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IN SITU X-RAY FLUORESCENCE AND CALIFORNIUM-252
NEUTRON ACTIVATION ANALYSIS FOR
MARINE AND TERRESTRIAL MINERAL EXPLORATION

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ABSTRACT

Instrumentation has been designed for in situ analysis of marine and terrestrial minerals using the techniques of X-ray fluorescence and neutron activation analysis. The energy-dispersive X-ray fluorescence analyzer allows more than 20 elements to be quantitatively measured at the 10 ppm level in water depths to 300 m. The analyzer consists of a solid cryogen-cooled Si(Li) detector, a 50 mCi ^{109}Cd or ^{57}Co excitation source, and an analyzer-computer system for data storage and manipulation. The neutron activation analysis, which is designed to measure up to 30 elements at parts per hundred to ppm levels, utilizes the man-made element ^{252}Cf as its neutron activation source. The resulting radioelements which emit characteristic gamma radiation are then analyzed in situ during 2-to 200-s counting intervals with Ge(Li) or NaI(Tl) detector systems. An extension of this latter technique, which uses a ^{252}Cf - ^{235}U fueled subcritical multiplier, is also being studied. The subcritical facility allows the neutrons from the ^{252}Cf source to be multiplied, thus providing greater neutron flux. Details of these in situ analysis systems, actual in situ spectra, and recorded data are discussed with respect to the detection of minerals at their varying concentration levels. The system response of each illustrates its usefulness for various rapid environmental mineral exploration studies. These techniques can be utilized on terrestrial surfaces and marine or fresh water sediments.

INTRODUCTION

The discovery and potential utilization of our seabed and terrestrial resources have recently become important as a means of helping fill the increasing demands for raw materials in our industrialized society [1]. At the present time, ocean mineral utilization is limited to continental shelf areas. However, much of the mineral needs of the future may have to be met by the use of deposits on the deep ocean floor or from those as yet undefined recesses of our terrestrial surface. Measurements of the major, minor, and trace element concentrations in marine, fresh water, and terrestrial surfaces could produce information for resource evaluation [2]. These measurements should ideally be accomplished with a detection system which continuously records the concentrations of the elements of interest as it moves across the mineral surface. This instantaneous analytical information is of benefit to the geologist since it allows him to: 1) modify his exploration plan; 2) map the extent and quality of the resource; 3) obtain data on mineral type through multielement ratios; and 4) provide an inexpensive analysis technique.

Of techniques which exist for elemental analysis, two can be applied to the in situ measurement of elements on terrestrial or water-covered surfaces. The first is neutron activation analysis [3-10]. The second is energy-dispersive X-ray fluorescence analysis [11,12]. Both systems have been developed and applied to the measurement of elements of economic interest in terrestrial and marine exploration programs.

Neutron activation analysis has come to the forefront as a laboratory analytical tool since it can analyze many elements simultaneously with little sample preparation [9]. It normally involves activation of milligram quantities of the substance by a reactor, followed by photon detection with a variety of spectrometric systems. This communication discusses the design and application of the state-of-the-art in situ X-ray fluorescence and neutron activation analysis technologies which can be applied to terrestrial and water-covered exploration areas.

IN SITU NEUTRON ACTIVATION ANALYSIS INSTRUMENTATION

Two major developments during the past few years have dramatically changed the potential of neutron activation analysis for both the quantitative measurements performed in mineral assay laboratories and for a variety of in situ mineral analyses. They are: 1) the production of useful quantities of the isotopic neutron source ^{252}Cf ; and 2) the development of high resolution Ge(Li) gamma ray detectors for measuring the neutron activation products. Californium-252 emits 2.34×10^9 n/s/mg and has a physical half-life of 2.63 a. It has been studied for its applicability in a variety of neutron irradiation applications, including analysis of the elemental content of various minerals using both prompt and delayed gamma rays which are emitted following neutron capture by the elements.

In situ ^{252}Cf activation analysis normally uses 1 million-fold less neutrons than a reactor, yet the use of as many neutrons as that of a reactor is desirable. In order to circumvent this problem as well as to minimize the cost involved in the purchase of Cf (\$10,000 USA/mg), an alternative source of neutrons is presently being studied. A subcritical assembly has been designed to multiply neutrons for laboratory analysis [13-15]. A subcritical assembly operates on the principle that for every neutron that is introduced into it, many neutrons are generated [16]. Technology exists to allow the use of this technique in field applications. Some results of this activation technique are compared in this paper to those obtained by reactor activation.

In recent studies at Battelle, Pacific Northwest Laboratories, we have demonstrated that the elements in various mineral and commercial-grade ores at levels of economic interest can be readily identified by ^{252}Cf neutron activation analysis procedures [2,3,7]. A particularly promising application of ^{252}Cf activation analysis is in the area of in situ seafloor elemental analysis. A prototype stationary nuclear probe incorporating this technology has been designed, evaluated, and employed in a variety of studies of marine sediments [7]. The seabed probe as employed includes a 0.2 to 1 mg ^{252}Cf neutron source, a 15% efficiency Ge(Li) diode detector, and a minicomputer which serves as a central processing unit for data collection and analysis. The present Ge(Li) unit is designed to operate at water depths to 300 m and is cooled with a solid cryogen (a freon-propane mixture which permits up to 80 h of continuous subsurface operation). The underwater cable connecting the seabed probe to the surface vehicle transmits the detector signal, a video signal, control signals, and preamp power and AC power for lights and underocean hydraulic services. The Ge(Li) detector, through its 1000 ft of cable, has a resolution of 3 keV at 1.33 MeV. A set of basic software programs for the computer allows the analysis of S, Ca, Cl, Mo, Mg, Al, F, K, Na, In, Ga, Nd, Ni, Cu, Co, Ba, Sn, V, I, Eu, Ti, Mn, W, Sb, Dy, Ag, Os, Br, Rh, Pt, La, Ir, and As.

