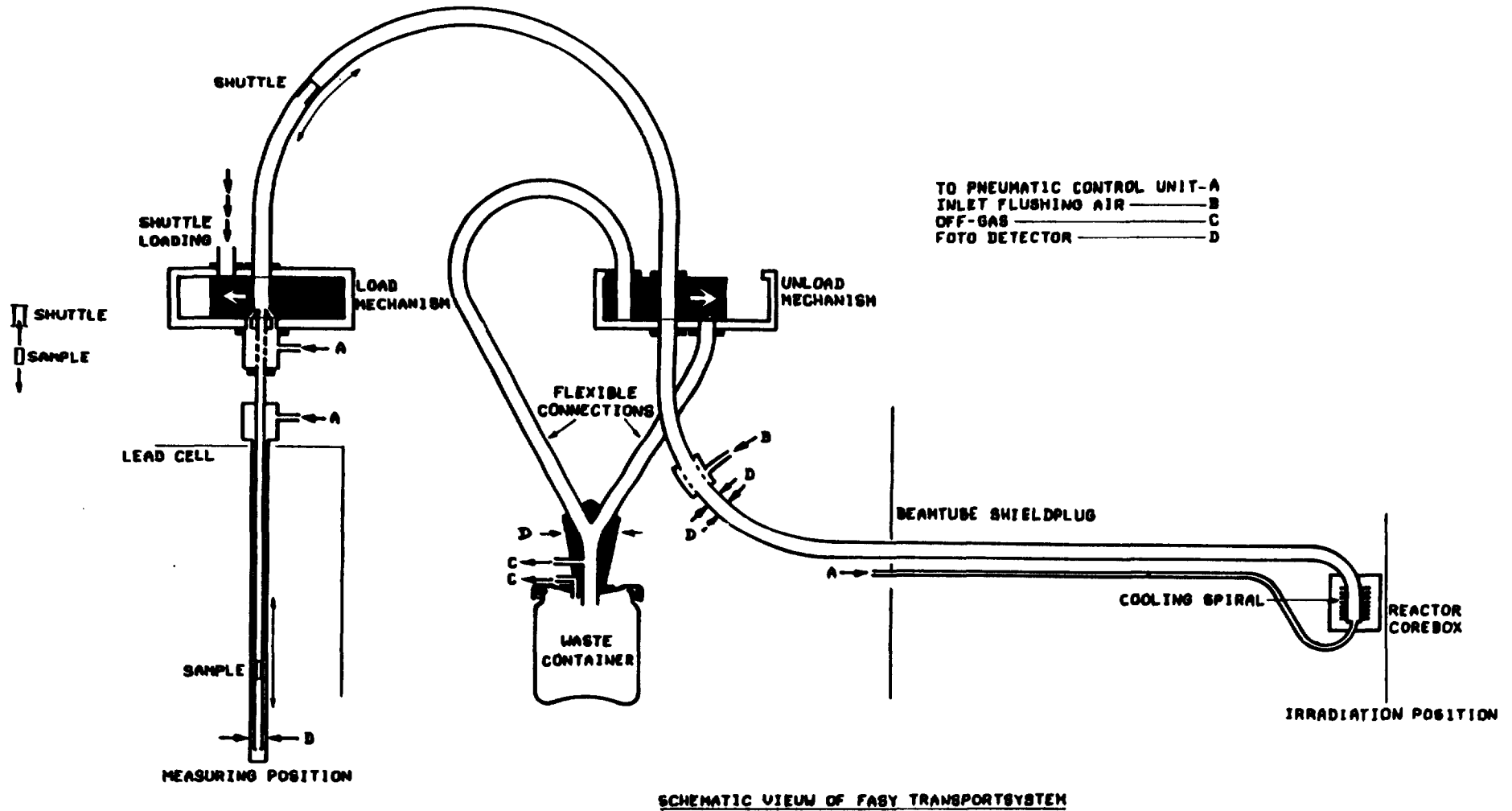
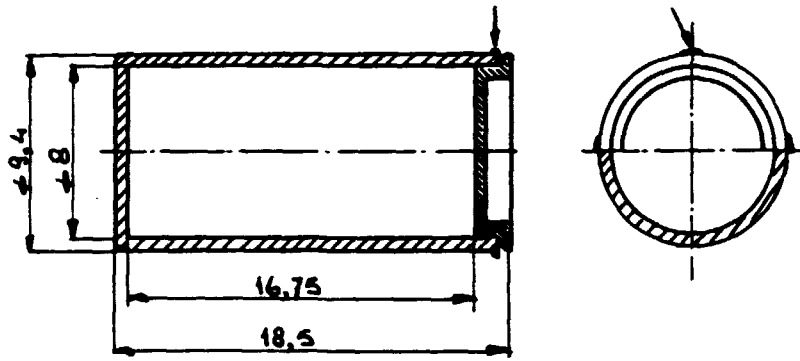


