PRNC-142 PUERTO RICO NUCLEAR CENTER ACTIVATION ANALYSIS AS A METHOD FOR TRACING SUSPENDED SEDIMENTS, Braulio Mejia Avilés and Knud B. Pedersen 7 ormario by unavinsrry OF PUERTO RICO UNDER CONTRACT (NO, AT [40-11-1839 FOR U. 1, ATOMIC ENERGY COMMISSION ---Page Break--- LEGAL NOTICE ssccount of Goversmeat ss with respect to the use of, oF for damages avun, soethod, oF process ---Page Break--- ACTIVATION ANALYSIS AS A METHOD FOR TRACING SUSPENDED SEDIMENTS by Braulio Mejfa avilés ane Knud Borge Pedersen ---Page Break--- ABSTRACT Neutron Activation Analysis was applied to the problem of sedimentation in the Mayaguez Bay. The method was chosen as an attempt to eliminate the cumbersome chemical methods normally employed, and because it offered the opportunity to increase the sensitivity greatly. 24 ana ci? were eliminated by the masking effect of Na filtering the samples through 0.45 u millipore filter paper. The papers were allowed to dry in a closed hood to minimize airborne contamination and dust from entering the samples. The weight of the particulate matter in the filter paper was determined by weighing the papers before and after filtration. The filter papers were placed in one inch polyethylene vials and irradiated for 3 sec, together with aluminum standards. They were analyzed 30 sec later, using a NaI (Tl) crystal. The samples and standards were counted in alternate order for 40 sec live time, for a period which did not exceed 5 min. Aluminum was found to be present in all the samples in different concentrations. The results demonstrated that aluminum may be used for tracing the sediments contributed by river waters, offering the opportunity of determining their distribution pattern and settling rate. ---Page Break--- TABLE OF CONTENTS Page Introduction 2... . sees teed Review of Literature... 2 Neutron Activation Analysis... 4 Quantitative Analysis... 5 Description of Electronic Equipment... 7 Pneumatic Transfer System... 9 Detector Shield... +2 Sample Collection and Preparation... Sequence of

Analys - 18 Results seetesesees 18 References..+..ese0+ 28 ---Page Break--- Table No. LIST OF TABLES Summary of Results, ---Page Break--- w ua LIST oF FIGURES Illustration for Calculating Efficiency. Block Diagram of Electrical Equipment Modification Done to Pneumatic System, The Detector Shield. Diagram of the Detector Shield, Sample Collector and Bottle. Spectrum From 1 ml Seawater. ae Peaks From Sample and Standard, Decay Curves for Sample and Standard... Approximate Locations of Sampling Station....+-.++++ Alnusinus Concentrations v. Locations. 2 23 4 ---Page Break--- INTRODUCTION Many new techniques have developed almost as by-products of nuclear fever, Activation Analysis is one of them. “Activation” by some type of nuclear reaction is used to produce a radioisotope from the element to be determined. There are two major advantages in using activation analysis: first, since the instrumentation available nowadays allows the detection and measurement of very small amounts of radioactivity, this proves to be a very sensitive method; second, since the radioisotope formed decays with its own characteristic radiations and half-life, it is feasible to make activation analysis very specific. Besides its high sensitivity, activation analysis is a fast and economical method of analysis. Of all the possible nuclear reactions, the neutron reactions have been most often used. In the analysis of complex mixtures of nuclei, the major constituents with high neutron cross sections mask the spectra of other trace activation products. Most of the methods that are used to analyze complex mixtures by neutron activation employ suitable chemical separations to eliminate the interfering induced activities. If they are done before irradiation, some of the interfering activities would be intensified or new ones would be introduced. In general, these chemical operations are time-consuming and therefore, if done after irradiation, are not practical when analyzing for short-lived isotopes. When analyzing for short-lived isotopes entirely.