As is shown in Fig. 1, the detector-irradiator unit of the probe is a box-shaped structure. The irradiator contains the Cf source near the bottom and is filled with paraffin which serves as a moderator. This assembly is alternately shifted between a radiation and detection position by an hydraulically-driven system. This system is typically operated by irradiating the seabed for 120 s, allowing a 40-s decay, then analyzing the resultant photons for from 2 to 500 s. A second device using this same neutron activation analysis technique is being evaluated presently. This device allows continuous movement of the activation analysis facility over the seafloor surface. It is composed of a hinged skid. The forward half of the skid houses the ^{252}Cf source, while 4 m to the rear the Ge(Li) detector is housed on the skid. In this fashion continuous irradiation and continuous detection are accomplished. Typical towing speed anticipated is 1 knot/h.

Modification of the irradiating technique is also being considered. The laboratory neutron multiplier which is being considered for portable in situ activation uses a subcritical lattice of enriched U rods with a central cylindrical flux trap [13]. A total neutron multiplication factor of 66 is achieved with this design which precludes criticality at elevated temperatures, from void spaces, or from the insertion of graphite, U, or other media. Subcritical systems are now being sold commercially but have not been used for field analysis.

IN SITU X-RAY FLUORESCENCE INSTRUMENTATION

The system in Fig. 2 [11,12] for in situ energy-dispersive X-ray fluorescence analysis includes a 50 mCi ^{109}Cd or ^{57}Co source, an 80 mm² Ag collimator, an 80 mm² Si(Li) diode as the detector, and a combination field and laboratory analyzer-computer network. This network consists of a portable 4096-word analyzer, portable tape deck and a PDP-15 computer with multidisc memory capability. The resolution of the prototype X-ray fluorescence system is 225 eV full width half maximum at 5.9 keV. This resolution is achieved with the system in its in situ operational mode underwater, using 20 m of cable. To date this system has been used to depths of only 20 m; however, its operational design allows it to be used at depths to 300 m. It is cooled with a solid cryogen Freon-22, permitting 24 h of continuous sub-surface operation. The detector assembly has a 0.1 mm Be window which is protected against the water pressure by a secondary 0.5 mm Be window or Ti window, depending on depth parameters required. The outside dimensions of this device are 70 cm x 70 cm x 85 cm with a water weight of 20 kg. The ^{109}Cd source and detector are located immediately above the window.

In field operation (Fig. 3), the system is placed aboard a surface vessel or submarine containing portable generators (110 V), voltage stabilizers, and the electronics necessary for data handling. The detector system is lowered to the ocean floor by a winch connected to the analyzer through underwater cables. Typically the analyzer records the spectral response of the Si(Li) detector for 5 min. Afterwards the sample position is changed by lifting the X-ray fluorescence system, moving to a new position, and re-positioning the analyzer on the sediment surface. X-ray fluorescence techniques are, of course, only used for surface identification of the elements. The surface identification allows one to view from mm to cm depths within the material depending upon the K or L X-rays being used. These photons generally vary from 5 to 100 keV in energy and, of course, vary as a function of the element.

In this fashion, the analyst has immediately available the relative concentrations of Pb, As, Hg, Zn, Ni, Cu, Fe, Mn, Rb, Br and Sr, plus many others. This in-field data capability allows variations in elemental concentrations to be pursued, permitting sampling decisions while the data are being obtained.

IN SITU APPLICATION AND EVALUATION

These in situ techniques have been evaluated in laboratory and field programs. The in situ X-ray fluorescence system is calibrated in the laboratory for 20 elements of interest. Calibration is accomplished by analyzing thin element standards (50-120 μg per cm evaporated onto 0.013 mm Mylar films, Micromatter, Inc., Seattle, Washington). The resulting peak areas per unit mass of element are then plotted as a function of X-ray energy from which a smooth multielement curve is established. This thin sample calibration is then applied to fixed sample matrices using an iterative matrix correction procedure which has been described and evaluated separately [19]. The method utilizes the incoherent and coherent scatter peaks obtained in X-ray spectral analysis to estimate the amount of low Z material to be considered in computing the total self-absorption factors. This permits the calibration of the X-ray fluorescence probe to vary with large changes in sample matrix which are encountered in real field situations. Typical sensitivities for the X-ray fluorescence analysis system are compared to those obtainable from neutron activation analysis using ^{252}Cf neutron irradiation in Table I.

In general, the X-ray fluorescence allows analysis of the sedimentary matrix at the 5 to 20 ppm element concentration level, whereas the activation analysis system normally measures concentrations from % to ppm levels. Through the use of a subcritical facility in a field situation, 10 ppb of some elements could be identified. These in situ activation sensitivities are based on the nuclear parameters of each element.