Figure 1. General view of the fast rabbit system FASY in beam-tube No.10 of the HFR.

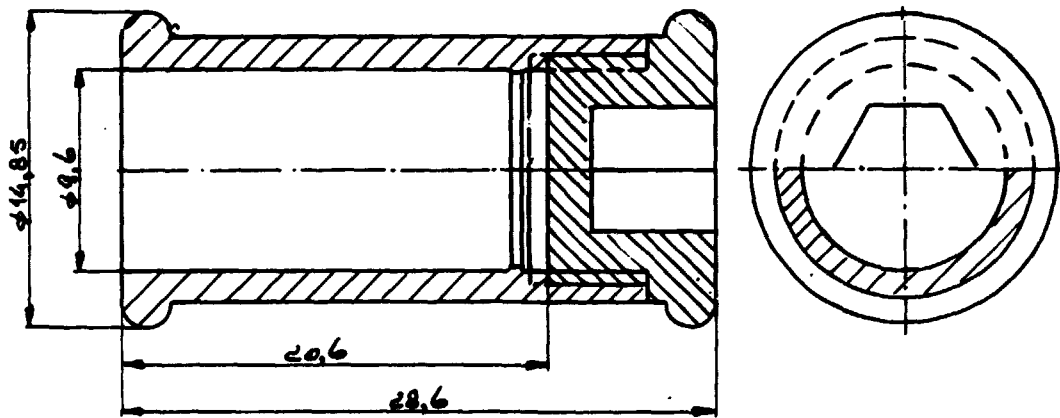
Fig.2. Schematic view of the fast rabbit system FASY.



notches for open shuttle only



TARGET HOLDER



OPEN RABBIT

Fig. 3. Targetholder and Rabbits.

