

Nuclear Techniques in Environmental Studies

EQUIPMENT NEEDED FROM EG&G ORTEC

Complete TEFA System
 311 Chamber for source-excited x-ray fluorescence
 SLP-06175 Si(Li) X-Ray Detector, CFG-SV, DWR-30
 Bin and Power Supply
 572 Spectroscopy Amplifier
 480 Pulser
 459 5-kV Detector Bias Supply
 ACE-2K System including suitable IBM PC (other
 EG&G ORTEC MCAs may be used)
 GEM-10195 Coaxial Detector System, CFG-SV, DWR-30

301 Air Pollution Filter Standards for x-ray fluorescence analysis
 302 Portable High-Velocity Air Filter Sample Collector
 308 Neutron Howitzer and Activation Chamber
 Excitation Sources for source-excited x-ray fluorescence:
 50 mCi each of ^{55}Fe , ^{109}Cd , and ^{241}Am
 X-Ray Source Kit SK-1X
 3 Ci Am-Be Neutron Source
 100 μg to 100 mg ^{252}Cf neutron source, $\sim 10^{12}$ neutrons/g
 Oscilloscope

Introduction

During the last several years many atomic and nuclear techniques have been developed to study environmental problems. These techniques have been applied to air and water pollution studies for the most part. The two techniques that have received the most attention are x-ray fluorescence (source- or tube-excited) and neutron activation analysis. Both of these methods can be nondestructive and, in many cases, show very good analytical sensitivity. Generally, sample preparation is simple and accuracies of $\pm 5\%$ are achievable with the proper standard samples.

There are about 20 elements for atmospheric samples that can be studied with neutron activation analysis, using thermal neutrons from a research reactor. This method has sensitivities for some of these elements as low as $0.01 \times 10^{-9} \text{ g/m}^3$ for air particulate material. Depending on the interferences in the spectra and local concentrations, it is also possible to observe and quantify 22 additional elements by this technique.

Source- and tube-excited x-ray fluorescence analysis is also being used commonly for atmospheric pollution studies. For thin air pollution samples, investigators have observed up to 18 elements in a given sample with concentrations high enough to quantify for the indicated measurement. In general, this method is not as sensitive as neutron activation analysis but for many studies it is an ideal analytic technique. It is rapid and, as was mentioned for air pollution studies, there is virtually no sample preparation. Many air pollution studies measure only a few selected elements for a large number of samples. In many cases this technique is the best analytical method that can be used.

Purpose

Experiment 23 is intended to point out the relevant techniques and also to encourage science departments in univer-

sities to become involved in environmental measurements using nuclear technology.

EXPERIMENT 23.1

A Study of Environmental Samples by Tube-Excited Fluorescence Analysis

Purpose

The purpose of this experiment is to study the applicability of tube-excited fluorescence analysis for trace environmental samples.

Procedure

1. Use the Model 302 Portable Air Filter Sample Collector to obtain air particulate samples for the area to be studied. These samples are usually collected for a 3- or 4-hour collection period. The flow rate meter on the Model 302 should be monitored periodically to assure an accurate air volume measurement.
2. The EG&G ORTEC TEFA System will be used to evaluate the elemental content and concentrations of the elements present on the filter sample. The main features of a TEFA system are shown in Fig. 23.1.

The TEFA system comes complete with a detailed set of instructions for energy calibration and determination of elemental concentration. It is assumed that the student performing this experiment is familiar with the TEFA system.

3. Adjust the excitation energy and calibration range of the TEFA system so that the main features of your spectrum can be observed for the air pollution filter sample. Table 23.1

