

NEUTRON ACTIVATION ANALYSIS OF AIR
FILTER SAMPLES - THE DETECTION OF ARSENIC

E. R. Samuels and J. M. Quinn

Radiation Protection Division

RPD - 81

Published by authority of
the Honourable John Munro
Minister of National Health and Welfare

June 1970

CONTENTS

	<u>PAGE</u>
INTRODUCTION	1
EXPERIMENTAL	2
RESULTS AND DISCUSSION	3
ACKNOWLEDGEMENTS	6
REFERENCES	6
TABLE	8
FIGURES	9 - 21

ABSTRACT

Neutron activation analysis techniques have been used to analyze air filter samples for trace elements of public health interest. Samples collected from 24 stations across Canada are irradiated in a nuclear reactor at a thermal neutron flux of about 1.5×10^{13} n/cm²/sec for 72 hours. The irradiated samples are analyzed by direct gamma-ray spectrometry using a Ge (Li) detector and a 1600 channel pulse height analyzer. Several elements have been detected but the present report deals only with the presence of arsenic. Relatively high levels of this element were found in the air filter samples from Yellowknife. Concentrations up to 0.04 µg/m³ of air were estimated. Relevant sections of the spectra are presented and the implications discussed.

NEUTRON ACTIVATION ANALYSIS OF AIR FILTER SAMPLES -

THE DETECTION OF ARSENIC

INTRODUCTION

The increasing incidence of atmospheric pollution has been a cause of great concern within recent years, with attention being directed primarily towards gaseous pollutants and various pesticides. However, little consideration has been given to the presence of trace elements which are being introduced continuously into the atmosphere through industrial and other pursuits. Some of these trace elements are highly toxic or are otherwise of public health interest, and information on their presence and concentrations in the air around populated areas should contribute to a better assessment of the possible health hazards associated with the problem of air pollution.

Because of the low levels at which many elements occur in the atmosphere, they cannot be detected by most conventional analytical methods. They can be readily determined, however, by the highly sensitive method of neutron activation analysis which allows the quantitative determination of several elements down to the parts per billion range.

Trace elements in the air can be conveniently collected on suitable type filters. By irradiating small portions of these air filter samples in a nuclear reactor and non-destructively analyzing the activated samples by gamma-ray spectrometry several of the constituent elements can be measured simultaneously. Pertinent details of such a technique have been outlined in a previous report (1).

The method has been used in some countries (2,3,4) to study the concentrations of stable elements in the air around large cities and industrial sites. The technique is now being employed by our laboratory to determine trace elements of public health interest in air filter samples collected at several centres across Canada. Several elements have so far been identified in these samples and detailed results will be published shortly.

The present report deals only with the detection of arsenic in the samples measured.

EXPERIMENTAL

The samples were collected daily from 24 stations across the country (Fig. 1) under the Division's air monitoring program (5). After the samples were measured for radioactivity, a $1\frac{1}{2}$ inch diameter circle is taken from each of the 2 inch discs counted. Since the total volume of air sampled over a 24-hour period was found to be 900 m^3 , the size of sample taken for irradiation represents a volume of 126 m^3 of air sampled. The $1\frac{1}{2}$ inch sample is wrapped in aluminum foil, placed in an aluminum capsule and sent for irradiation in the McMaster nuclear reactor. Irradiation is carried out in a thermal neutron flux of about $1.5 \times 10^{13} \text{ n/cm}^2/\text{sec}$ for 72 hours. After a suitable cooling period of 1-2 days, the samples are returned to the Radiation Protection Division's laboratory for analysis. Blank filter paper samples were irradiated under the same conditions as the air filter samples.

The irradiated samples as contained in the aluminum foil were transferred to plastic planchets and covered with mylar film for

counting. Counting was done in a 17.6 cm³ Ge (Li) detector (resolution 3.2 kev per channel for the 1.33 Mev Co⁶⁰ γ -ray) with a 1600 channel Victoreen pulse height analyzer.

The samples were counted immediately on arrival at the laboratory for short times (usually less than five minutes) to obtain an idea of the level of the induced activities and to ensure detection of the shorter-lived products. All the samples are then recounted for longer periods to permit better identification of the constituent elements. Recounting is again performed after a few weeks delay when the shorter-lived components would have all decayed and the longer-lived isotopes would have become more evident.

The data were printed out using a Model 32 Teletype printer and the spectra recorded by means of an Omnigraphic point plotter.

RESULTS AND DISCUSSION

The glass fiber filter used for collection of the samples contain several elemental impurities with high thermal neutron cross sections which contribute substantially to background activity. Such a filter is not suitable for thermal neutron activation analysis, since the induced activities in the filter itself would seriously interfere with the identification of elements in the sample particularly at the trace levels at which they are likely to occur. However, many elements have been positively identified in the irradiated samples from various stations of the air monitoring network. As this report is concerned primarily with the presence of arsenic in the air samples, only the portions of the spectra of interest are reproduced in Figures 2-12.

All the samples represented, excepting that in Fig. 12 which was collected April 6-7, 1970, were collected February 27-28, 1970. The data, with estimated arsenic concentrations, are summarized in Table I.

The spectrum of the blank filter is shown in Figure 2. Figures 3 and 4 represent the gross spectra of a Yellowknife sample two days and nine days respectively after irradiation. The net spectra two and four days after irradiation are shown in Figures 5 and 6, respectively. Figures 7-11 give the spectra of Resolute, Coral Harbor, Vancouver, Ottawa, and Halifax, respectively.

It is clearly evident that Yellowknife is the only station with a relatively high concentration of arsenic. The arsenic-76 peaks at 0.559 Mev and 0.657 Mev are quite prominent, with the former being the dominant peak in the spectrum. This is even more so when it is considered that arsenic-76 has a half-life of 26.5 hours and would have decayed through approximately two half-lives at the time of the first measurement. The other major constituent bromine-82, has a half-life of 35.7 hours, which is about one and one-half that of arsenic-76.

Bromine is the main element observed in the samples from the other stations over the relevant portion of the spectrum. No arsenic is indicated in the samples from Coral Harbour and Halifax, but traces are quite likely present in the samples from the other stations as suggested by the edge on the bromine-82 peak at 0.55 Mev.

Samples collected over different periods were irradiated to determine whether the observed elements were consistent constituents of the air around the sampling stations. The spectrum of a sample collected at Yellowknife on April 6-7, 1970 is shown in Figure 12. The

presence of arsenic in this sample is more strikingly demonstrated than in the previous sample (Figures 3-6). Although the spectrum was taken eight days after irradiation, the less intense arsenic-76 peaks at 1.216 Mev and 1.229 Mev are quite obvious, in addition to the peaks at 0.559 Mev and 0.657 Mev. This implies that arsenic was present originally at a relatively high concentration. It also strongly suggests that arsenic is a normal constituent of the air at Yellowknife and that it is present in easily measurable concentrations.

These initial measurements were all made on a qualitative basis in order to determine the optimum conditions for the detection of the trace elements which might be present and hence the procedure which should be followed for their quantitative estimation. Since detection was of primary interest, the samples were measured under varying geometries and without appropriate standard sources. However, from previous calibrations with pure arsenic trioxide solutions, the arsenic contents of the 24-hr. Yellowknife samples were estimated to be about 4 μg for the February sample and 32 μg for the sample collected in April. These values correspond to arsenic concentrations of 0.005 $\mu\text{g}/\text{m}^3$ and 0.04 $\mu\text{g}/\text{m}^3$, respectively. It should be emphasized that no correction has been made for the contribution of other isotopes to the arsenic peaks nor were standards irradiated at the same time and under the same conditions as the samples.

The threshold limit for arsenic in air has been set at 0.5 mg/m^3 for occupational exposure (6), which is related to exposure over a 40 hour week. The limit for continuous exposure, as would be the case when ambient air is being considered, would conceivably be much lower than the quoted value for occupational exposure. The concentrations observed at

Yellowknife might then be significant from a public health standpoint.