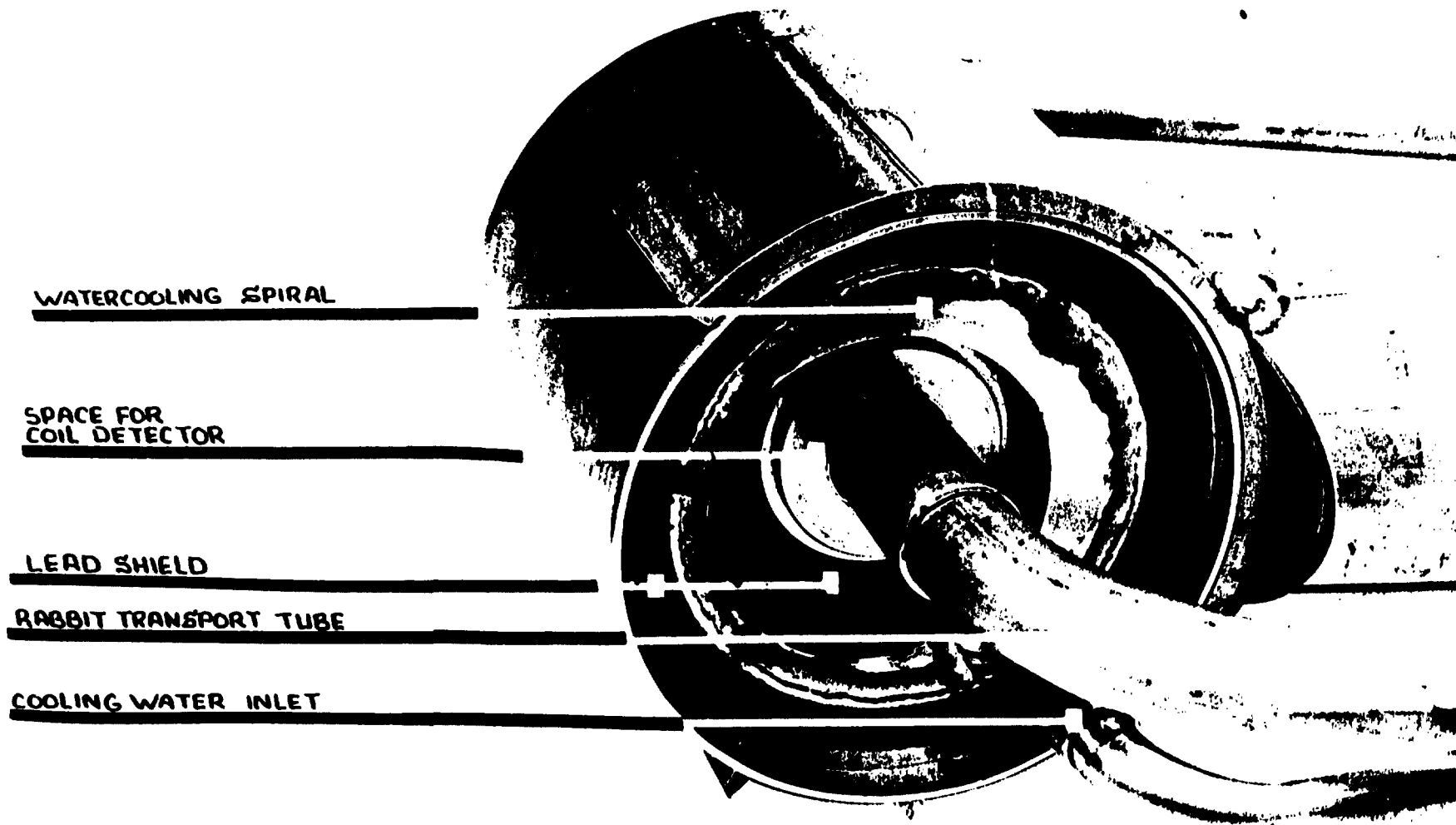


Figure 4.

VIEW OF IRRADIATION POSITION OF FASY (LEAD AND
TOP LID ARE NOT PRESENT ON THE PICTURE)