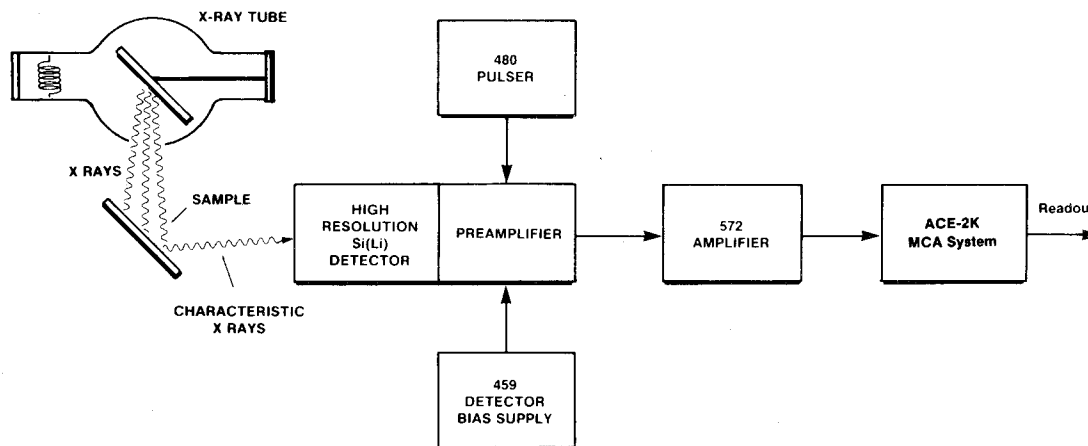


Fig. 23.1. Main Features of EG&G ORTEC's Tube-Excited X-Ray Fluorescence Analysis System.

Table 23.1. Typical Concentrations of Major Trace Elements of Airborne Particulates in an Industrial Area.

(Note: These numbers can change appreciably from one industrial area to another.)

Element	Concentration $\mu\text{g}/\text{m}^3$	Element	Concentration $\mu\text{g}/\text{m}^3$
Na	9.0	Zn	0.07
Al	0.75	As	1.0×10^{-4}
Si	1.00	Se	6×10^{-5}
Cl	5.00	Br	0.40
Ca	2.50	I	0.08
Sc	6.00×10^{-4}	Sb	5.0×10^{-4}
Ti	1.5×10^{-4}	Cs	4.0×10^{-4}
Cr	0.02	Ba	3×10^{-4}
Mn	0.50	La	7×10^{-4}
Fe	0.72	Ce	2×10^{-3}
Co	2.0×10^{-4}	Sm	2×10^{-4}
Ni	0.052	Eu	3×10^{-5}
Cu	0.80	Th	4×10^{-5}

shows typical concentrations of the major trace elements of airborne particulates in an industrial area.

Table 23.2 shows the presence of elements observed on atmospheric particulate samples by x-ray fluorescence.

4. Use the techniques outlined in the TEFA Instruction Manual to determine the elements present on your sample and the concentrations of each element.

In this measurement we have assumed that the pollution sample is thin. In other words, the matrix and attenuation corrections have been ignored. This is generally satisfactory for elements heavier than titanium for air filters. For lighter elements and thicker samples, refer to refs. 2, 3, and 9 for the necessary corrections to the data.

Table 23.2. Elements Observed on Atmospheric Particulate Samples.

X-RAY FLUORESCENCE	
Routinely	Marginal
K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Cd, Br, Pb	Au, Hg, Sr
NEUTRON ACTIVATION ANALYSIS	
Na, Al, Ca, Sc, V, Mn, Fe, Co, Cu, Zn, Se, Br, Sb, La, Ce, Sm, Eu, Hf, Th	Mg, S, Cl, Ti, Cr, Ni, Ga, As, Mo, Ag, In, I, Cs, Ba, Yb, Lu, W, Re, Ir, Au, Hg

Figure 23.2 is a spectrum similar to that which might be measured in this experiment. The technique outlined above for air pollution studies is equally applicable for water pollution data or any number of environmental measurements. Figure 23.3 is a spectrum that was measured on whole blood from a patient who showed lead poisoning symptoms. This tube-excited sample showed that the patient had several times the normal concentration of lead in his blood, indicating lead poisoning.

Figure 23.4 shows the results of some experiments studying the heavy element environmental pollution of mercury in fish. This figure is a good example of the ability of this state-of-the-art technique to do multielement analysis of an environmental sample in counting times of only 10 minutes.

