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Comparison of Germanium Detectors For Neutron Activation Analysis For Mercury

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COMPARISON OF GERMANIUM DETECTORS FOR NEUTRON ACTIVATION ANALYSIS FOR MERCURY

by

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ABSTRACT

Two types of lithium-drifted, solid-state, germanium detectors were compared for their ability to detect and measure mercury in matrices of different complexity. We compared (1) a large, coaxial detector with relatively high efficiency and a good peak-to-Compton ratio, and (2) a thin wafer detector, called a low energy photon detector (LEPD), which has a good resolution for low energy photons. In samples with relatively few elements primarily of low atomic number, the large detector is preferred because of its greater counting efficiency. In complex samples containing many elements that interfere with the mercury peak, e.g., samarium, thorium, barium, and tungsten, the detector of choice is the LEPD because of its ability to resolve the gamma photons. The choice of detector for intermediate samples would depend on the quantity of interfering elements present.

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SECTION I

CONCLUSIONS AND RECOMMENDATIONS

In instrumental neutron activation analysis (INAA) for mercury in samples composed primarily of water or organics with relatively few metallic elements, the large coaxial, lithium-drifted, germanium, solid state detector is preferred because of its greater efficiency. In complex samples containing many elements, especially those containing samarium, thorium, barium, and tungsten, the low energy photon detector (LEPD) is preferred because of its significantly better ability to resolve low energy photons.

The laboratory using instrumental neutron activation analysis should be equipped with germanium detectors of both types. The large detector will provide information over a wide energy range with better accuracy and precision. In the analysis of complex samples in the low energy range (below 150 keV), the LEPD is mandatory in order to resolve the multitude of gamma and x-ray emissions.

When a sample containing a large quantity of phosphorus is activated, it emits large amounts of bremsstrahlung that can prevent instrumental analysis of all low energy emissions.

SECTION II

INTRODUCTION

Mercury continues to be a problem in environmental pollution. Mercury in sediments, in water, in fish, and in other environmental samples is measured by cold vapor atomic absorption and other analytical methods in which the mercury must be separated from the sample prior to measurement. Loss of mercury during separation is a problem to the analyst. A method that does not use pre- or post-treatment is desirable to referee the usual analytical methods. Instrumental neutron activation analysis (INAA) is such a method. INAA is a nondestructive, multielement, qualitative and quantitative method. It would probably be the preferred method for determination of mercury at low concentrations if more nuclear reactors were available.

When mercury is irradiated with thermal neutrons, two radioisotopes are produced, Hg-197 and Hg-203. Hg-197, which has a higher activity, is usually the preferred isotope for measurement. Hg-203 is used for confirmation when necessary. The primary gamma photon of Hg-197, with an energy of 77.3 keV, is in the range of maximum interference from Compton scattering, natural background, x-rays, and bremsstrahlung. In addition, the sample matrix may contain elements whose decay produces photons that would interfere with the measurement of the 77.3 keV gamma of Hg-197.

Two types of detectors are available for INAA, both of which are of the Ge(Li) type. Sodium iodide detectors, NaI(Tl), are not suitable for INAA because of their poor resolution. The first Ge(Li) type is a relatively large coaxial or modified coaxial detector designed to have a relatively large active volume, the purpose of which is to increase the efficiency of detection of gamma photons over a large range of energies. The second type is a thin wafer Ge(Li) called a low energy photon detector, LEPD. It was designed to allow most high-energy photons to pass through undetected, and has its greatest efficiency of detection for low-energy photons, i.e., below 150 keV. The more notable difference in these two detector types is in their ability to resolve energies. The larger types have resolutions of the order of 2 to 7 keV full-width-half-maximum (FWHM) of the photopeak. The LEPD's have resolutions in the 0.2 to 0.7 keV FWHM range.

This paper compares the two Ge(Li) detectors for INAA of mercury in various matrices.

SECTION III

EXPERIMENTAL

MATERIALS

Mercury standards were made from reagent grade mercury dissolved in nitric acid and maintained in solution in 1.6 N nitric acid to prevent adsorption onto the glass vessel. Serial dilutions gave solutions ranging from 10^{-5} to 10^{-9} g Hg/ml of solution. Dilutions were made in distilled water, water from the Chattahoochee River taken just north of Atlanta, Georgia, and ocean water taken near Charleston, South Carolina.