It is quite clear, that on a comparative basis the arsenic concentration at Yellowknife is the highest of all stations measured. If this element is present in the air at such levels, it seems justified to conclude that it could be present in other environmental materials as well as in humans in higher-than-normal concentrations. It is suggested therefore that these preliminary results form the basis for an investigation of the general levels of arsenic around Yellowknife.

ACKNOWLEDGEMENTS

The advice and assistance of Dr. S.K. Ghosh and Mr. M. Diotte of the Development Physics Unit in the measurement of the samples and the interpretation of the results are gratefully acknowledged. Our thanks also to Dr. H. Taniguchi, Head of the Chemistry Section, for his continued interest and support in this work.

REFERENCES

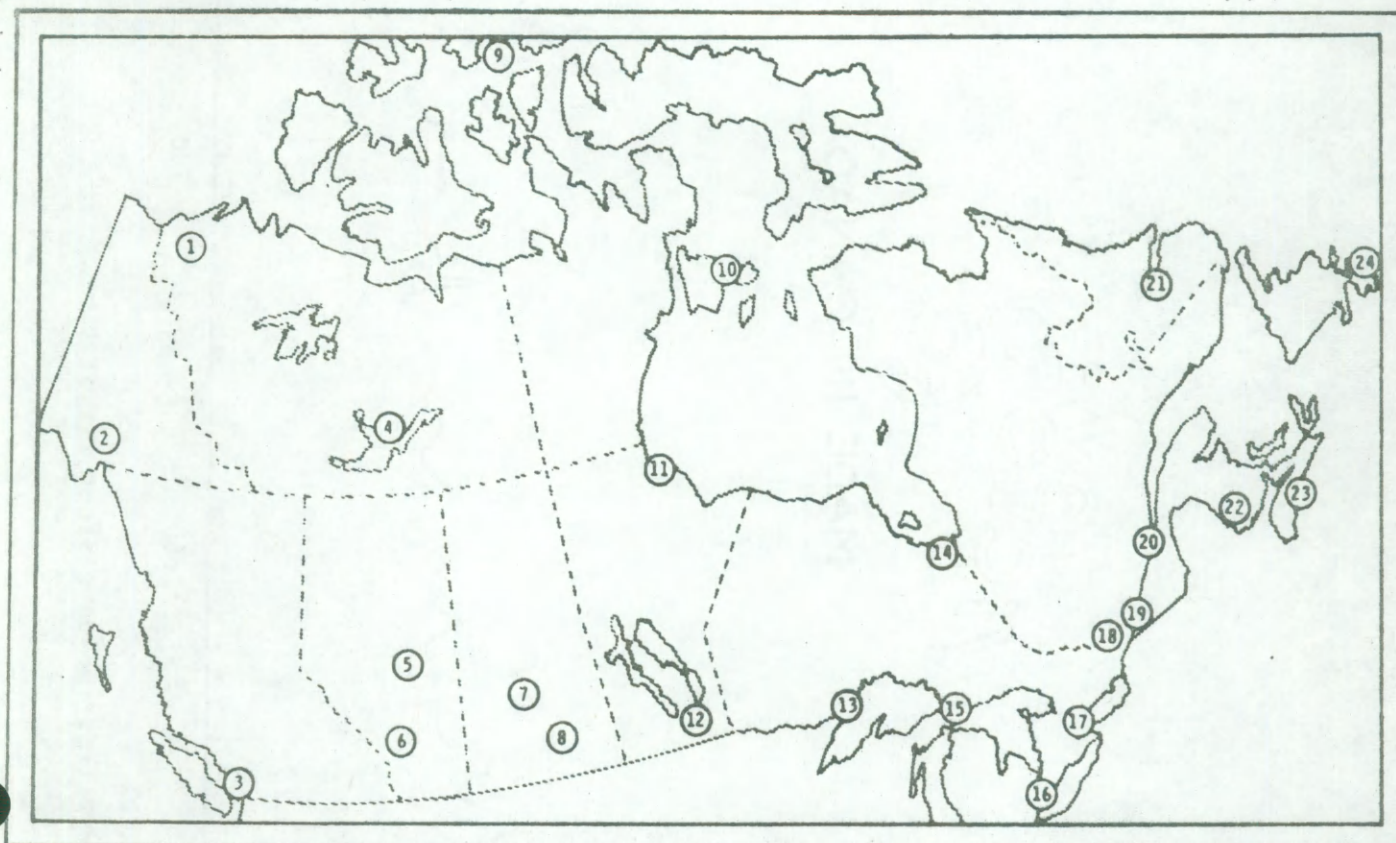
1. Samuels, E.R.
The Application of Neutron Activation Analysis for the Determination of Trace Elements of Health Significance.
IR-58. August 1969.
2. Altshuller, A.P.
Air Pollution
Analytical Chemistry 41 # 5: IR-13R (1969)
3. Brar, S.S., Nelson, D.M., Karabrocki, E.L., Moore, E.E.,
Burnham, C.D., and Hattori, D.M.
Thermal Neutron Activation Analysis of Airborne Particulate Matter in Chicago Metropolitan Area. The 1968 International Conference Modern Trends in Activation Analysis. October 7-11, 1968. National Bureau of Standards, Gaithersburg, Maryland.
4. Dudey, N.D., Ross, L.E., and Noshkin, V.E.
Application of Activation Analysis and Ge (Li) Detection Techniques for the Determination of Stable Elements. Ibid

5. Beale, J., and Gordon, J.
The operation of the R.P.D. Air Monitoring Program.
RPD-11, July 1962.
6. Threshold Limit Values for 1961.
Occupational Health Bulletin.
Vol. 16 No. 11 1961.

TABLE I
ARSENIC IN AIR FILTER SAMPLES

Sampling Station	Collection Date	Estimated As Conc ⁿ ($\mu\text{g}/\text{m}^3$)
Yellowknife	Feb. 27-28, 1970	0.005
"	April 6-7, 1970	0.04
Resolute	Feb. 27-28, 1970	< 0.001
Coral Harbor	Feb. 13-14, 1970	NI
Vancouver	Feb. 27-28, 1970	< 0.001
Windsor	Feb. 27-28, 1970	< 0.001
Toronto	Feb. 27-28, 1970	< 0.01
Ottawa	Feb. 27-28, 1970	< 0.001
Halifax	Feb. 27-28, 1970	NI

NI = Not indicated



- | | |
|-------------------|----------------------|
| 1. INUVIK | 13. FT. WILLIAM |
| 2. WHITEHORSE | 14. MOOSONEE |
| 3. VANCOUVER | 15. SAULT STE. MARIE |
| 4. YELLOWKNIFE | 16. WINDSOR |
| 5. EDMONTON | 17. TORONTO |
| 6. CALGARY | 18. OTTAWA |
| 7. SASKATOON | 19. MONTREAL |
| 8. REGINA | 20. QUEBEC CITY |
| 9. RESOLUTE | 21. GOOSE BAY |
| 10. CORAL HARBOUR | 22. FREDERICTON |
| 11. FT. CHURCHILL | 23. HALIFAX |
| 12. WINNIPEG | 24. ST. JOHN'S |