Instrumental methods must be used. By analyzing the sample immediately after irradiation, very small amounts of these short-lived isotopes can be measured. In this work, a technique was developed to measure small amounts of aluminum present in seawater samples. ---Page Break--- [REVIEW OF LITERATURE Increasing interest has been shown in purely instrumental methods of neutron activation analysis, and a number of studies not involving chemical separations have been reported. (1D) Jap published a review of some recently developed v.P. Guinn instrumental methods and techniques which are now in use. Some of these methods employ pneumatic tubes to analyze the samples as short as two seconds after irradiation. Fo. V. Anders(3*4) has applied the concept of gamma-ray difference spectrum to suppress the longer-lived components in the gamma spectra of activated samples. The method consists of analyzing the samples shortly after irradiation and also after the short-lived isotopes have decayed. By subtracting the second spectrum from the first, the effect of the longer-lived isotopes is almost entirely removed from the gamma-ray spectrum. “Dik, Robertson, L.A. Renicelli and RW. Perkins”) used neutron activation and direct counting techniques to measure concentrations of numerous trace elements in seawater, marine organisms, and pelagic sediment. Rit, Caldwell and W.R. Mitie, Jr. have used rapid neutron activation techniques for quantitative determination of Silicon, Aluminum, and Magnesium in rocks. The accuracy and reproducibility of the analyses and interferences from other elements are given. Nit. Creene has reviewed the use of activable stable isotopes with various types of activation analysis for tracing. Advantages and disadvantages of the method are given, and several examples of applications ---Page Break--- in medicine, pollution studies, and hydrology are described. P. Marrenoes has described the use of radioisotopes in tracing the effluent diversion at a proposed site for sewage disposal. Tracer injections

at different sites permit a selection of the most economical site according to the required purification of the sewage. ---Page Break--- when a stable nuclide captures neutrons and forms a radioactive product which has a relatively low absorption cross section, the rate of change of the number of atoms of the radioactive product will be given, and, N(t) = Number of radioactive atoms = Avogadro's number = Weight of the stable nuclide = Neutron activation cross section A = Atomic mass number of stable nuclide = Neutron flux = Decay constant of the radioactive product multiplying both sides of equation 4 by dt. Then integrating, and assuming N(0) = 0. ---Page Break--- where A N(t) is the activity of the radioactive product. The activity after irradiation time t and a decay time is given by $N(t) = Ni\ e^{(-\lambda t)}$ and the count rate will be, $R(t) = \varepsilon\ A\ N(t)$ where ε is the efficiency of the detector. For a point source on the axis of a cylindrical scintillator as in Fig. 1 it is given by, $\Omega = 2\pi(1 - \cos(\theta))$ where Ω is the solid angle subtended by the crystal measured from the point source, and μ is the total absorption coefficient. Quantitative Analysis In order to perform quantitative analysis of any sample using activation analysis, we can measure the flux, cross section and efficiency of our system, or compare our samples with known samples of standards. In order to compare the activity of the sample with that of a standard, they must have been exposed to the same neutron energy spectrum and neutron flux, and have similar count rates, thus producing essentially the same detector dead time. To obtain the same detector efficiency, the geometries must also be equal. ---Page Break--- ILLUSTRATION FOR CALCULATING EFFICIENCY ---Page Break--- by irradiating the sample and standard for the same time and essentially in the same place we can assure the same value of the flux and the same neutron.

energy spectrum. By choosing the weight of the standards so that their count rate will be similar to that of the samples, similar dead times can be obtained. If the standard and the sample are located in the same place relative to the detector, and have essentially the same dead time, the same efficiency can be assumed. Taking the ratio of the count rate of the sample to that of the standard we get, tens = Eta woot ne ey a stp SMa Ksrmetca - e7Myg AV A Therefore, if the decay time is the same where Wir is the weight of the standard. THE EXPERIMENT! Description of Electronic Equipment 1. Scintillation Detectors A 2" x 4.2" sodium iodide crystal activated with thallium was used for the detection of gamma rays. It was coupled to a 10 stage, ---Page Break --- photomultiplier tube which was operated at 935 volts. 2. Preamplifier The purpose of the preamplifier is to increase the signal amplitude from the detector and provide impedance transformation; that is, it transforms the voltage which is developed across the small capacity at the input of the preamplifier into an approximately equal voltage across the high capacity output cable. Canberra Industries Model 805 Scintillation Preamplifier was used for these experiments. It is a charge sensitive, all silicon transistor device which integrates the charge output signals from scintillation/photomultiplier detectors, for presentation to the pulse shaping main amplifier. 3. Amplifier The function of this instrument is to increase further the signal amplitude from the preamplifier. The gain can be adjusted to obtain the desired energy scale in the analyzer. C.1, Model 810 double delay amplifier was used for this experiment. It accepts the pre-amplified signals from proportional counters, scintillation, or semiconductor detectors. It yields in turn output signals suitable for single channel or multichannel analysis, and for leading edge timing. 4. High Voltage D.C. Supply This instrument transforms the 115 Volt, 60 Hz A.C. voltage to high D.C. Voltage to be