Mercury analyses were performed on three types of organic matter: orchard leaves, National Bureau of Standards standard reference material 1571; bovine liver, National Bureau of Standards standard reference material 1577; and three fish samples used in the "Mercury-in-Fish Round Robin, 1972," Environmental Protection Agency, Surveillance and Analysis Division, Chemical Services Branch, Athens, Georgia.

Twenty-one sediment samples were analyzed, eighteen sediments from various sources[1] and three samples from the "Sediment Round-Robin, Mercury--1972," Environmental Protection Agency, Surveillance and Analysis Division, Chemical Services Branch, Athens, Georgia.

EQUIPMENT

The large Ge(Li) detector was manufactured by Nuclear Diodes, Incorporated. It is a cylindrical, modified coaxial detector with a diameter of 38.5 mm and a depth of 35.5 mm. The well is 6.9 mm in diameter. The window is composed of aluminum 0.5 mm thick. Relative to a 3 x 3 inch NaI(Tl) detector, its efficiency for the 1.333 MeV gamma of cobalt-60 was 7.9% with a peak-to-Compton ratio of 33/1. Its resolution was 1.40 keV FWHM at 122 keV. The preamplifier and linear amplifier were manufactured by Nuclear Diodes, Inc.

The LEPD used was obtained from Ortec Incorporated. Its dimensions are 16.0 mm active diameter by 4.76 mm active depth with an 0.13 mm beryllium window. The resolution was 0.502 keV FWHM at 122 keV. The preamplifier and linear amplifier were also manufactured by Ortec Inc.

The amplifier signals were processed by a Nuclear Data, Incorporated ND 2200 multichannel analyzer system with a 4096 channel resolution and a 1024 channel memory. The ADC had a 100 MHz digitizing rate. The multichannel analyzer was calibrated so that the gamma peak occupied 5 memory channels when either detector was used.

PROCEDURES

All samples were encapsulated in quartz vials to prevent the loss of mercury experienced with plastic vials.[2] Eight one-gram replicates of each liquid sample and four half-gram replicates of each solid sample were analyzed. In the preparation of the encapsulated samples for irradiation, two vials containing samples were packaged with two vials of standard in a square configuration in alternate positions. One gram of solution containing 1.0811×10^{-6}g Hg/ml was placed in each standard vial. This standard concentration was chosen to give a good statistical count in moderate counting time. All samples and standards were weighed, as it was impractical to deliver a quantitative volume into a quartz vial. The density of the standard was close enough to 1 that the concentration differential was negligible.

Thermal neutron irradiations were made in the one-megawatt experimental nuclear reactor at the Nuclear Research Center, Georgia Institute of Technology, Atlanta, Georgia. Irradiations were made in a vertical thimble inside the reflector for periods of 5 to 9 hours at a flux of 8.6×10^{12} neutrons/cm^2/sec.

Irradiated samples were allowed to decay three days or longer, depending on the sample matrix. A minimum of three days was necessary to permit decay of the activated elements in the quartz. Solutions of mercury in distilled water or river water could be analyzed after three days of decay. Ocean water and the sediments required at least 10 days of decay before they could be counted. The organic material could be counted after 6 days if absorbers were used to attenuate moderate amounts of bremsstrahlung originating from the phosphorus-32. If the phosphorus-32 concentration is too large, bremsstrahlung obscures the mercury-197 peak.

During gamma analysis each replicate and standard was counted with the quartz vial mounted as close to the detector face as possible for the best available geometry that would permit no more than 10% dead-time. (Dead-time is the time spent by the multichannel analyzer to process gamma photons.) The

replicates and their standards were counted in the same position and were rotated during counting to minimize geometry effects, especially for the solids. Each replicate and standard was counted by both detectors.

SECTION IV

RESULTS AND DISCUSSION

Table 1 presents the results of analysis of the solutions of mercury made up in distilled water, river water, and ocean water. The data show that the large detector is better in both accuracy and precision. In ocean water an increase in background diminishes the sensitivity of the method as demonstrated by the failure to detect mercury in the 10^{-9}g Hg/g range.

Table 2 presents the data for the biological samples. The nominal values for orchard leaves and bovine liver are taken from the Certificate of Analysis of the National Bureau of Standards. Those for the fish samples were the mean values from the round-robin results. The determined values were higher than nominal values except for bovine liver, in which mercury could not be detected because of bremsstrahlung from phosphorus-32. No specific reasons can be ascribed for the higher values. Results for the two detectors are essentially equivalent.