Fig. 1. Location of Air Sampling Stations

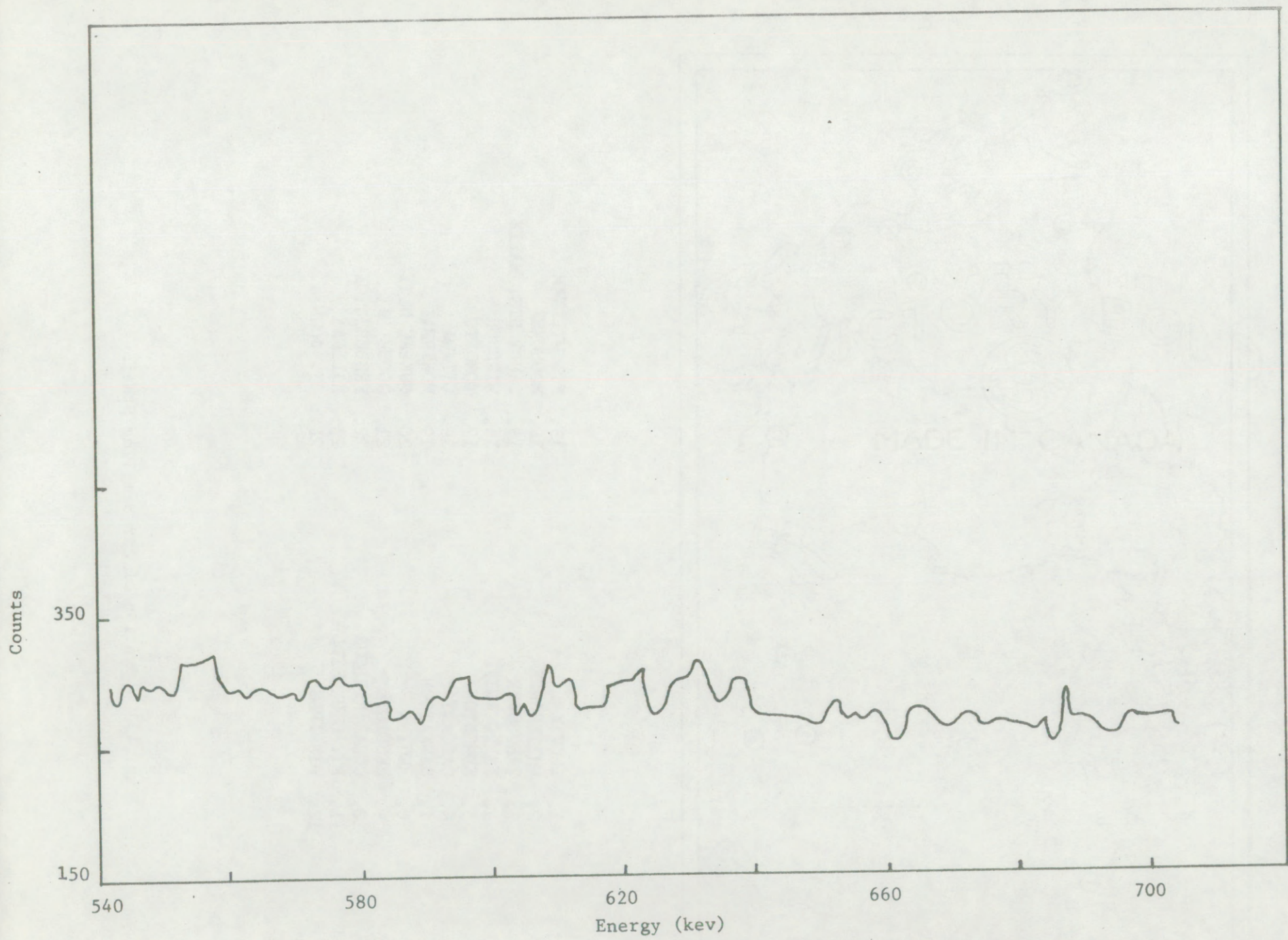


Fig. 2. Ge (Li) spectrum of Glass Fiber Filter two days after irradiation

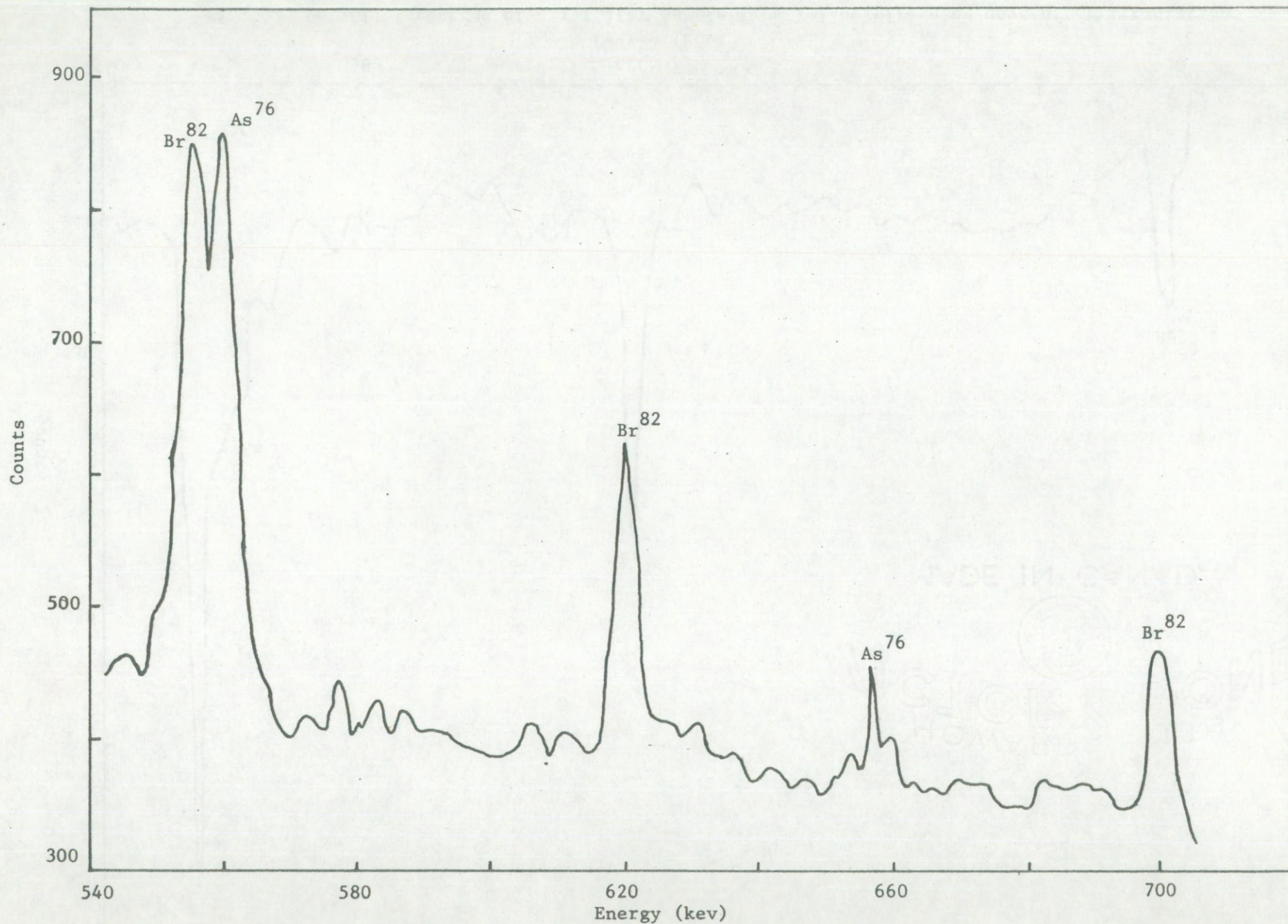


Fig. 3. Ge (Li) spectrum of air filter sample from Yellowknife two days after irradiation.
Sample collected Feb. 27-28, 1970.