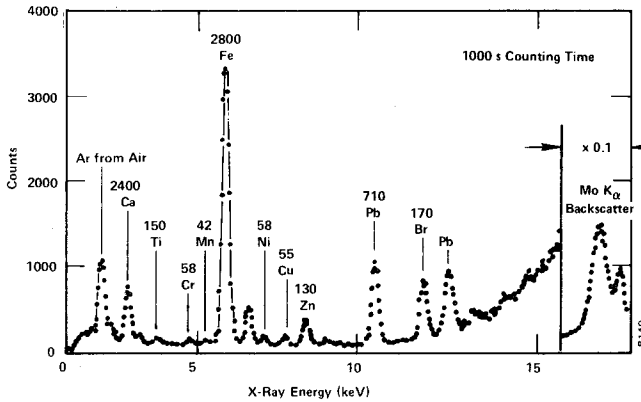


Fig. 23.2. Tube-Excited X-Ray Fluorescence Spectrum for an Air Pollution Filter. The numbers above the peaks are the measured concentrations in ng/cm² (taken from ref. 9).

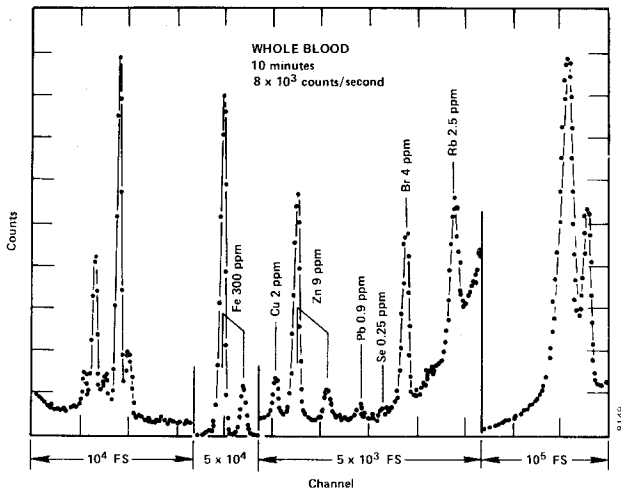


Fig. 23.3. Tube-Excited X-Ray Fluorescence Spectrum of a Whole Blood Sample. In this spectrum the measured concentration of lead is several times normal, indicating lead poisoning (taken from ref. 9).

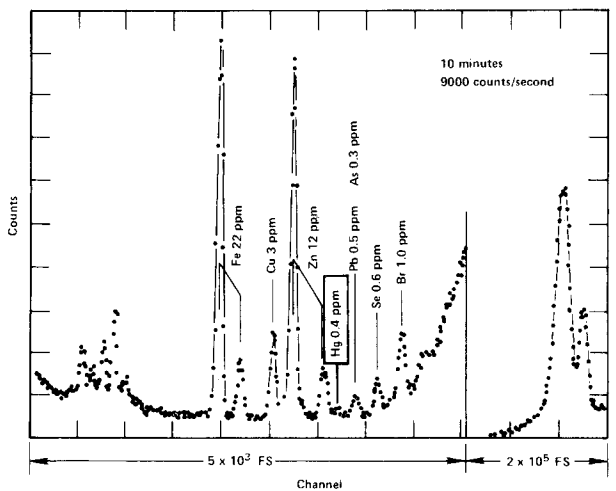


Fig. 23.4. Tube-Excited X-Ray Fluorescence Spectrum of a Fish taken from Water that has a High Mercury Content (taken from ref. 9).

EXPERIMENT 23.2

A Study of Environmental Samples by Source-Excited Fluorescence Analysis

Purpose

The purpose of this experiment is to study the applicability of source-excited x-ray fluorescence for trace analysis of environmental samples.

Description

The only difference between this experiment and Experiment 23.1 is the source of x rays. Sample preparation and other data comparative techniques are the same. Figure 23.5 shows the experimental arrangement for the EG&G ORTEC SEFA electronics, the MCA, and some detail of the method by which the sample is irradiated and fluoresced.

In order to produce the maximum sensitivity for trace analysis studies, it is necessary to select the excitation source carefully. Figure 23.6 shows a plot of photoelectric excitation cross section vs energy. As is expected from the theory, the maximum cross section for the K-shell excitation occurs at an energy equal to the K-shell binding energy for that element. For example, assume that all elements lighter than vanadium in our sample are to be studied with maximum sensitivity. The maximum photoelectric cross section for vanadium occurs at 5.463 keV (Fig. 23.6). Therefore, from a theoretical point of view, we would like to have an excitation source with exactly that energy. However, because of Compton scattering from the sample and other experimental reasons, it is best to have the excitation photons a little higher in energy than the binding energy listed above. For this problem, a source of ⁵⁵Fe, which emits photons of 5.895 keV, would be the best source. A general rule of thumb would