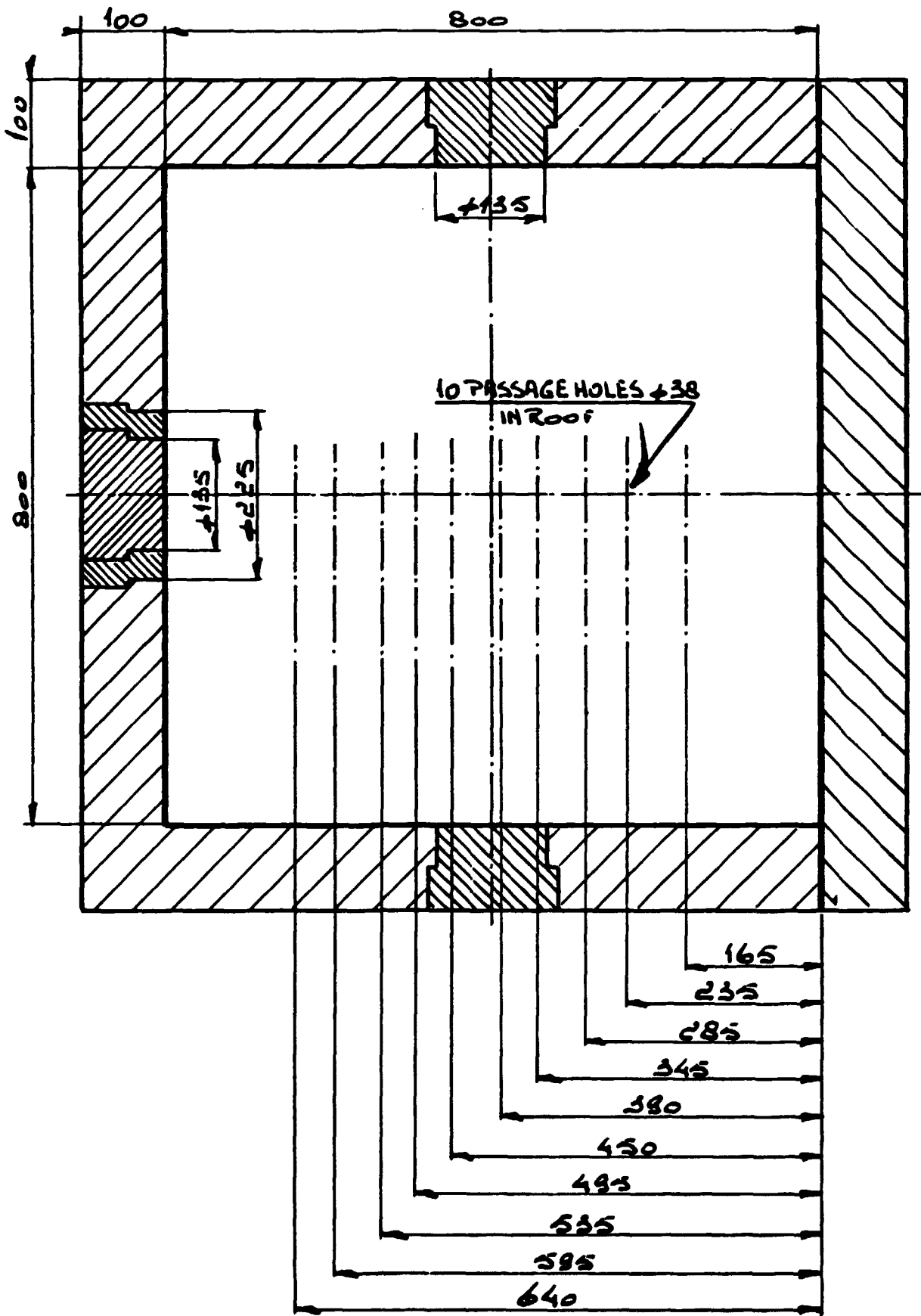


Figure 5. TOP VIEW OF LEADCELL WITH MEASURING PART POSITIONS

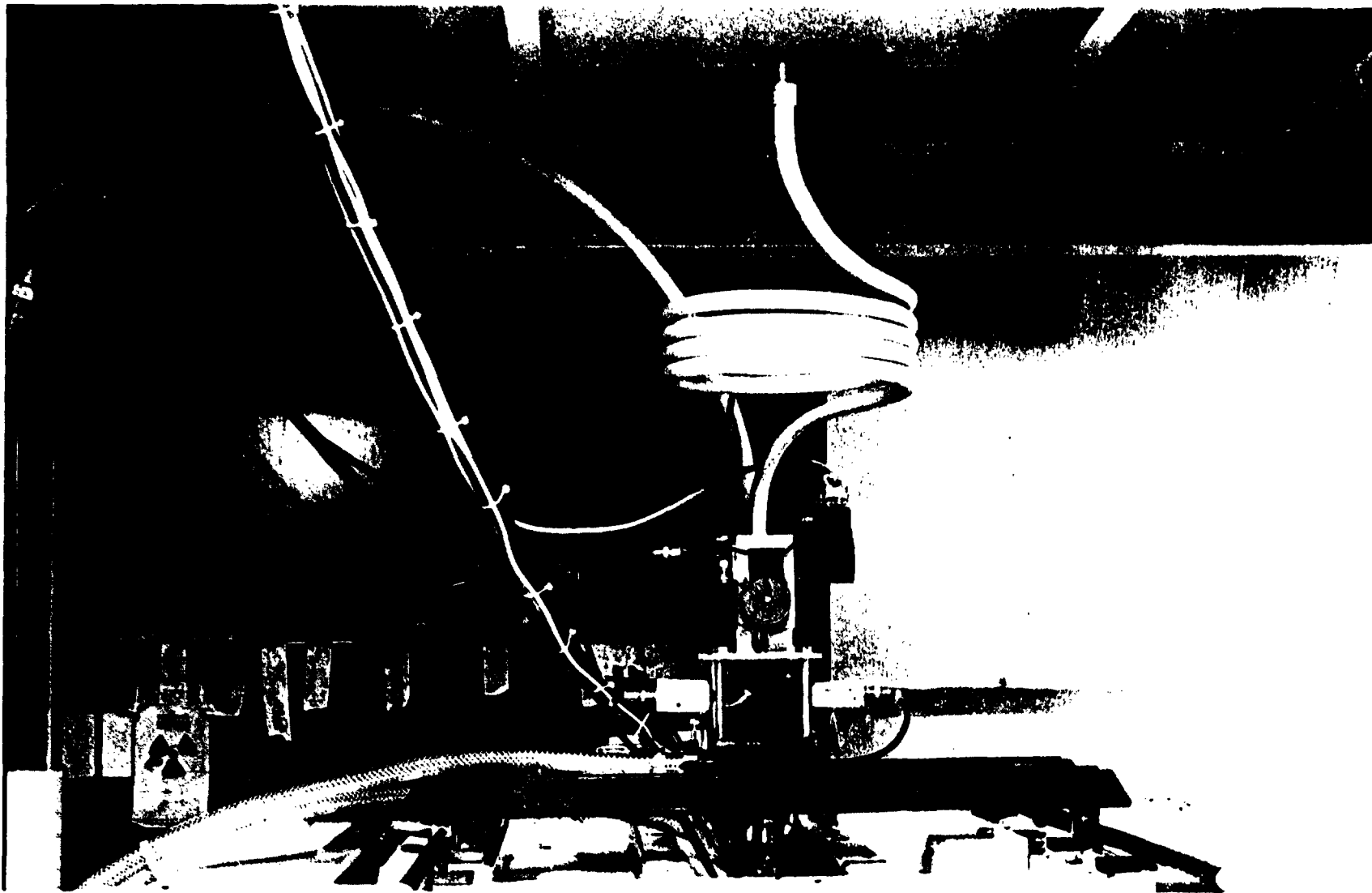


Figure 6. The loading mechanism of the fast rabbit system FASY. Samples are stocked in the spiral-loop.