Table 3 presents data for the sediments. Nominal values for the "Sediment Round-Robin, Mercury--1972" samples are the mean values of all the participants' results. The other samples, being natural sediments, have no nominal values. All of these sediments were complex in composition with measurable quantities of many rare elements. Consequently, the background was high and direct interference was appreciable. Since many of the elements had half-lives as long or longer than that of mercury, the background and interference did not decay away. This background made the INAA for mercury less sensitive in sediments than in the solutions or biological samples tested. The better results for the LEPD can be attributed to its ability to resolve the many peaks. The LEPD was at least one order of magnitude more sensitive than the large detector.

"Not detected" was noted rather than "less than" values for those samples in which mercury was not detected, because the limitation of measurements was not primarily a function of the detector but was largely a matter of the composition of the individual sample. For two samples, 37933 and 37934, mercury is listed as "present". The 77.3 keV gamma did not produce a peak with enough counts to justify a concentration computation, but, along with the x-rays, was sufficient to indicate that mercury was present in the sample.

Table 1.

Standards		Detector Results			
		LEPD		Coaxial	
Sample	Actual Conc.*	Conc.*	Rel.% S.D.**	Conc.*	Rel.% S.D.**
		Distilled Water			
A	1.0811×10^{-5}	1.06×10^{-5}	5.0	1.07×10^{-5}	3.0
B	1.0811×10^{-6}	1.10×10^{-6}	3.7	1.08×10^{-6}	1.9
C	1.0811×10^{-7}	1.09×10^{-7}	3.9	1.05×10^{-7}	2.3
D	1.0811×10^{-8}	1.23×10^{-8}	7.2	1.12×10^{-8}	6.9
E	1.0811×10^{-9}	3.17×10^{-9}	19.	1.82×10^{-9}	31.
		River Water			
A	1.0811×10^{-5}	1.06×10^{-5}	4.8	1.06×10^{-5}	3.4
B	1.0811×10^{-6}	1.06×10^{-6}	3.7	1.09×10^{-6}	2.7
C	1.0811×10^{-7}	1.08×10^{-7}	3.2	1.06×10^{-7}	1.8
D	1.0811×10^{-8}	1.35×10^{-8}	8.9	1.12×10^{-8}	6.3
E	1.0811×10^{-9}	2.51×10^{-9}	35.	1.59×10^{-9}	26.
		Ocean Water			
A	1.0811×10^{-5}	1.03×10^{-5}	6.0	1.05×10^{-5}	4.3
B	1.0811×10^{-6}	1.03×10^{-6}	4.8	1.07×10^{-6}	3.2
C	1.0811×10^{-7}	1.12×10^{-7}	6.7	1.06×10^{-7}	6.2
D	1.0811×10^{-8}	1.14×10^{-8}	64.	1.46×10^{-8}	40.
E	1.0811×10^{-9}	Not Detected		Not Detected	

* Concentration g Hg/g sample

** Relative per cent Standard Deviation

Table 2.

Biological Samples

Sample	Nominal Value		Detector Results			
			LEPD		Coaxial	
	Conc.	Rel. % S.D.	Conc.	Rel. % S.D.	Conc.	Rel. % S.D.
Orchard leaves	1.55×10^{-7}	9.7	2.08×10^{-7}	25.	2.95×10^{-7}	18.
Bovine liver	1.6×10^{-8}	12.5	Not Detected		Not Detected	
Fish						
72c1222	2.06×10^{-6}	40.	2.71×10^{-6}	13.	2.84×10^{-6}	8.1
72c1223	5.75×10^{-6}	28.	7.63×10^{-6}	5.0	7.00×10^{-6}	2.9
72c1224	7.23×10^{-6}	28.	9.21×10^{-6}	2.7	8.57×10^{-6}	5.2

Table 3.