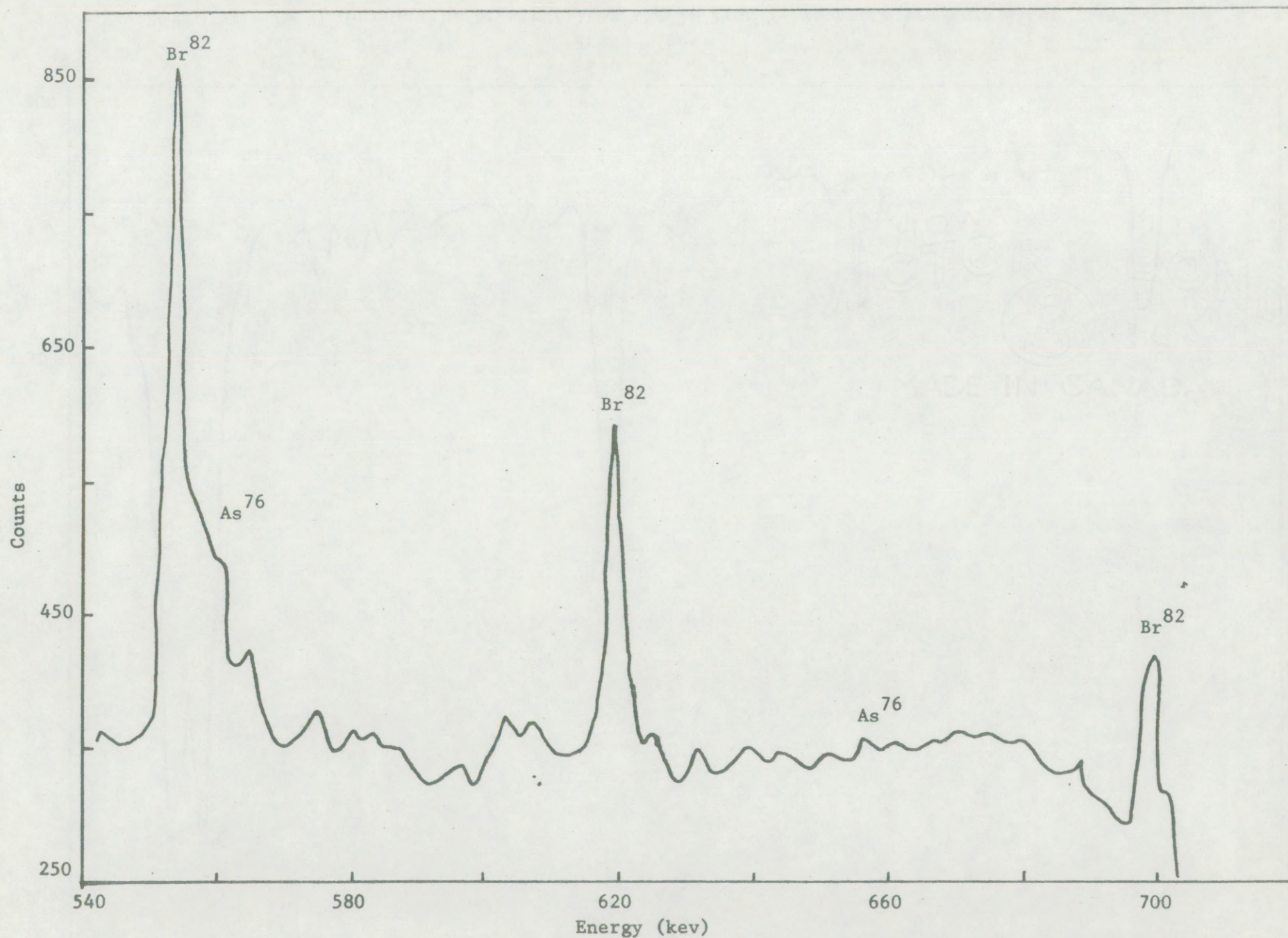


Fig. 4. Ge (Li) spectrum of air filter sample from Yellowknife nine days after irradiation.

Sample collected Feb. 27-28, 1970.

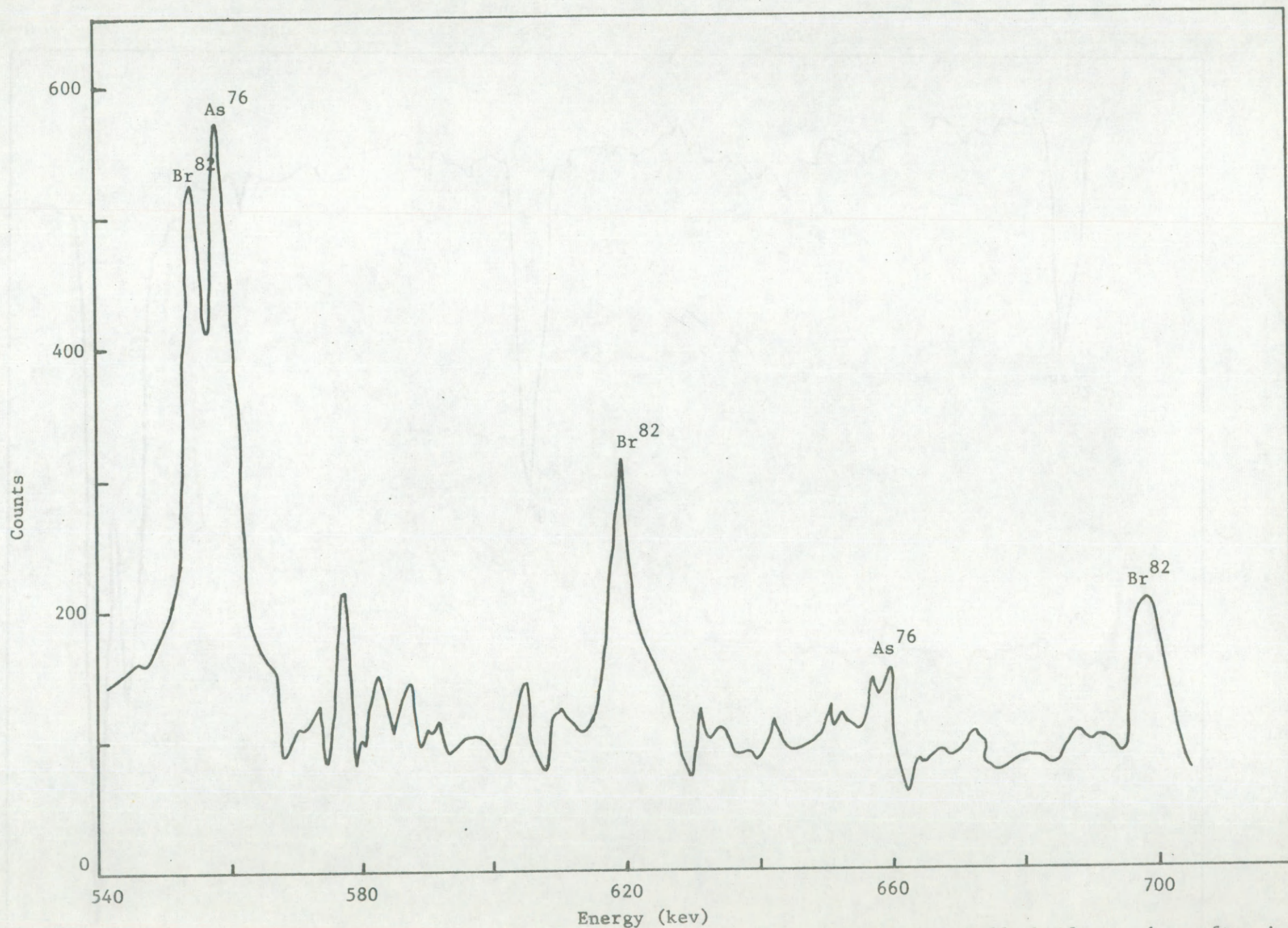


Fig. 5. Ge (Li) spectrum (background subtracted) of air filter sample from Yellowknife two days after irradiation. Sample collected Feb. 27-28, 1970.