used by the photomultiplier tube, ‘the one used for this experiment was a Fluke Model 409 A, whose output ranges to 1,500 volts D.C. with less than 0.02% ripple and ina. output. ---Page Break--- 5. in and Power Supply Ortec Model 401 A Modular System Bin was used to provide power for the amplifier. It can provide plus or minus 12, or 24 volts D.C. and 115 A.C, delivered to assigned module connector pins. 6. Multichannel Analyzer The Multichannel Analyzer consists of the following elements: (1) the analog to digital converter that associates each input signal with a specific amplitude channel, (2) the memory, of data which contains the information of the number of pulses in each channel, and (3) the oscilloscope, typewriter, and curve plotter which provide for the display of the data which is stored in the memory. The system for this experiment was a Nuclear Data series 2201 system analyzer, which is a completely modular multichannel analyzer. A block diagram of the electronic equipment is shown in Fig. 2. ALL the irradiations were done at the T.R.N.C. research reactor at a power level of 1. Transfer System 1, Description of the system The system consists of a pipe through which the “rabbit," (the vehicle where the samples are placed), travels to and from the reactor. The time of irradiation can be adjusted from one second up to thirty minutes. When the rabbit dispatch button is pressed, vacuum is applied at the reactor end of the pipe, thus pulling the rabbit in toward the reactor. When vacuum is applied instead at the other end of the pipe the rabbit is made to return. 2. Modification Done to the System Fig. 3 illustrates the modification done to the pneumatic ---Page Break--- 10 just a bsuemauasl cha uazateny TaNNYHO Poa agans uaMod NIG sagans_¥3Mod BOULION HOIH L woisai3a XL yalanany algianv-3ud AN3WeINOS JINOYL2IT3 IHL 40 WYDVIG 0078 saws ---Page Break--- u MODIFICATIONS DONE TO THE PNEUMATIC system ! To the Reactor Butterfly Valve — switch i 7 | Short Pipe Connection Detector Shields Fig 3 ---Page Break--- 2 transfer

systes. When the system was set on "rabbit return," the vacuum applied above the receiving box to make the rabbit return from the reactor also pulled the rabbit back after it had passed the vacuum connection, which made the rabbit lose almost all of its speed, making it impossible to reach the end of the pipe. In order to remove the vacuum effect, a butterfly valve was installed in such a manner that it was activated by the rabbit as it approached the vacuum connection. By installing a curved pipe below the receiving box, the rabbit was transferred from the reactor directly into the detector shield. A short pipe intern was placed inside the receiving box, allowing the rabbit to bypass the box. The detector shield used for this experiment is shown in Fig. 4. It was made from solid lead in the form of a hollow cylinder. The circular walls are four inches thick and have three circular cavities, two for the detectors and one for the rabbit tube. The two detector cavities, which extend beyond the outer wall of the cylinder, provide space for detectors of different sizes. The walls of the external cavities are two inches thick, and two lead plugs of the same thickness are located behind each detector. The inner walls of the shield were covered with .027" of cadmium and .0625" of copper to absorb the characteristic lead X-rays, which are produced in the walls of the detector shield. Since the shield was coupled to the pneumatic system, it had to be sealed airtight so that the vacuum would effectively pull the rabbit from the reactor. ---Page Break--- ---Page Break--- Two styrofoam layers were placed inside the shield to provide support for the detectors. The detector was embedded in the top layer, thus remaining in a fixed position. Figure 5 shows the dimensions of the table and the relative position of the detector. D. Sample Collection and Preparation. Ten water samples were collected using the sample collector shown in Fig. 6. Glass bottles were previously washed with 4N Nitric Acid and distilled water, by holding the