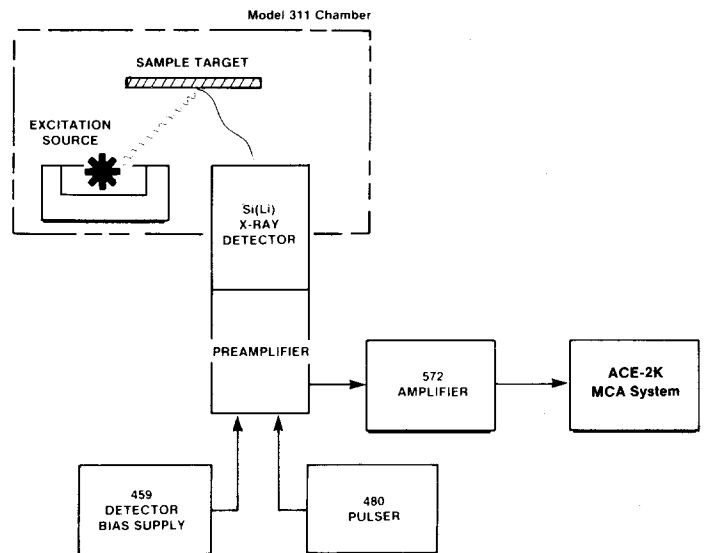


Fig. 23.5. Equipment Arrangement for Experiment 23.2.

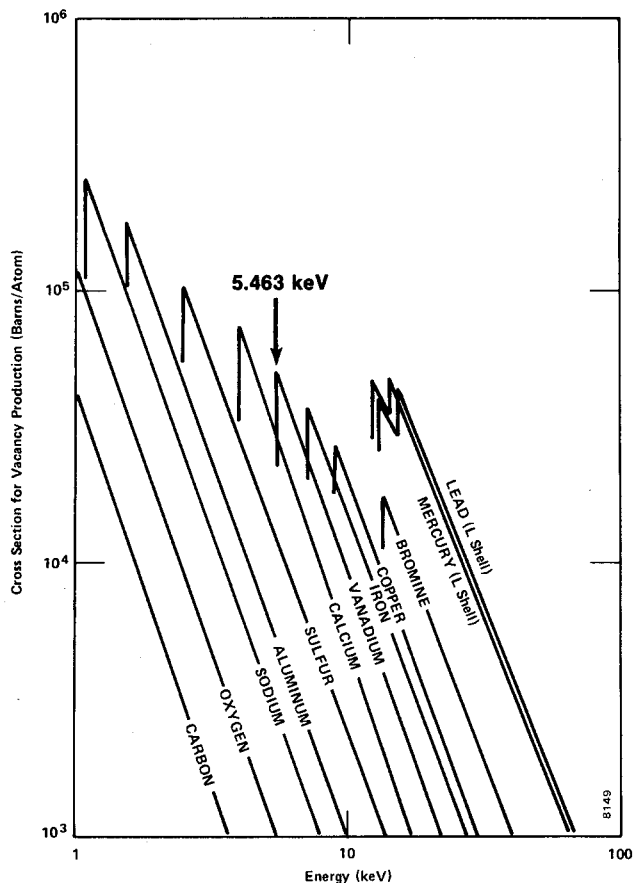


Fig. 23.6. Photoelectric Excitation Cross Sections for Twelve Elements Plotted as a Function of Energy.

say that the excitation photons from the source should be ~2 keV higher in energy than the K_{α} peak from the heaviest element in the environmental sample being studied. From the preceding statements and a careful analysis of Fig. 23.6, it should be obvious that it is advisable to study any given sample with several different excitation sources. The low-energy sources give maximum sensitivity for low-atomic-number elements, while the higher-energy sources, such as ^{109}Cd , are quite effective for heavier elements.

Procedure

1. Set up the electronics as shown in Fig. 23.5. Use the techniques learned in Experiment 12 to calibrate the system over the desired range with Source Kit SK-1X.
2. You may now fluoresce your first air- or water-pollution sample. For air pollution samples the Model 302 Portable High Velocity Air Filter Sample Collector can be used as outlined in Experiment 23.1. For the techniques of preparing other samples, refs. 2, 7, and 9 are helpful.
3. Figure 23.7 shows a typical source-excited x-ray fluorescence spectrum of residue from water that was taken from a municipal treatment plant.