Figure 4 shows the in situ X-ray fluorescence spectra of one sample of Puget Sound, Washington sedimentary material, illustrating the peak areas associated with 17 elements. In this study, surficial sediments were investigated near a large smelter which ostensibly is the source of significant amounts of Pb and As to the environment. Specifically, the study was to evaluate whether materials from the old slag pile were contaminating the area and whether the slag pile could be re-refined to provide an additional economic recovery of minor elements. A summary of the measurements made by in situ X-ray fluorescence is compiled in Table II. An analysis of Puget Sound water was also made at the same time for comparison with the surficial element concentrations in the same area. In the harbor, which was built with slag on one side and normal sedimentary rock from the coast of Washington on the other, Pb was 70 ppm. The Br concentration of 280 ppm in the water is above that normal seawater value of 65 ppm. The difference may be ascribed to colloidal or soluble material which was locked in the small bay between these two sedimentary sides. Results of the analyses of other elements were consistent with this assignment. For example, Sr at 56 ppm could be compared to normal sea water containing 8 ppm. Yttrium is normally at the sub-ppm level, yet was detected at 2 ppm. Niobium also was high.

Iron which is normally at the 10 ppb level was detected at the 0.06% level. These values all indicated colloidal material or particulate material in the water column. Other applications of the X-ray fluorescence in situ technique are immediately apparent.

Recent advances in intrinsic Ge detectors have allowed a sensitive system to be designed for the determination of heavy elements through K shell X-rays. For the detection of photons from the heavy elements, intrinsic Ge diodes are superior to Si(Li) detectors. This latter technique was evaluated for U and Th in laboratory experiments [20] utilizing a 40-mm² x 5-mm thick intrinsic Ge diode. The basic materials analyzed were 0.29% U ore and 1% simulated Th ore. The data illustrated that a 0.01% U ore can be analyzed in 10 s with a statistical uncertainty of only $\pm 7\%$, where Th could be detected at the same level in the same unit of time with an uncertainty of $\pm 11\%$. This type of in situ system would be designed just like the existing X-R-F unit except it would use a Ge detector and a ⁵⁷Co excitation source.

In Table I the detection sensitivity of the ²⁵²Cf neutron activation analysis probe has been calculated for a 1 mg ²⁵²Cf source. The detectable concentrations are based on 2-min irradiations, a 1-min decay, and a 2-min analysis with a 15% efficiency Ge(Li) detector. Experiments accomplished in the laboratory and in the field program have shown that the majority of induced radioactivity as seen by the nuclear probe assembly is obtained in a 15-cm-radius hemisphere of the ocean floor. For example, 90% of the 1.810 MeV gamma rays and 95% of the 0.847 MeV gamma rays from ⁵⁶Mn which are seen by the detector are emitted from this volume.

Through the use of a subcritical multiplication assembly, the sensitivity for detection of an element by neutron activation analysis can be reduced 100-fold, if a subcritical multiplication system is used with a multiplication factor of 100. For example, if one were identifying Au with in situ X-ray fluorescence, he could detect 5 ppm (Table I). If he were using in situ neutron activation analysis for Au, the concentration detectable is 10 ppm. However, if a subcritical device were used in the same configuration with the in situ activation analysis system, 0.1 ppm could be identified. The detectable concentrations in Table I are defined as twice the square root of the background in a field matrix.

For the analysis of ore bodies at great ocean depths, in situ activation analysis is the method of choice. Manganese nodules, for example, are found primarily at 6000 m or greater depths. These are depths beyond which the X-ray fluorescence system can operate. In Figure 5 is shown the spectra of Mn nodules taken in a field program. In this study, the existing prototype neutron activation analysis stationary system was used to analyze Mn nodules seeded in an ocean floor at 50 m depth. Optimum time periods for neutron irradiation, decay, and counting were evaluated for the detection of each

element of interest by the seabed probe. The gamma ray spectra shown in Fig. 5 illustrates the quality and type of information that were developed. The photopeaks are due to gamma rays emitted from the radionuclides formed by activation of the parent elements. The energies of the gamma rays are given in keV. The photopeak areas are proportional to the concentrations of the elements in the seabed. The analyzer can be programmed to integrate these photopeak areas and with proper efficiency factors provide a visual printout of the elemental concentrations.

As is shown in Fig. 5, the detection of Mn, Al and V is quite obvious under a variety of decay and counting periods with 7 mg of ^{252}Cf . Cobalt and Cu are best observed with short irradiation periods, such that ^{56}Mn does not build up. Nickel was not detected.

Efficiency factors for the in situ analysis of the major elements in this Mn nodule set were determined from irradiated (^{252}Cf for 20 s at a flux of 6×10^7 neutrons/cm/s) one gm samples of Mn, Co and Cu. The ^{56}Mn peak had 857 keV in 680 counts; the ^{60}Co , 150 counts; and ^{64}Cu , 425 counts, with a counting time of 200 s following a decay of 200 s. Using these efficiency factors, the calculated elemental concentrations for the irradiated nodules were 24% Mn, 0.5% Cu, and 0.2% Co, which agrees well with the results obtained by the United States Geological Survey for 150 lb of these nodules (Mn 23.8%, Cu 0.51%, and Co 0.18%). Although Ni was not identified with this small neutron source, it would be easily identifiable if the ^{252}Cf sub-critical multiplier facility were used to increase the number of neutrons irradiating the material.