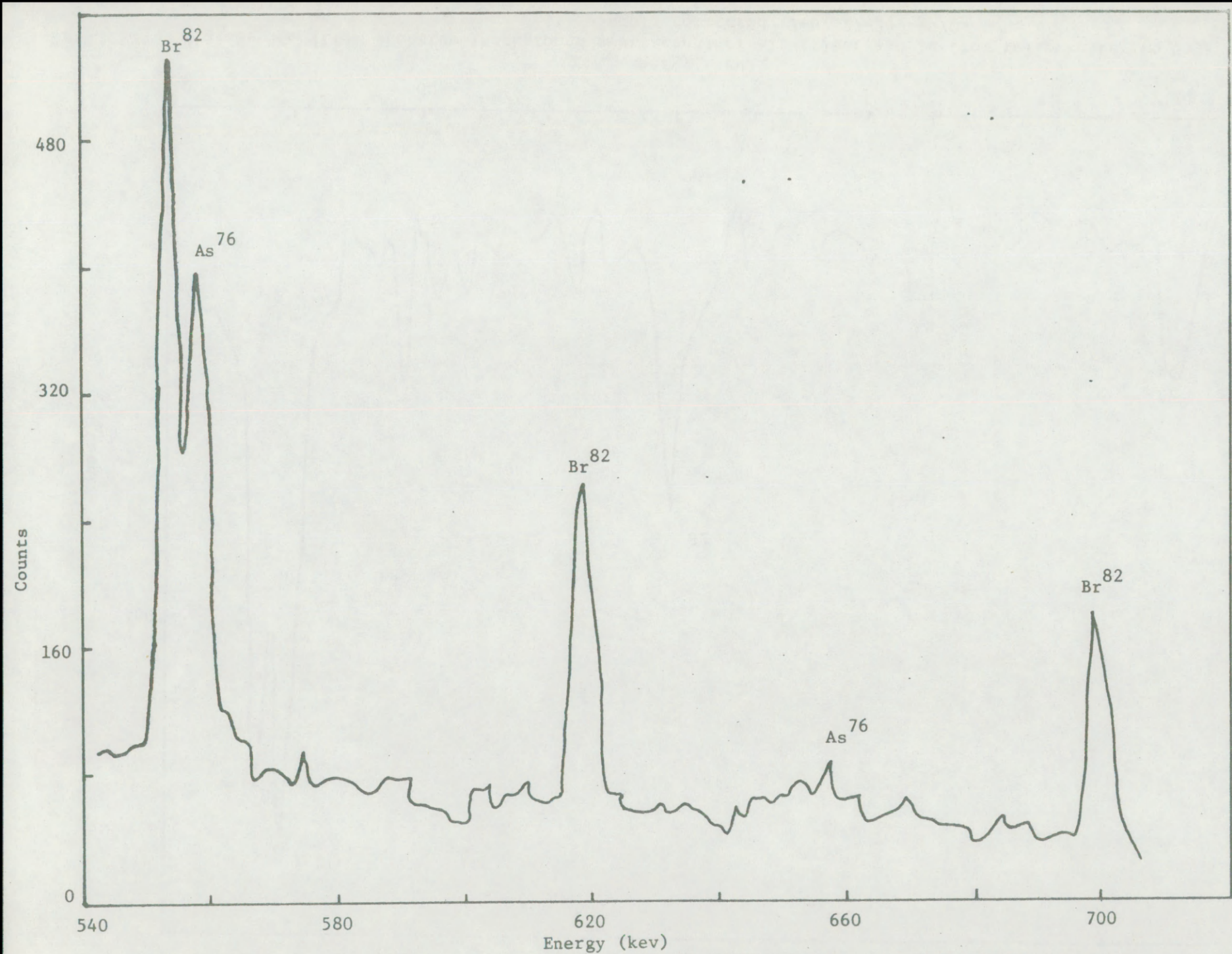


Fig. 6. Ge (Li) spectrum (background subtracted) of air filter sample from Yellowknife four days after irradiation. Sample collected Feb. 27-28, 1970.

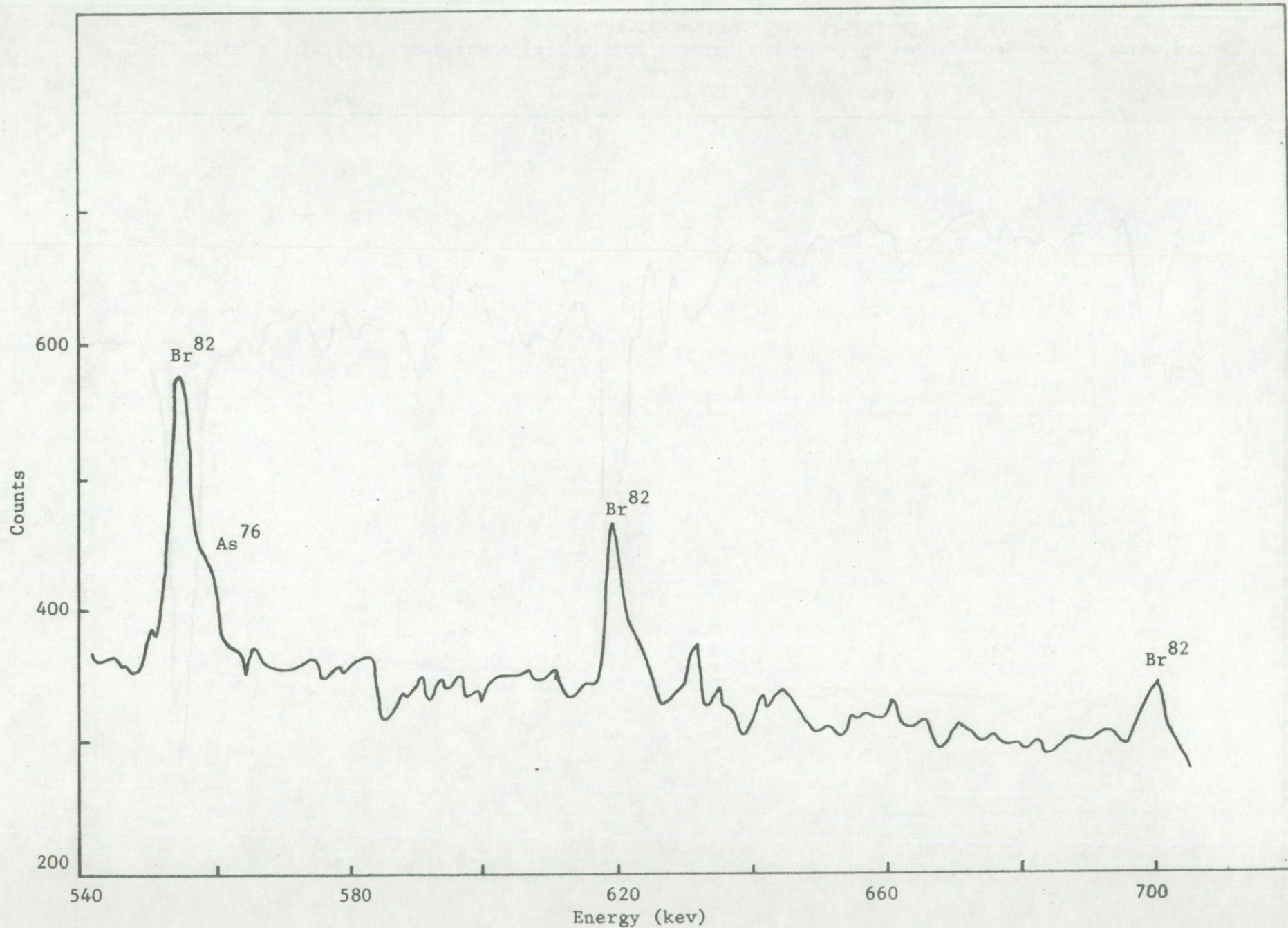


Fig. 7. Ge (Li) spectrum of air filter sample from Resolute two days after irradiation.
Sample collected Feb. 27-28, 1970