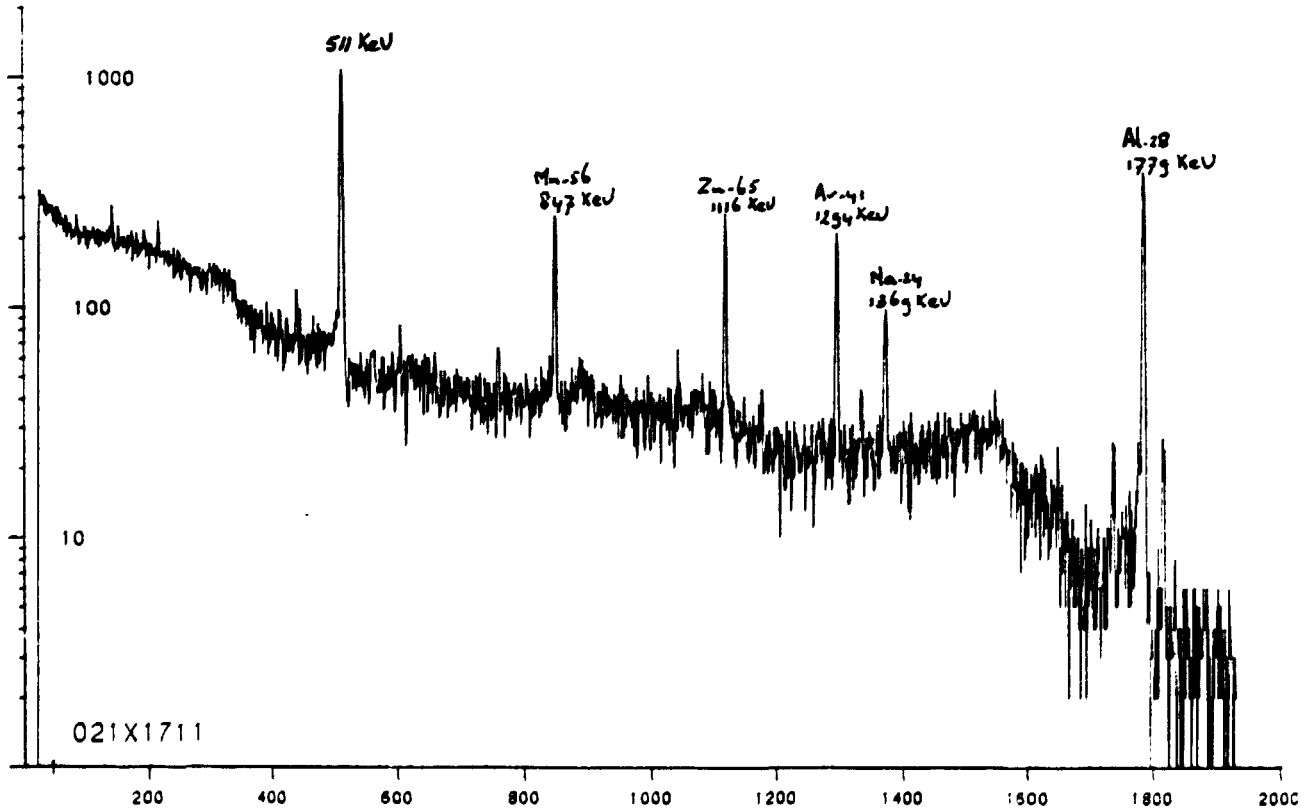
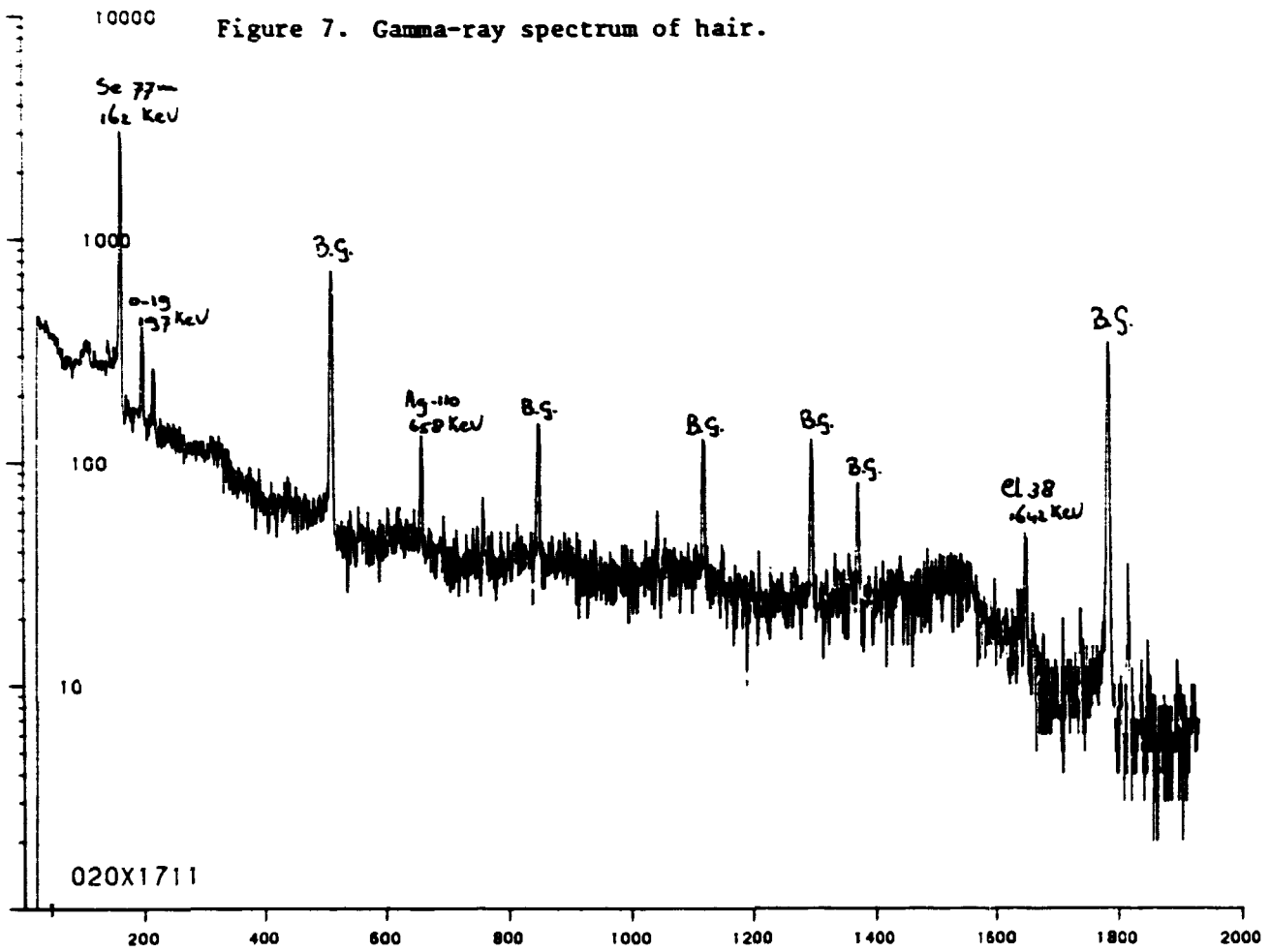