This in situ neutron activation ocean study indicated that Na, Fe, La, Sm, Br, Co, Sc, Cr, Eu, Hg, Th, Rb, Ta, Cs, Sn, Sb and Zn do not mask detection of the more important elements of Mn, Co and Cu in the nodule deposits. Although sea water contains about 3.6% NaCl, there were no significant interferences from neutron-induced ^{24}Na and ^{38}Cl in the sea water or the sediment interstitial waters. Historically, bulk samples are collected to allow the determination of mineral concentrations. Grab samples have thus been obtained in all field program studies for comparison of the laboratory and in situ data to allow an interpretation of the accuracy of the in situ techniques. In both in situ X-ray fluorescence and neutron activation procedures, the laboratory and in situ data have agreed to within $\pm 30\%$ for some 40 elements studied.

SUMMARY

From these studies, we have shown that it is feasible to determine in situ the major, minor, and trace elements in a wide-ranging terrestrial or marine exploration program. This multielement analysis from X-ray fluorescence and neutron activation analysis techniques is exceedingly important in the interpretation of how the material must eventually be handled. In

some cases a given ore would be beneficiated for minor elements as well as the major elements. Data are obtained to determine if a change in chemical procedure is required to eliminate an interfering element. These in situ systems measure: 1) major elements, and 2) minor and trace elements at levels of economic interest. These measurements are made with the X-ray fluorescence technology for the top millimeters of surface and at depths to 15 cm with the neutron activation analysis technology. Some 20 to 30 elements can be measured with either technique, with concentrations ranging from % to ppb levels. These real-time measurements can be accomplished in fresh water or marine sediments or on terrestrial surfaces.

These two field studies proved that concentration changes vary within a few meters as transverse segments were observed across various sediment areas. The program also illustrated that these probes monitor different chemical compositions not normally detected by bulk analysis procedures. This is especially true of the X-ray fluorescence technology which measures surface phenomena.

With these systems analysis is achieved in real-time periods of 5 min. The data in Table I can be used to show that the elements of value in minerals such as barite, bauxite, caserite, phosphorite, scheelite, metal-bearing muds and Mn nodules can all be detected at their respective economic levels. This in situ technology is now being used to design probes to fit down bore holes for exploration purposes. These nuclear techniques allow useful, rapid and economic measurements to be made in the exploration of our terrestrial and freshwater or marine minerals.

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TABLE I

SENSITIVITY FOR MEASUREMENT
OF ELEMENTS IN SEABED OR ON TERRESTRIAL SURFACE

Element	Detectable Concentration X-ray Fluorescence ² (ppm)	Detectable Concentration by Neutron Activation ¹
Al	--	0.1%
Sb	10	1%
As	5	0.1%
Ba	20	0.1%
Cd	10	1%
Cr	5	4%
Co	5	0.1%
Cu	5	0.1%
Dy	10	10 ppm
F	--	0.01%
Au	5	10 ppm
Hf	10	1 ppm
In	10	1 ppm
Fe	5	50%
La	20	0.01%
Mg	--	0.01%
Mn	5	0.01%
Hg	10	1%
Mo	5	0.01%
Ni	5	1%
Nb	5	1%
Sc	--	1 ppm
Se	5	1 ppm
Ag	10	10 ppm
Sr	5	0.1%
Sn	10	3%
Ti	10	10 ppm
W	10	0.1%
V	10	10 ppm
Zn	5	N.E.*
Ga	5	N.E.*
Ge	5	N.E.*

TABLE 1 (continued)

Element	Detectable Concentration X-ray Fluorescence ² (ppm)	Detectable Concentration by Neutron Activation ¹
Br	5	N.E.*
Rb	5	N.E.*
Y	5	N.E.*
Er	5	N.E.*
Ce	20	N.E.*
Pb	5	N.E.*
Hg	5	N.E.*

* Not evaluated to date

¹Based on ~~two-minute~~ irradiation with 1 mg ²⁵²Cf, 40-second decay, and 2-minute gamma-ray analysis with 15% Ge(Li) diode.

²Based on 50 mc ¹⁰⁹Cd excitation (or ²⁴¹Am where necessary) source and 80 mm² Si(Li) detector.

ELEMENTAL CONCENTRATIONS IN SURFICIAL SEDIMENTS ANALYZED BY IN-SITU X-RAY
FLUORESCENCE IN PUGET SOUND-POINT DEFIANCE, WASH, U.S.A.