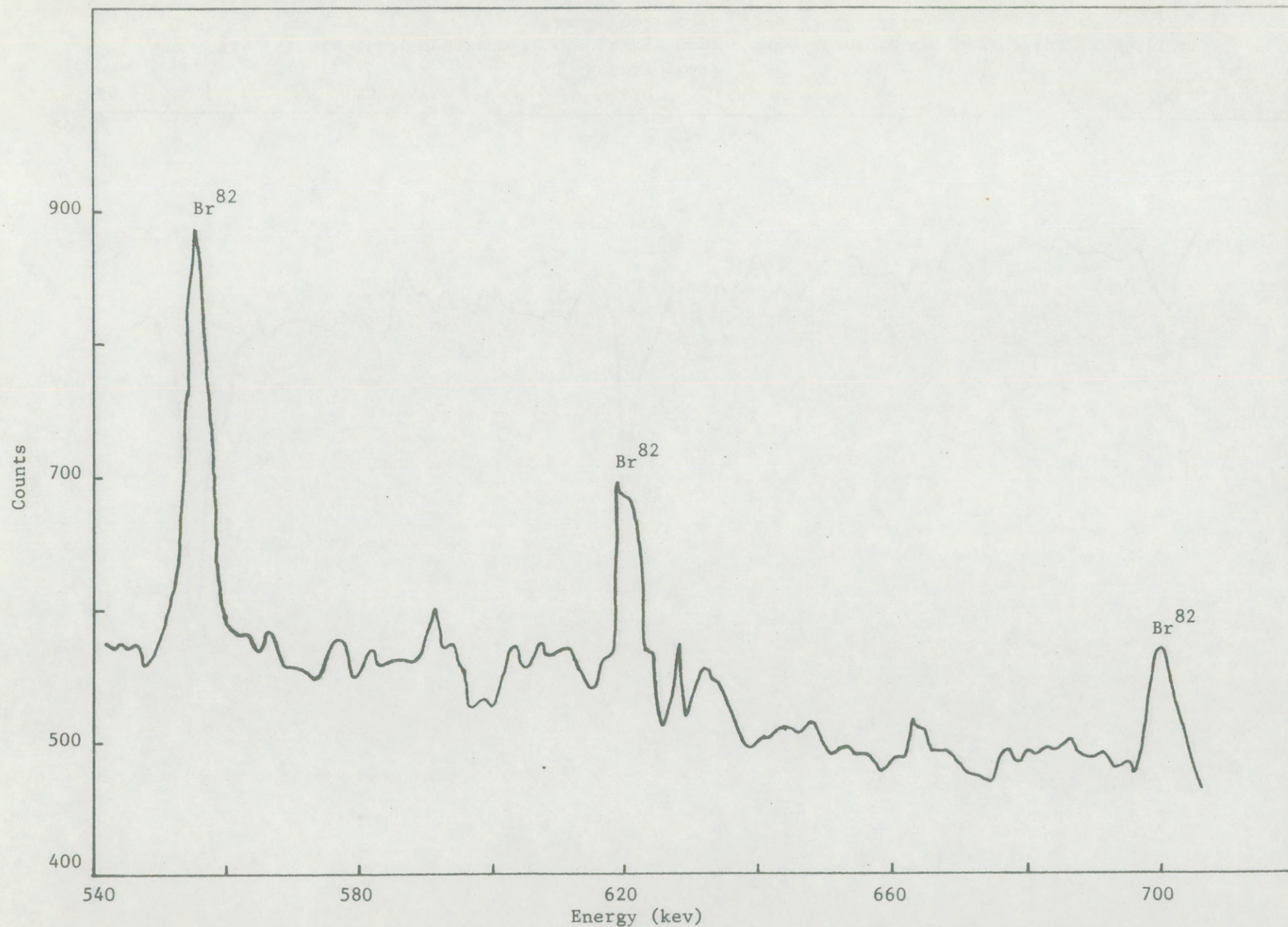


Fig. 8. Ge (Li) spectrum of air filter sample from Coral Harbor two days after irradiation
Sample collected Feb. 13-14, 1970.

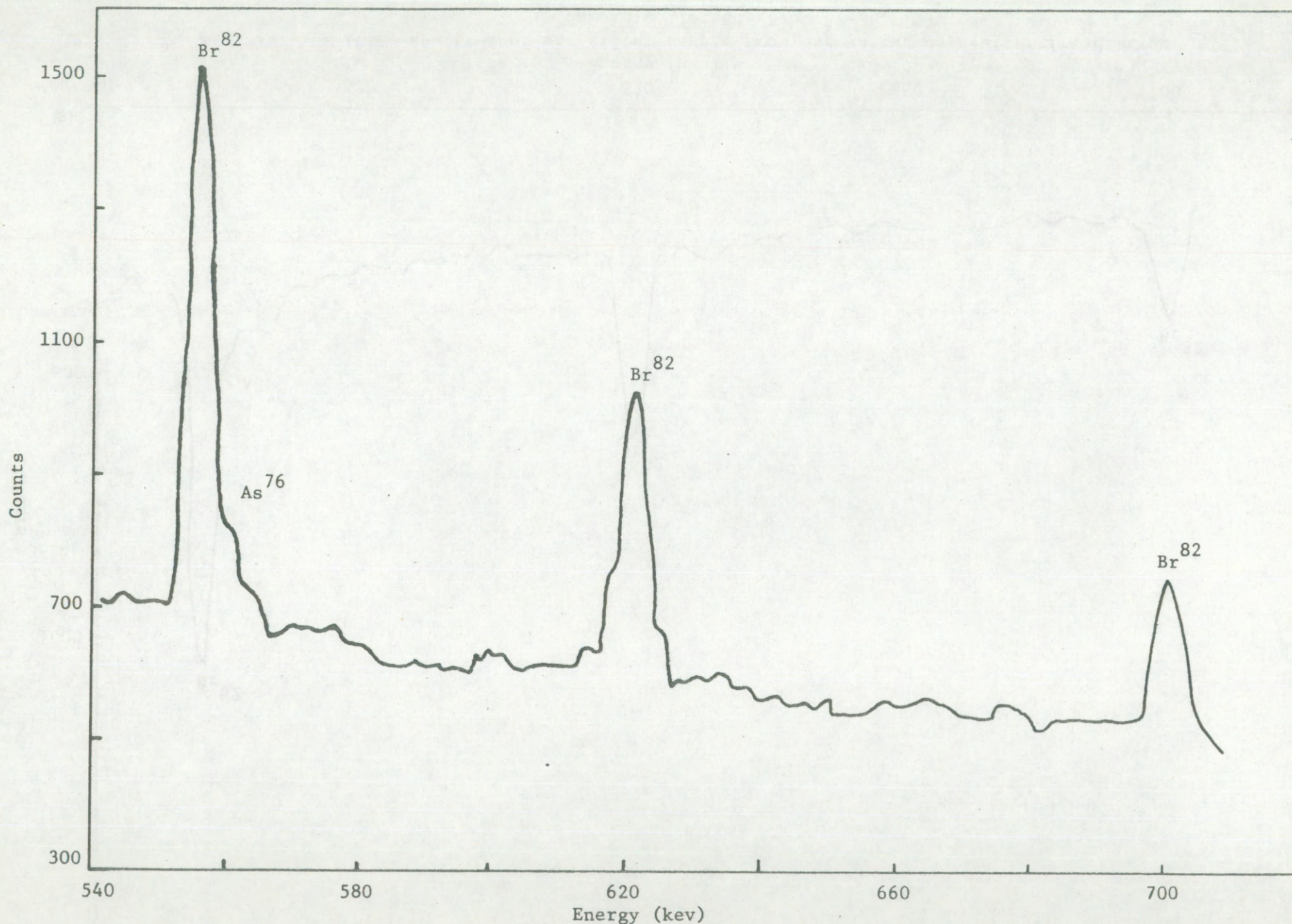


Fig. 9. Ge (Li) spectrum of air filter sample from Vancouver two days after irradiation
Sample collected Feb. 27-28, 1970