Figure 8. Blank spectrum

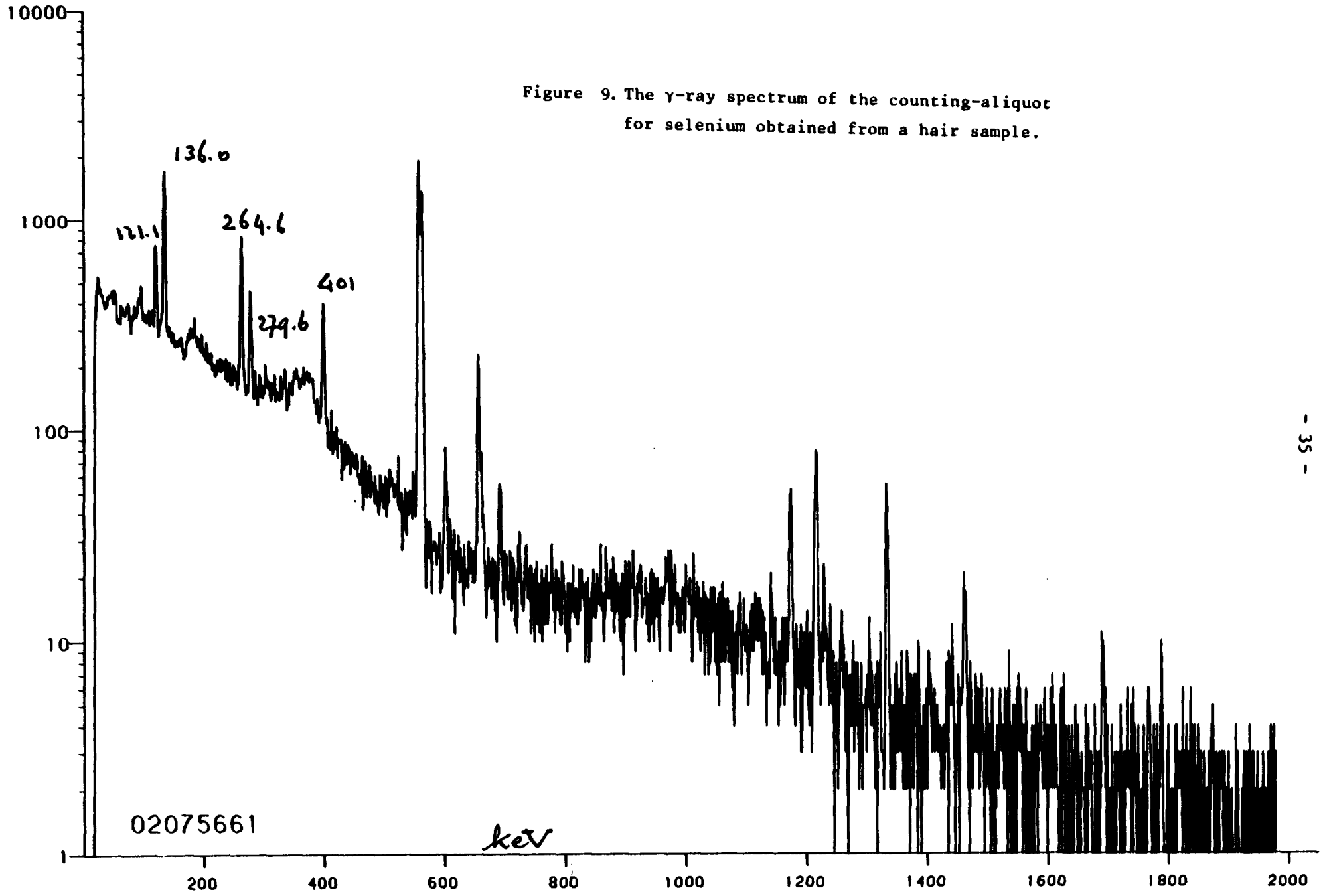


Figure 9. The γ -ray spectrum of the counting-aliquot for selenium obtained from a hair sample.