The concentrations of each element in the spectrum can be determined by comparing the peak area to that of a standard

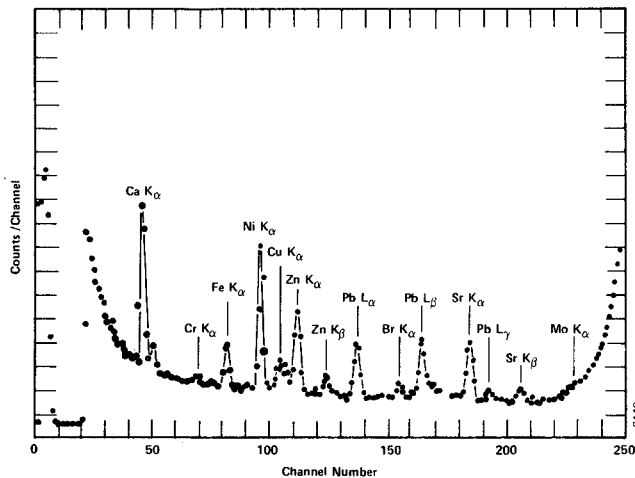


Fig. 23.7. ^{109}Cd Source-Excited X-Ray Fluorescence Spectrum of a Water Filter from the Effluent Water of a Municipal Treatment Plant.

that was fluoresced for the same conditions. For some of the major elements, the Model 301 Filter Standards can be used in this comparative mode.

EXPERIMENT 23.3

A Study of Environmental Samples using Neutron Activation Analysis and High-Resolution Gamma Spectrometry

Purpose

To study the applicability of neutron activation analysis with HPGe detectors to trace analysis measurements.

Discussion

There are four sources of neutrons that can be used for this experiment. These are: neutrons from research reactors, isotopic neutron sources, ^{252}Cf sources, or accelerator-produced neutrons. For thermal neutron cross-section measurements, the neutrons from any of the above sources will have to be thermalized before being used. A neutron howitzer, such as the EG&G ORTEC 308, can be used for this thermalization as well as to provide an activation chamber for the experiment. Figure 16.2 shows the spectrum of neutrons that must be thermalized for a typical isotopic source such as Am-Be. Figure 23.8 shows the fission spectrum of neutrons from the ^{252}Cf sources that have become popular. Most accelerators that are used for neutron activation analysis are Cockcroft-Walton machines that use 14-MeV neutrons from the $^3\text{H}(d,n)^4\text{He}$ reaction. These fast neutrons can be thermalized with the 308 Howitzer, or they can be used directly, depending on the elements being studied in the environmental sample.

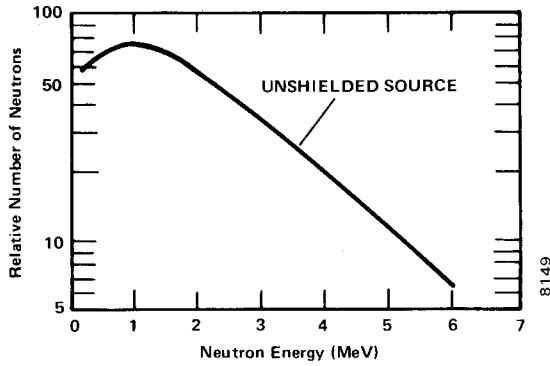


Fig. 23.8. Typical Fission Neutron Distribution from an Unshielded ²⁵²Cf Source.

Procedure

1. Set up the electronics as shown in Fig. 23.9. Use the procedures outlined in Experiment 7 to calibrate the electronics system so that 2 MeV falls near full scale, using 1024 channels in the analyzer.
2. Determine the proper activation and counting times for the first environmental sample. Use the data in Experiment 17 and in Table 17.2 as a guide.
3. Activate the samples in the irradiation facility and count for the best calculated times. Identify the elements present by the calibration curve and the Table of the Isotopes (ref. 8).
4. To quantify the elements in the sample, irradiate the standards of the observed trace elements under the same conditions as for the environmental samples and compare the peak measurements. These techniques are outlined in Experiment 23.2 and refs. 4 and 6.