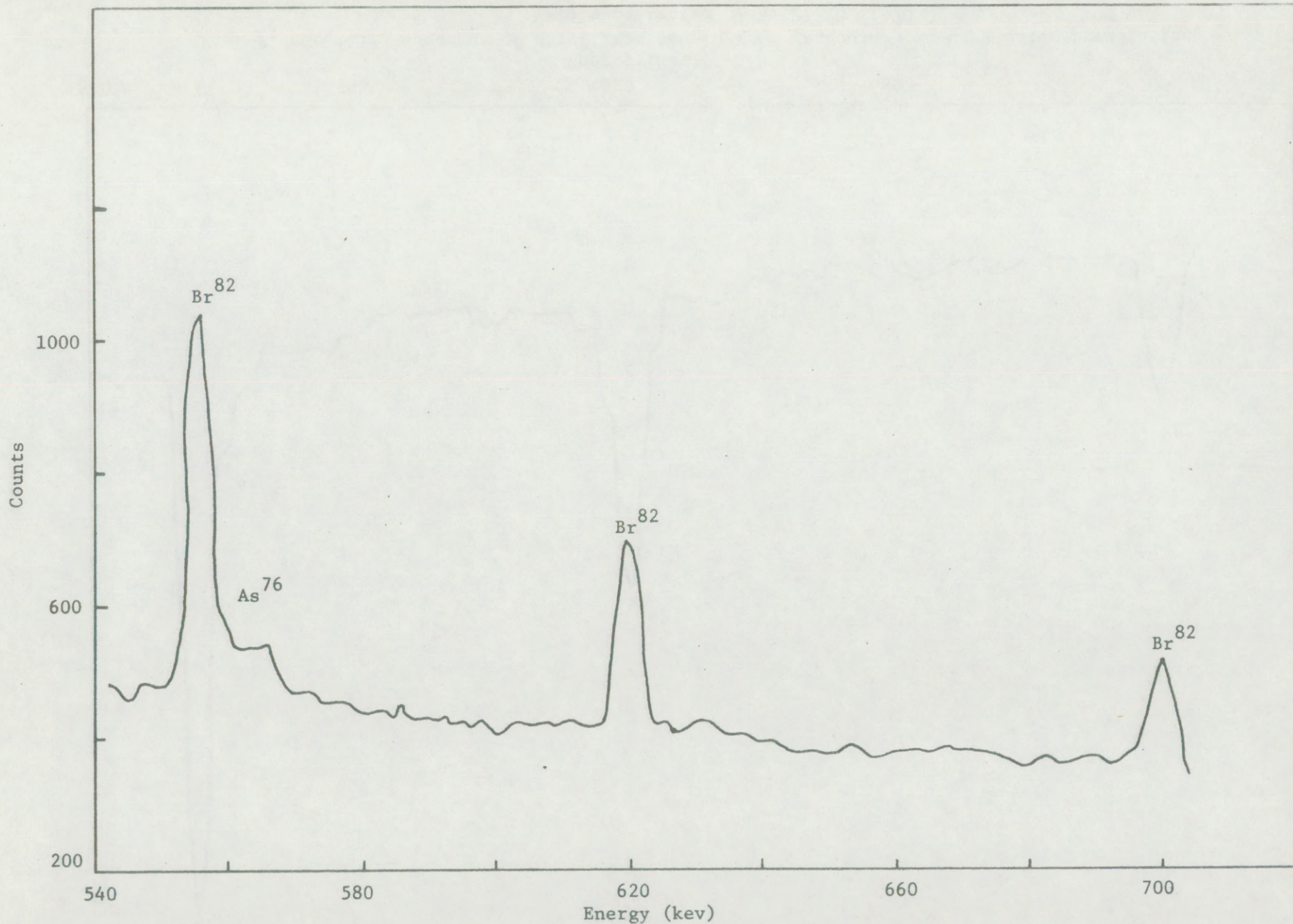


Fig. 10. Ge (Li) spectrum of air filter sample from Ottawa two days after irradiation.
Sample collected Feb. 27-28, 1970.

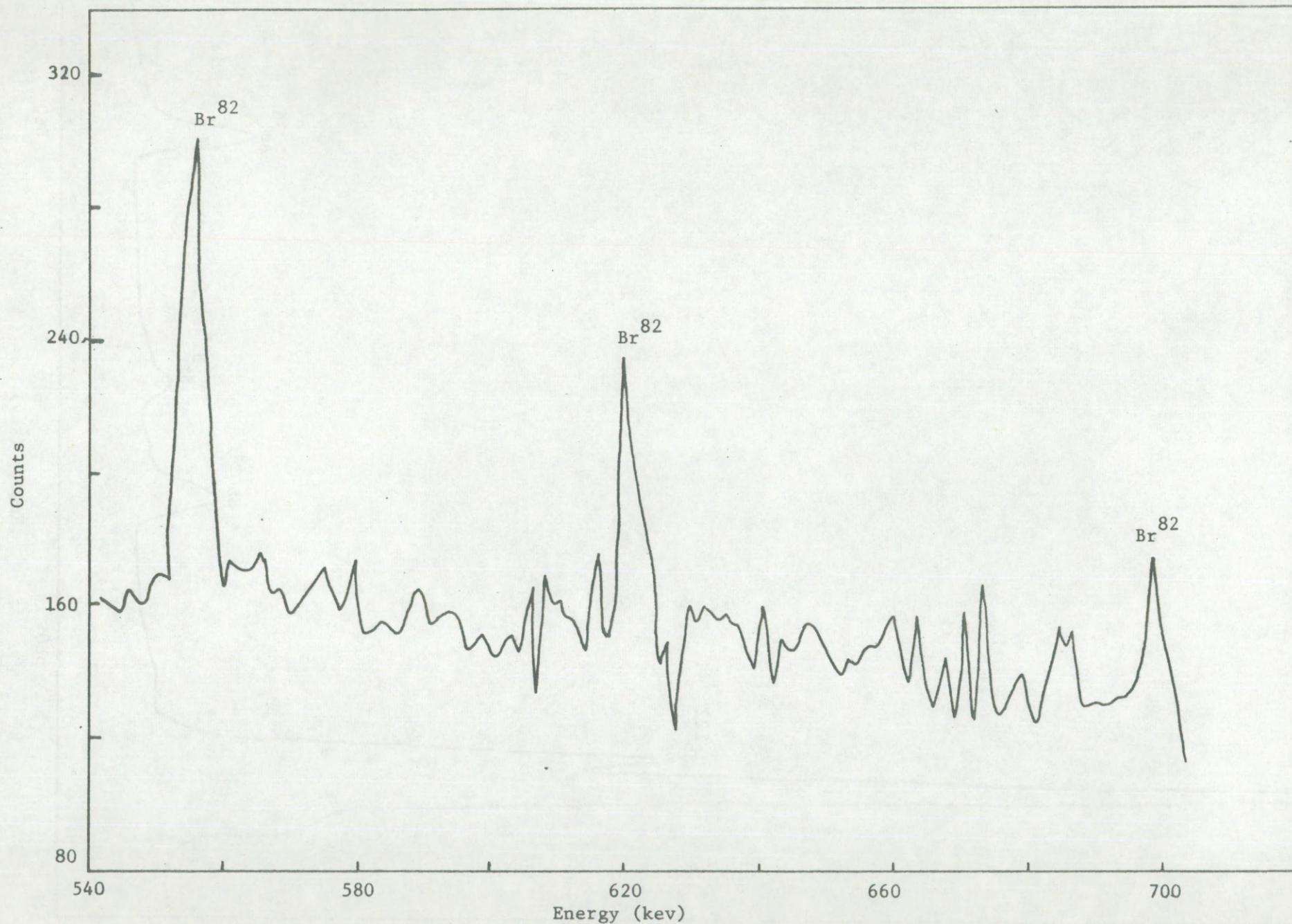


Fig. 11. Ge (Li) spectrum of air filter sample from Halifax three days after irradiation.
Sample collected Feb. 27-28, 1970.