sample collector at the desired depth a bottle placed in the sample collector will be completely filled with surrounding water. Samples were collected at different locations and at different depths in the vicinity of a sewage outfall in the Navaquee Bay. Since the purpose of this project was to develop a technique so that the samples could be irradiated and analyzed without chemical separations, I will sample the water were irradiated, using anal polyethylene vials, and were then directly analyzed. The water samples were irradiated for three seconds and analyzed after thirty seconds of decay. Only Sodium Chloride could be detected as can be seen in Fig. 7 where one such spectrum is shown. The remainder of the seawater samples were filtered, using 0.45 µm millipore filter paper, measuring one inch in diameter. The filter papers were allowed to dry in a closed hood to minimize airborne contamination and dust from entering the samples. The weight of the particulate matter in the filter paper was determined by weighing the ---Page Break--- DIAGRAM OF THE DETECTOR SHICLO DETECTOR STYROFOAM LL | LAYERS. red 5 ---Page Break--- ---Page Break--- was Jo my “ona u3ennN TaNNeHO tasn 99 9 (nan zen, ON ose S4nnoa 40 w3awnN 10008 _ ---Page Break--- 1 papers before and after filtration. Sense of Analysis ‘The filter papers were folded and placed in cylindrical polyethylene vials, one inch long and 1/2 inch in diameter where they were irradiated for 3 seconds together with vials containing aluminum standards. The aluminum standards consisted of small pieces of aluminum foil which were accurately weighed. Both the samples and standards were located at the bottom of the vials in order to sustain the same geometry relationship with the detector. They were analyzed in alternate order for 40 sec live time, for a period of time which did not exceed five minutes. The multichannel analyzer had been calibrated to read from 0 to 3 MeV in the four sections of the memory using an aluminum standard. identified and integrated from 6

channels ‘The aluminum: photopeak x: before to channels after the peak channel. The result of these integrals were then plotted on semi-log paper. Since the decay times have to be equal in order to make equation 16 valid, the ratio of the integrals has to be taken at a fixed decay time. For this work, the value of the integrals 2 min after irradiation was taken; by substitution in equation 16, the weight of aluminum in the samples was determined. Results The results of this work show that the amount of aluminum present in the particulate matter suspended in seawater can be measured using instrumental neutron activation analysis. A summary of the results is presented in Table 1. ---Page Break--- ---Page Break--- 20 A typical representation of the Al"® photopeaks (1.78 MeV) obtained from the activation of the particulate matter, as compared to that obtained from the aluminum standard, is illustrated in Fig. 8. The first and third correspond to the suspended sediment sample while the second and fourth were obtained from the aluminum standard. In Fig. 9, the integral over the Al® peak for the sample and the standard is plotted as a function of the decay time. Similar graphs were obtained from all the samples of particulate matter and the amount of aluminum was found to be dependent on location and depth. The area where the samples were collected and the collection points are shown in Fig. 10. In Fig. 11, the concentration of aluminum is plotted for different locations and depths. The shape of the curve for samples taken at a depth of 1 meter shows that the waste discharged at the sewage outfall, and in particular the suspended matter carried by the Yaguez River, contains large amounts of aluminum. Curve segments which are also plotted in Fig. 10 show that the aluminum concentration increases with depth. This effect is more significant in the vicinity of the Yaguez River where rapid settling of the sediment carried by the river is occurring. The fact that sulfate and chlorine exist in seawater in high concentrations.

constitutes the first foreseeable problem when analyzing marine samples. When the samples are activated, the washing effect of xa and ca™# does not allow the detection of the = ‘This problem was successfully overcome by filtering the water samples with ---Page Break--- (ON 73NNVHO a ---Page Break--- 2 [DECAY CURVES FOR SAMPLE AND STANDARD 10000|- ooo} yoo t 2 s = 3 DECAY TIME (min) Fig. 9 ---Page Break--- 23 APPROXIMATE LOCATION OF SAMPLING STATIONS Yvonra Yoouez River MAYAGUEZ Bay é 2 Location of sewage outfall Highway No.2 SCALE: 1115000 Fig. 10 ---Page Break--- Fy tr Sta (su313W) TIV4LNO ZOWMaS WOYs FONVISIG ZLVMIKONdAY a ee ae waimnt 9 su313N sz Hid3a. SS wie san anon yo wnow AL fame nudge HOHLY9OT SA ronAvEELN Ws) NOLLWELNBONOD NANIAMIV ---Page Break--- 25 OG n wfilipore filter paper. During filtration, the particulate matter which is not in solution is retained in the filter paper while the large amounts of sodium and chlorine which are in solution go through. This reduced to a negligible level the interference of these two major constituents, thus making possible the detection of small amounts of other active products. When using standards to perform quantitative analysis by neutron activation, one of the most important considerations is the fact that the shape and the size of the standard and of the sample should be similar. For very small samples, the variations in efficiency due to the difference in shape and size of the samples and standards are only significant when they are located close to the detector. When they are placed at a distance of 10 cm or more, the difference in efficiency becomes negligible(!2). Another important consideration in the use of instrumental neutron activation analysis is the choice of irradiation and decay times. These should be chosen so that the ratio of the activity of the desired radioisotope to the activity of the radioisotope which would create the greatest interference is a maximum. Calculations done to optimize these two parameters for this experiment show that