Figure 23.10 shows an air filter sample that was measured using this technique by the scientists at Battelle Memorial Institute in Richland, Washington. For comparison, the same sample's spectrum is also shown as it was analyzed with a 3-in. x 5-in NaI detector. Figure 23.11 is a spectrum of an Alaskan caribou liver (courtesy of Battelle Memorial Institute) with the observed isotopes.

Many other environmental, biological, medical, etc. spectra have been studied with this technique as well as with x-ray fluorescence. The student is encouraged to read the references listed for this experiment in order to appreciate the state-of-the-art contributions that these techniques have made to trace element analysis.

Table 23.2 lists elements that have been identified with both x-ray fluorescence and neutron activation techniques. Table 23.3 lists the major elements found in air filter samples that were obtained in Los Angeles, California.

Table 23.3. Typical Sources of Trace Elements on Air Pollution Filters.

(This is data for Los Angeles taken from ref. 7.)

Source	Source Strength	Major Elements
Power Plant and Petro Chemical	36%	S, V, Ni
Automotive	28%	Pb, Br, Fe, Si, S, Ca, Cl, Al, Zn, K, Cu
Airborne Soil	25%	Si, Fe, Al, Ca, K, Ti, Mn
Sea Salt	7%	Na, Cl, Mg, S
Other	5%	K, Zn, Mg, Ti, Mn, Cu

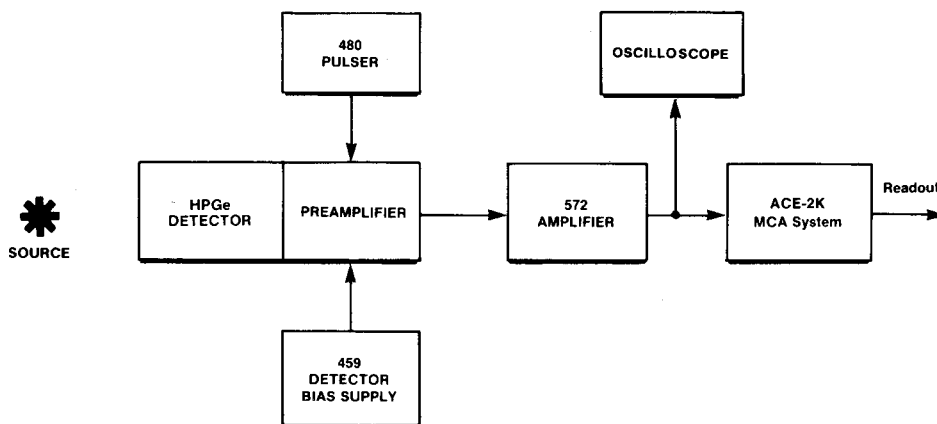


Fig. 23.9. Electronics Connections for Experiment 23.3.