	WATER DISTANCE DEPTH TO SHORE		ELEMENT ppm (UNLESS NOTED OTHERWISE) *										
	<u>11.111</u>	<u>11.111</u>	<u>Fe (%)</u>	<u>Ni</u>	<u>Zn</u>	<u>Hg</u>	<u>Pb</u>	<u>As</u>	<u>Br</u>	<u>Sr</u>	<u>Zr</u>	<u>Nb</u>	<u>Mo</u>
PUGET SOUND WATER	42	100 30	0.06	550	<100	<210	70	<45	280	56	<17	18	<23
EAST (PT. DEFIANCE)	217	100 30	0.03	150	30	<60	<20	<13	240	31	<6	<6	<9
" "	217	100 30	0.05	230	<30	<90	<30	<14	230	46	<6	<7	<9
LAUNCH (PT. DEFIANCE)	73	50 20	1.64	100	220	<60	150	60	70	480	180	<5	17
" "	73	50 20	2.02	160	100	80	90	30	15	500	190	8	<7
SLAG PILE (PT. DEFIANCE)	3712	100 30	0.85	120	500	<60	320	140	180	210	80	11	29
" "	3813	80 25	1.50	190	450	<60	350	270	190	270	100	<6	33

* THE ELEMENTS Ti, V, Cr, Ba, Cu, Ga, Se, AND U WERE BELOW THEIR DETECTION LIMITS OF 0.01%, 0.01%, 300 ppm, 1%, 30 ppm, 20 ppm, 10 ppm, and 10 ppm RESPECTIVELY

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Fig. 1. Design of the developed in situ neutron activation analysis probe for water depths to 300 meters.

Fig 2 — Schematic design of the developed in situ X-Ray Fluorescence Probe,

Fig. 3. In situ X-ray Fluorescence Probe being used for multielement analysis of slag pile wastes in Puget Sound, Washington, U.S.A.

Fig. 4. In situ X-ray fluorescence spectra of Puget Sound, Washington Sediments.

Fig. 5. Gamma-Ray Spectra of manganese nodules being analyzed in situ underwater with the neutron activation analysis probe.

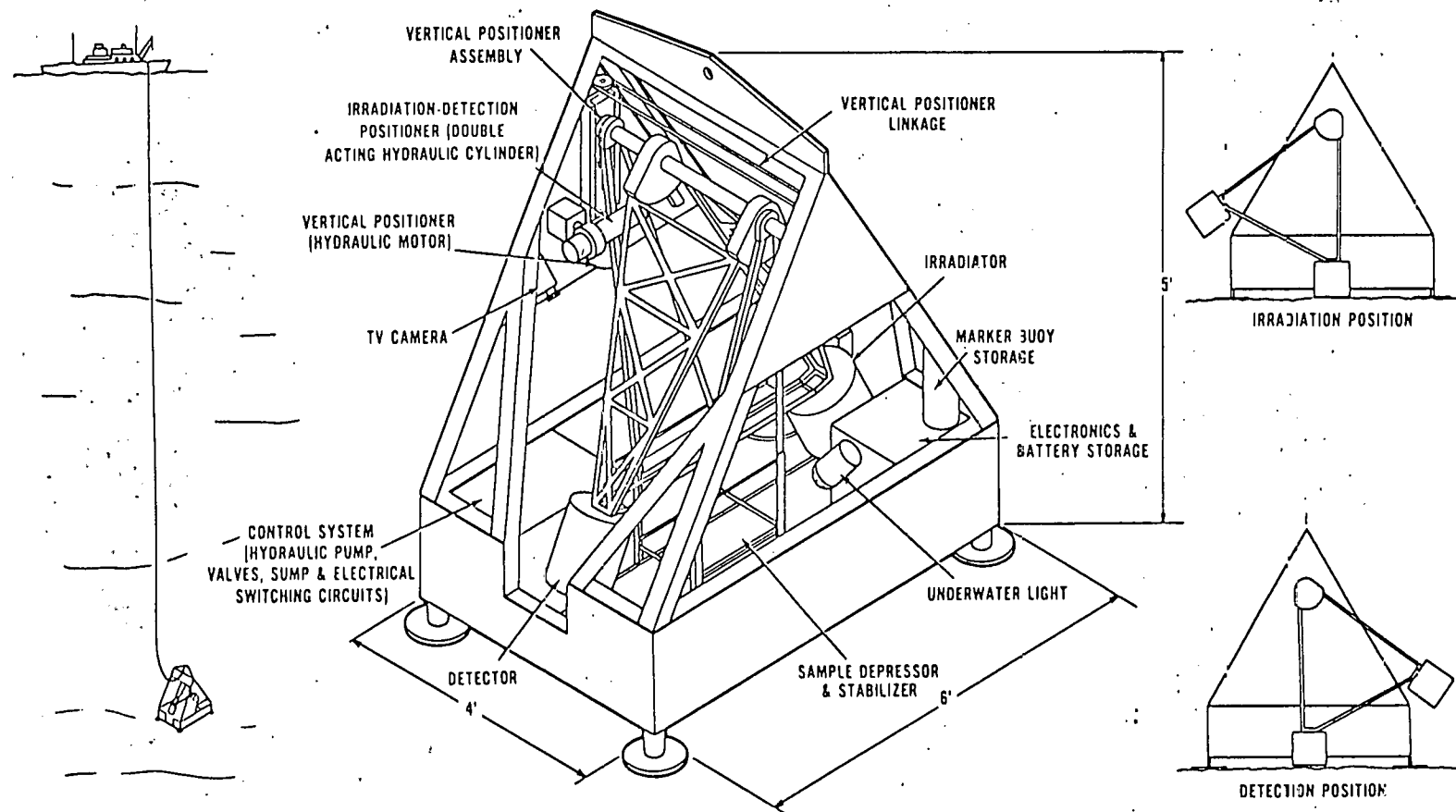
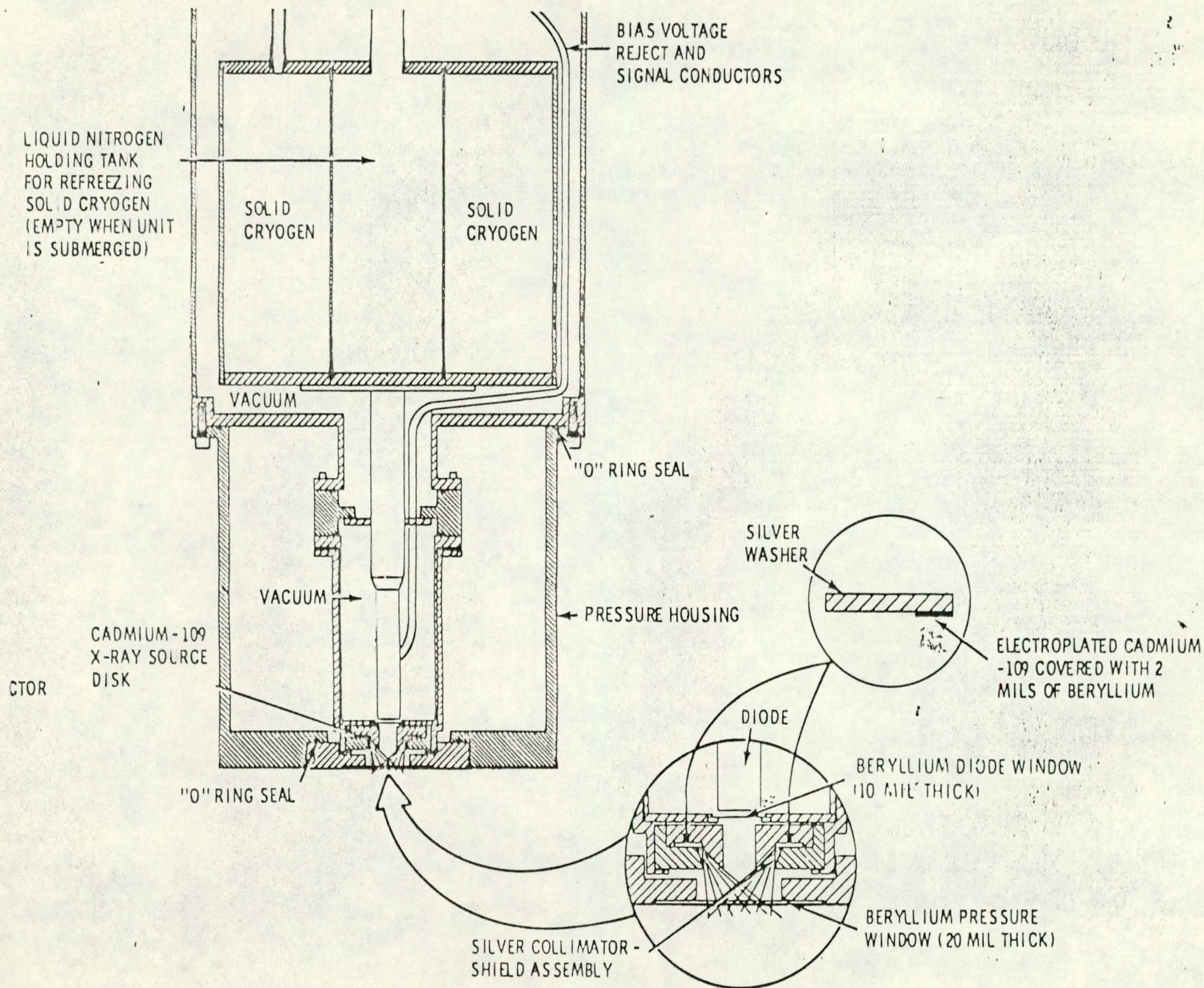