For ensuring elution in the presence of sodium, the shortest possible times of irradiation and decay should be used. The radioisotope which is going to be produced has a short half-life, like for example 4122 (xa * 2-3 min). Another consideration in the choice of the irradiation is to produce enough Al°® to be able to measure its activity during at least two half-lives. A considerable effort has been devoted to the study of these reactions that take place at the river-ocean interface which modify the composition of the nearshore waters. If the sediment coming from the rivers can be identified at the ocean-river interface, the pattern of sedimentation at the river mouth can be determined. In order to identify the sediment which is coming from the river, a tracer must be used. The fact that the concentration of aluminum in the suspended solids was found to increase in the vicinity of the Yaguer River sustains the possibility that aluminum may be used as a tracer for the river sediments. Since aluminum is an integral part of the river sediment, its rate of settling should be the same as that of the river. One of the advantages of knowing the pattern of distribution and settling rate of river sediments is that the blocking effect which is developed at the mouth of the river could be predicted, and preventative measures could be developed. It is of fundamental importance that the river waters are allowed to flow freely into the ocean, since the limitation of the water flow not only endangers its quality but may cause flooding during seasons of high precipitation. The technique which has been developed here is designed to use aluminum as a naturally occurring tracer. In situations where aluminum cannot be used as the tracer, other tracers can be developed by changing the times of irradiation and decay of the samples. A few improvements should be made to the water sampling technique, since for this research project the greatest effort was devoted to the laboratory.

analysis, the determination of the location where the sample was collected was done only visually. A more precise method would be used if a study of the ocean-water interface were to be conducted. Also, in order not to disturb the sample at the point of collection, a sample collector which could be opened and closed at the desired depth should be used. conclusions From the results of this work the following conclusions can be drawn: 1. By irradiating 1 ml of sea water and analyzing it after decay times up to 30 sec, only sodium and chlorine can be detected. 2. By filtering the water samples using 0.45 µ Millipore filter paper and analyzing the filter paper by neutron activation, the sodium and chlorine interference is reduced and the amount of aluminum present in the particulate matter suspended in the water can be measured. 3. The concentration of aluminum in the Mayaguez Bay area which was studied was as much as one hundred times greater than the value for standard sea water. The concentration of aluminum and the weight of particulate matter per liter of water increases in the vicinity of the sewage outfall and near the mouth of the Yaguez River. 5. The concentration of aluminum and the amount of particulate matter suspended in the water also increase with depth. 4. The method and techniques developed in this work can be used to trace the distribution and settling rate of the particulate matter contributed by certain river waters. ---Page Break--- L we. 28 REFERENCES vv.P. Ovinn, “Advances in Neutron Activation Analysis", Proceedings of the Third International Conference on Peaceful Uses of Atomic Energy, Geneva, 31 August - 9 September 1964, United Nations, 1963, Vol. 15, pp. 433-442. V.P. Oainn and C.D. Kagner, “Instrumental Neutron Activation Analysis", Anal. Chem., 32, 317-323 (1960). G.Y. Andera, “Determination of Fluorine by Neutron Activation", Anal. Chem., 32, 1368-1369 (1960). O.O. Pnders, "Use of Very-Short-Lived Isotopes in Activation Analysis", Anal. Chem., 33, 1706-1709 (1961) itis Roberton, L.A.

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