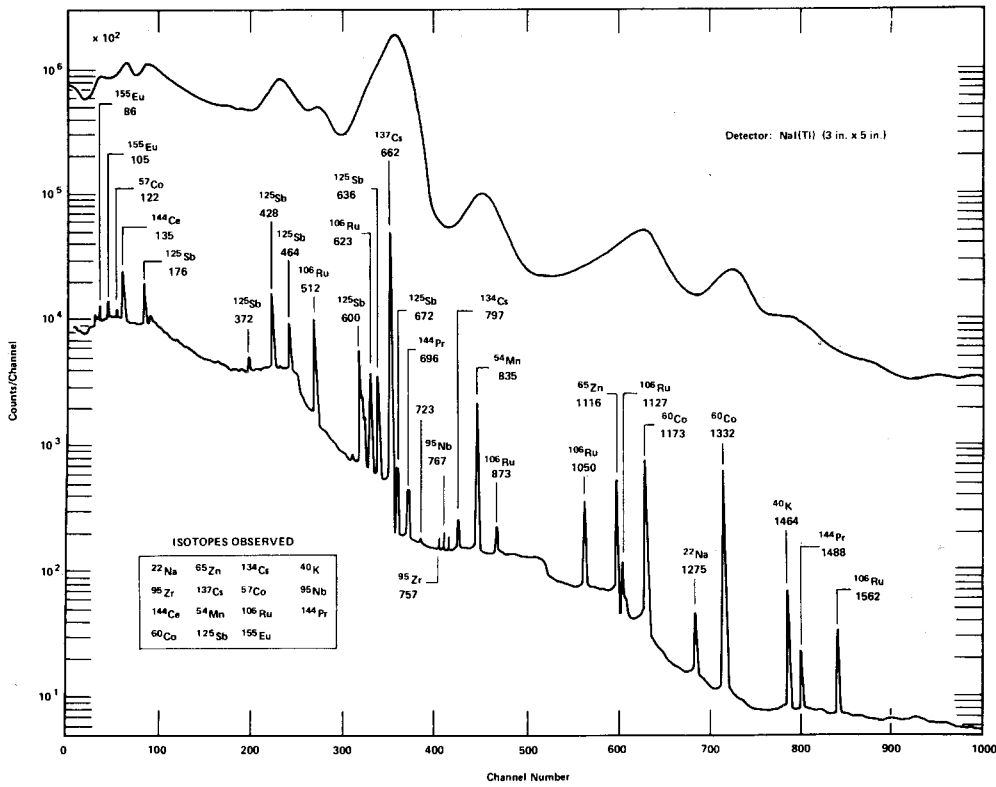


Fig. 23.10. High-Resolution Germanium Spectrum of an Air Filter Sample. Shown also on the figure for comparison is the 3-in. x 5-in. NaI spectrum of the same sample. (Courtesy of Battelle Memorial Institute.)

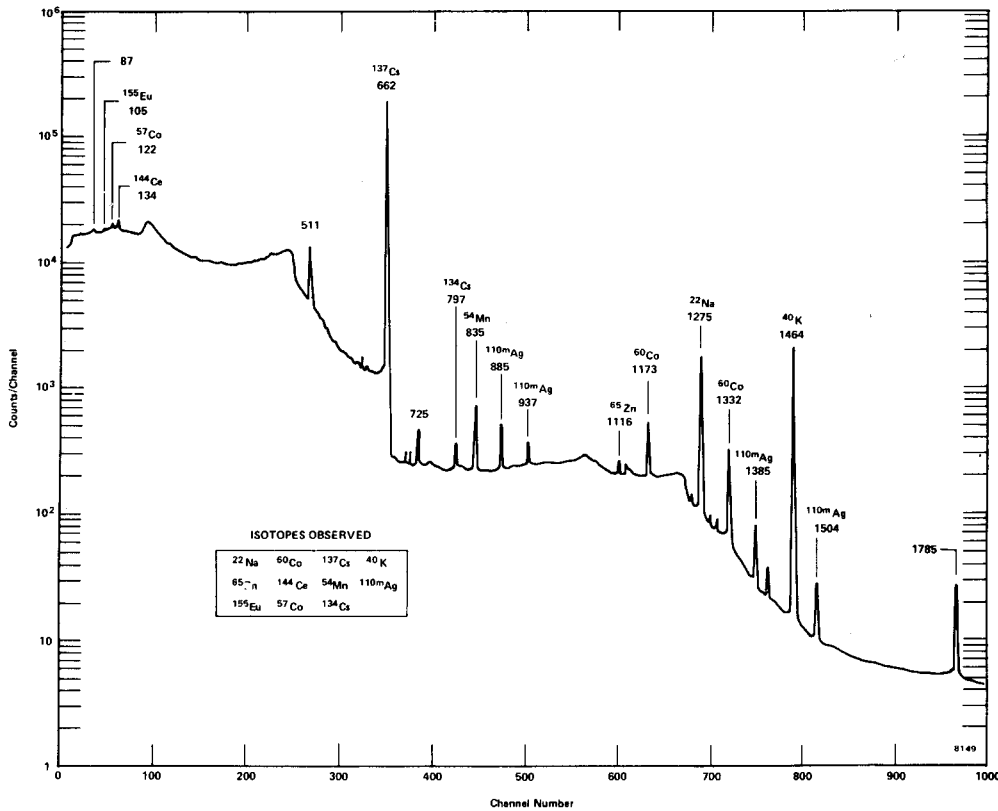


Fig. 23.11. High-Resolution Germanium Spectrum of Alaskan Caribou Liver Showing Isotopes Observed. (Courtesy of Battelle Memorial Institute.)

References

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