Fig. 1. Design of the developed in situ neutron activation analysis probe for water depths to 300 meters.



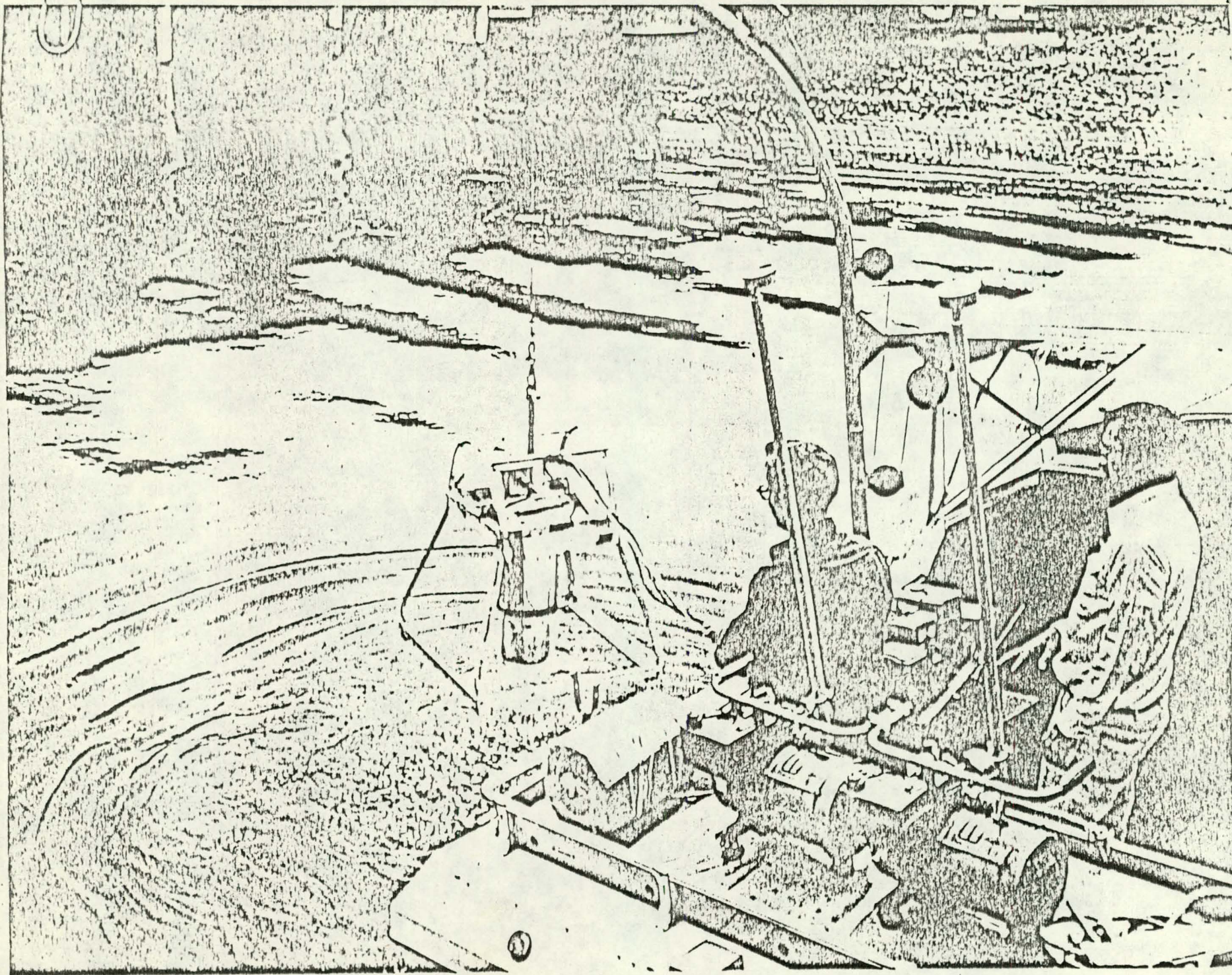


Fig. 3. In situ X-ray Fluorescence Probe being used for multi-element analysis of slag pile wastes in Puget Sound, Washington, U.S.A.