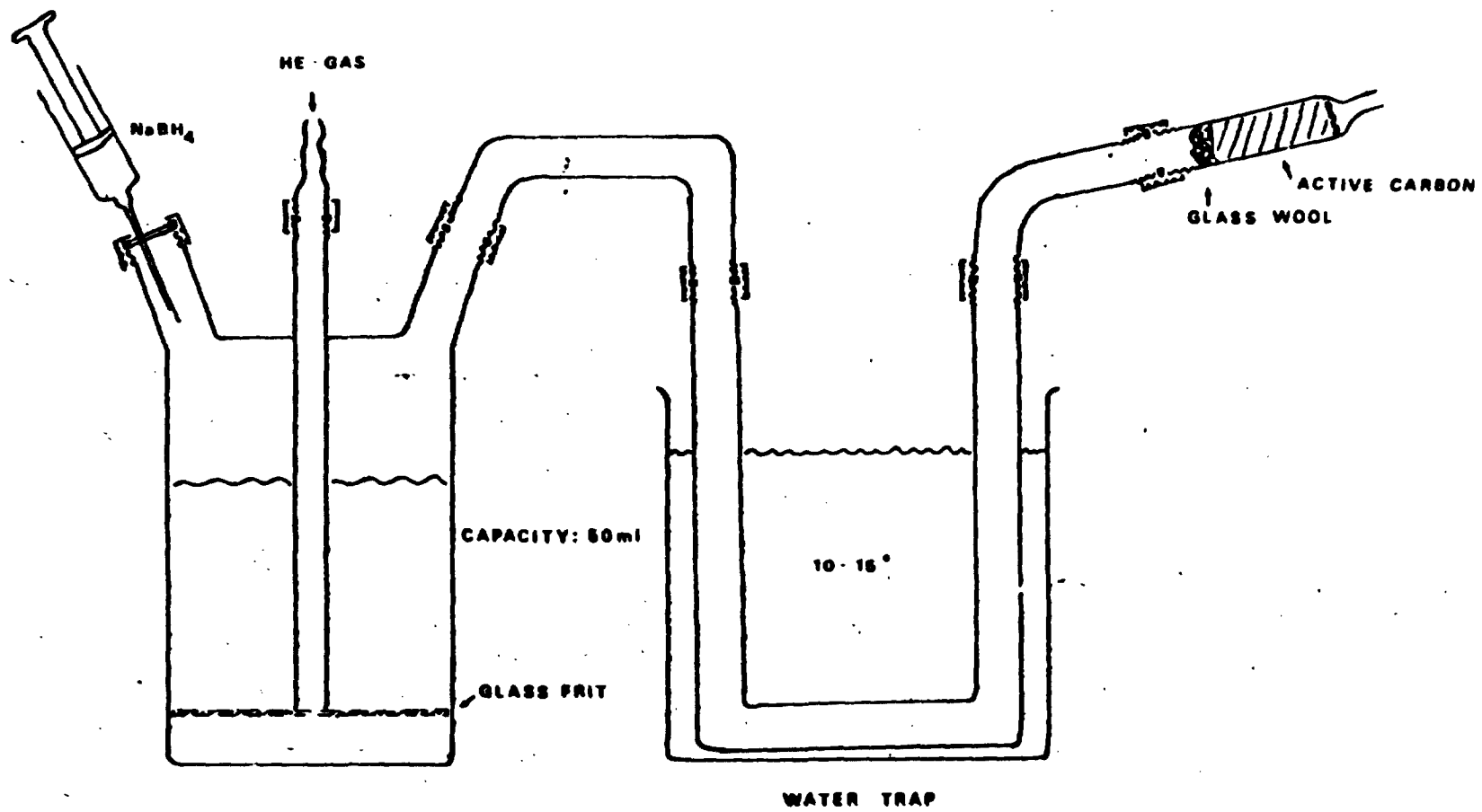


Fig. 10. The hydride generation vessel.