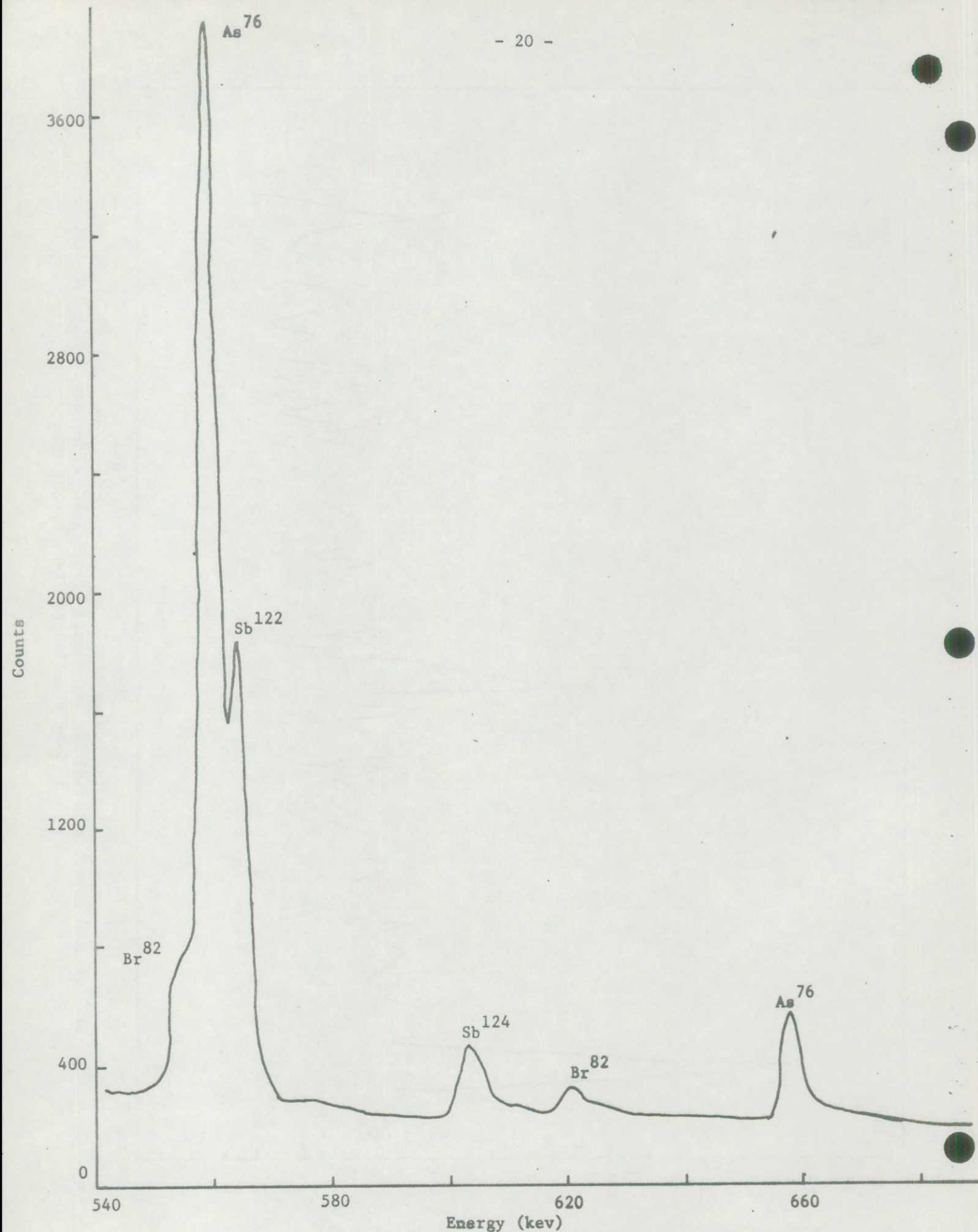


Fig. 12. Ge (Li) spectrum of air filter sample from Yellowknife eight days after irradiation. Sample collected April 6-7, 1970.

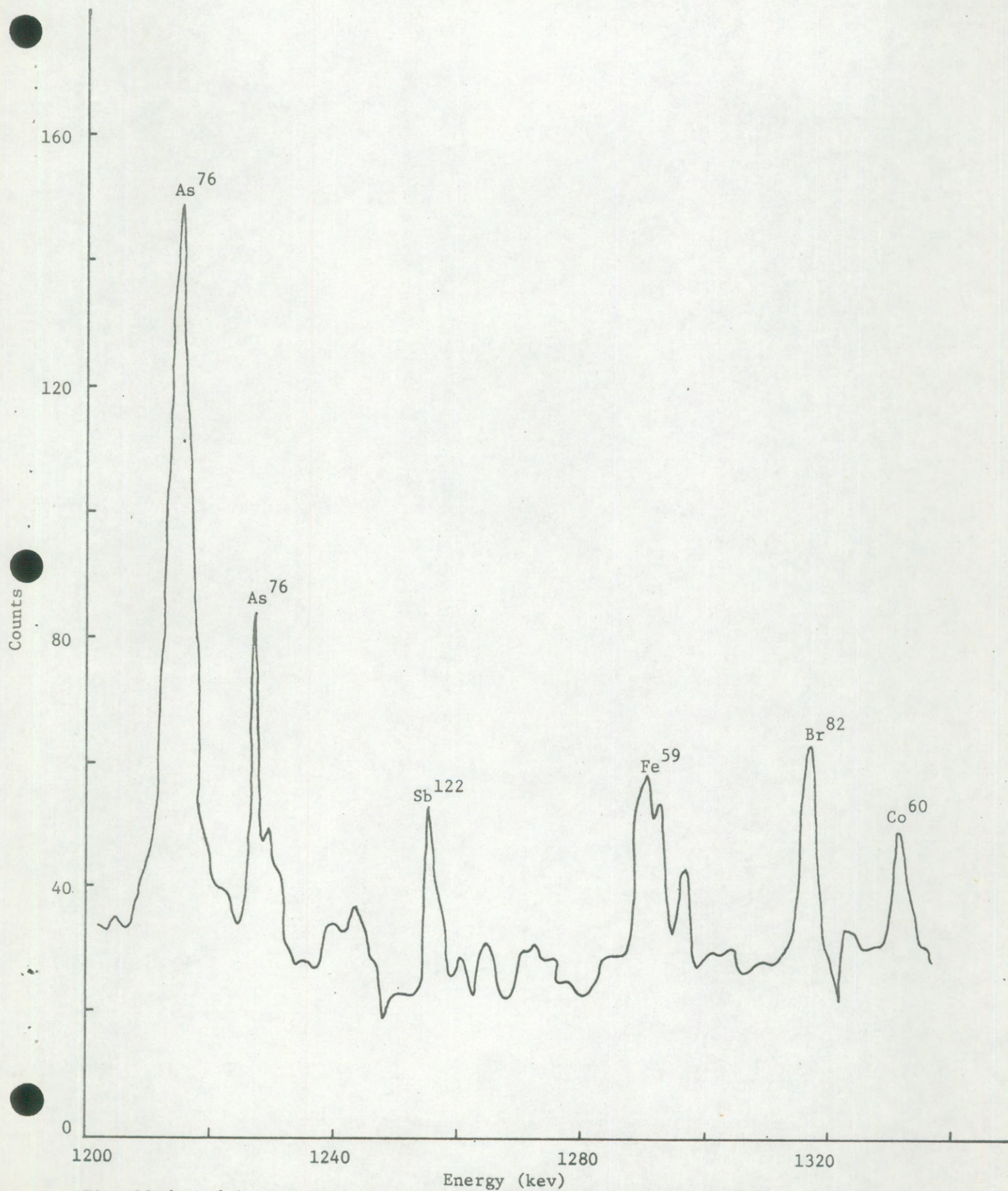


Fig. 12 (cont'd) Ge (Li) spectrum of sample from Yellowknife eight days after irradiation. Sample collected April 6-7, 1970.