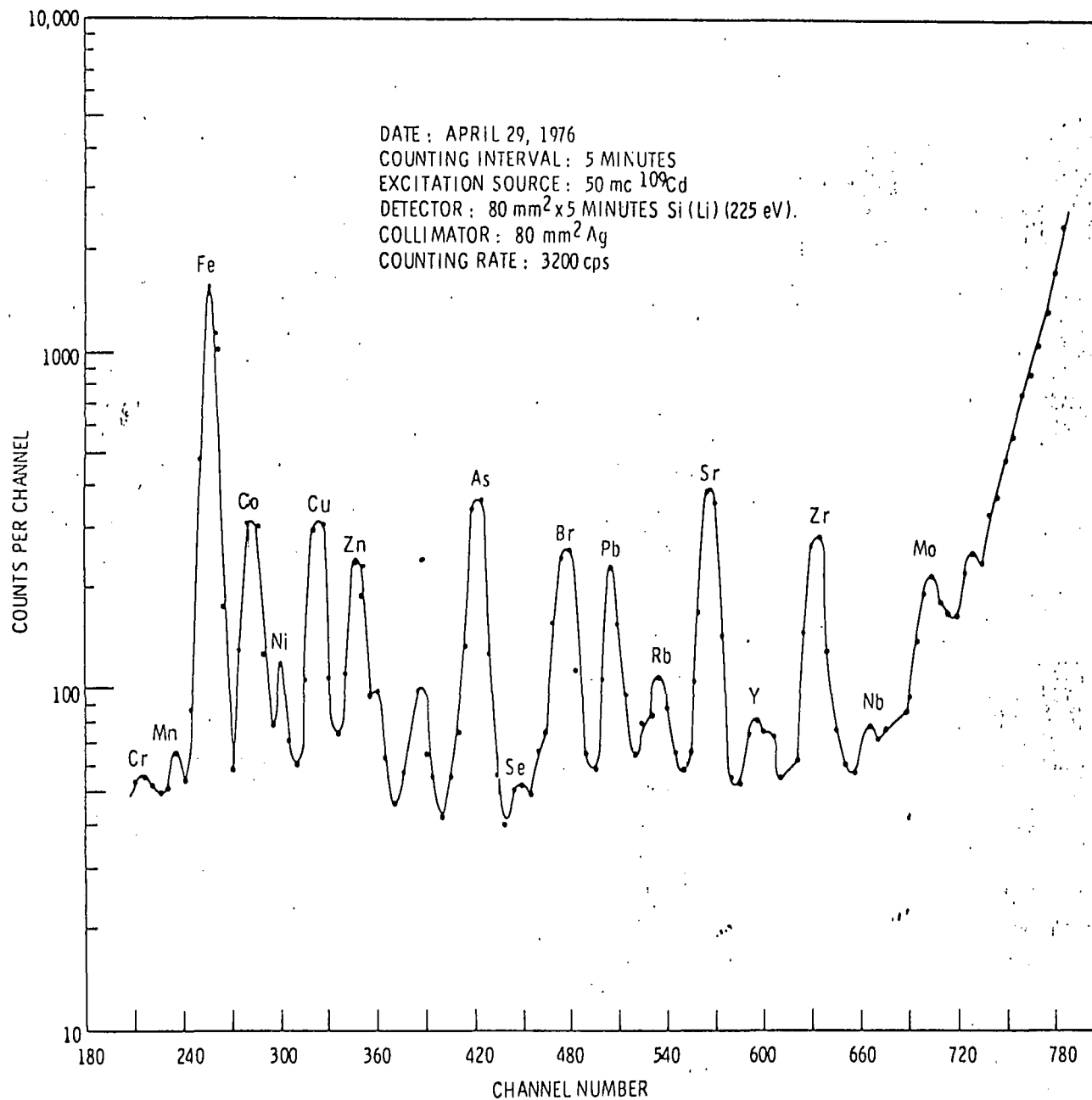


Fig. 8. In situ X-ray fluorescence spectra of Puget Sound, Washington sediments.

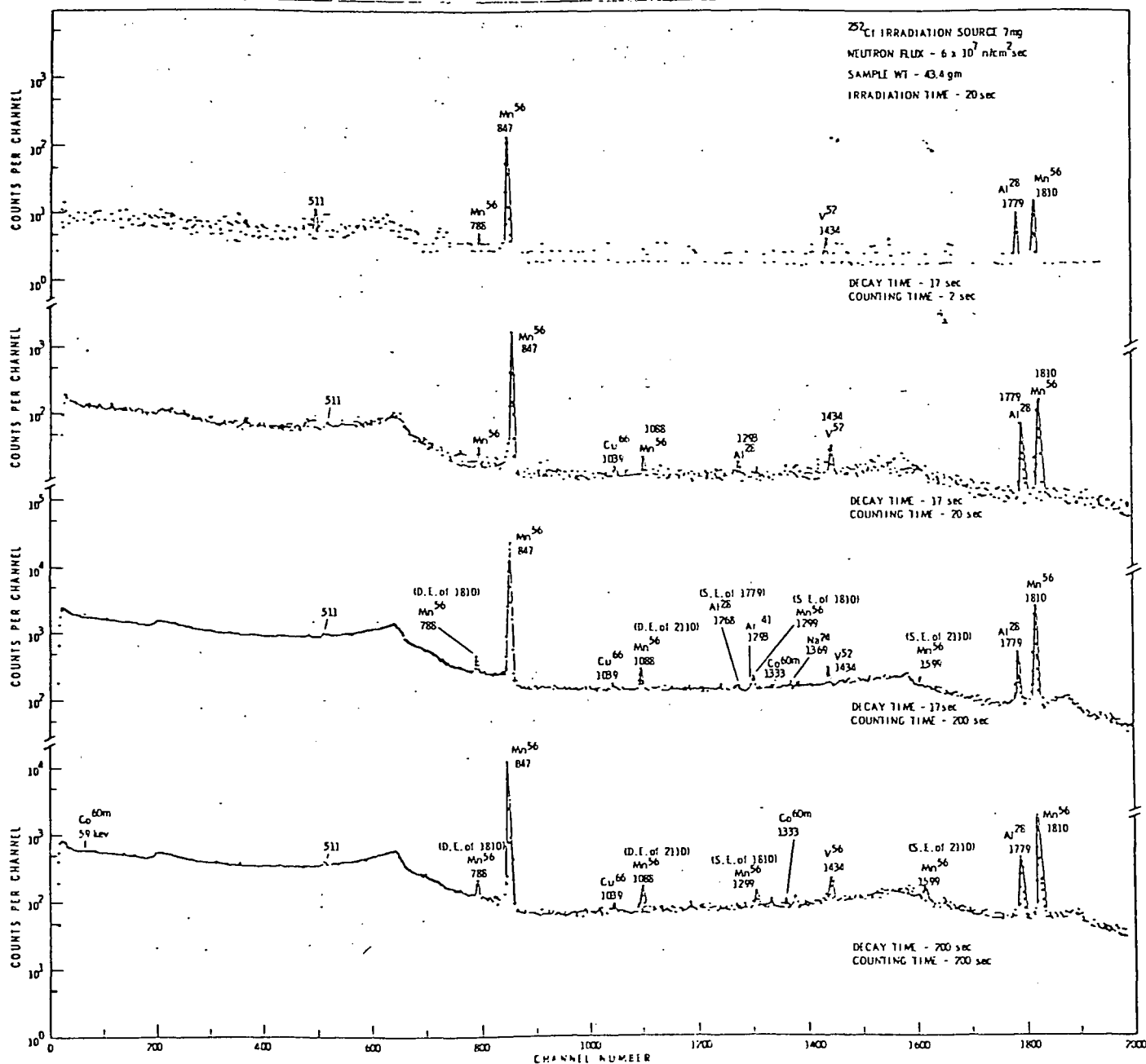


Fig. 4. Gamma-ray spectra of manganese nodules.