Sample	Nominal Value		LEPD		Coaxial	
	Conc.	Rel. % S.D.	Conc.	Rel. % S.D.	Conc.	Rel. % S.D.
Sediments						
Round-Robin						
72c5643	1.096×10^{-4}	20	1.60×10^{-4}	2.5	1.17×10^{-4}	5.3
72c5644	4.39×10^{-5}	21	6.19×10^{-5}	4.2	4.69×10^{-5}	1.3
72c5645	2.2×10^{-7}	170	Not Detected		Not Detected	
Natural						
37913			6.56×10^{-4}	4.0	5.55×10^{-4}	3.1
37914			1.11×10^{-3}	3.1	1.25×10^{-3}	3.9
37915			1.9×10^{-7}	53.	Not Detected	
37916			5.22×10^{-6}	8.6	3.36×10^{-6}	14.
37917			2.5×10^{-7}	48.	Not Detected	
37918			3.8×10^{-7}	42.	Not Detected	
37919			1.17×10^{-5}	9.4	1.23×10^{-5}	9.8
37920			Not Detected		Not Detected	
37921			1.41×10^{-7}	40.	Not Detected	
37922			3.36×10^{-4}	4.8	2.55×10^{-4}	3.8
37923			Not Detected		Not Detected	
37933			8.7×10^{-7}	31.	Not Detected	
37934			Present		Not Detected	
37935			Present		Not Detected	
39736			2.37×10^{-5}	11.	1.85×10^{-5}	7.6
37947			1.8×10^{-7}	56.	Not Detected	
37950			Not Detected		Not Detected	
37961			Not Detected		Not Detected	

Compton backscatter is the primary general source of interference in INAA. When a gamma photon interacts with any atom and transfers some of its energy to that atom, a degraded photon and an active atom result. The degraded photon, known as Compton backscatter, and the emission from the active atom, if detected, will add to the spectrum background. When the sample matrix is essentially hydrogen, oxygen, carbon, and nitrogen, as in water and biologicals, the background is low since these elements either are not activated or their half-lives are very short. As the complexity of the sample increases to include appreciable quantities of elements with atomic numbers greater than ten, the background goes up and the possibility of direct photon interference increases. For these reasons, sediment background problems are great.

Two elements that cause trouble in mercury analyses are samarium and thorium. Thorium-232 when activated, quickly decays to protactinium-233, which interferes with mercury-197. Other elements such as gadolinium and rhodium could also interfere but have not been encountered in the sediments tested in this laboratory. Samarium and thorium appear to be ubiquitous in nature. They are amenable to activation analysis, and they have half-lives that are appreciable with respect to that of mercury. The gamma photon energy for mercury-197 is 77.3 keV; for samarium-153 it is 75.4 keV, and for protactinium-233 it is 75.3 keV. If the ratio of detected gamma photons from the interfering elements is high with respect to number of detected mercury gamma photons, the mercury photons could be completely masked and thus mercury could not be distinguished using the large detector. The LEPD, because of its better resolution, can separate the interfering gamma photons from mercury gamma photons resulting in a positive analysis for mercury.

When a radioactive element decays to a new daughter element, the daughter element is in a metastable state. In decaying to the stable state, the daughter emits energy in the form of x-rays, which can have energies up to 120 keV depending upon the source. Mercury-197 decays to gold-197, which in turn emits four x-rays at 67.0, 68.8, 78.0 and 80.2 keV. The first, second, and fourth x-rays can make it difficult to determine the baseline. The third x-ray, 78.0 keV, is included in the count of the Hg-77.3 keV gamma; however, since the standard also includes it, it causes no error. Mercury-203 decays to thallium-203, which emits x-rays at 70.8, 72.9, 82.6, and 84.9 keV, adding to the background problem. The LEPD is able to resolve these x-rays, permitting the counting of the

77.3 keV gamma photons. Other possible sources of x-rays in the 77 keV range are osmium, iridium, platinum, lead, bismuth, polonium, astatine, and radon. Polonium, astatine, and radon are daughter elements of the decay of natural thorium and uranium and are so rare as to pose no problems. Osmium, iridium, and platinum are very rare, and normally will not be a problem. The weak polonium x-rays caused by bismuth, which is rare, also do not interfere. The large amounts of lead used in a detector shield absorb large quantities of energy and will produce interfering x-rays. However, these x-rays can be prevented from reaching the detector by proper cladding of the shield with copper and cadmium.

A few elements emit gamma photons that, while not interfering directly with the 77.3 keV gamma of mercury-197, can add to the difficulty of determining the baseline, since they have energies not far removed from 77.3 keV. For example, tungsten-187 has a 72.3 keV gamma and barium-133 has an 81.0 keV gamma. The LEPD resolves these energies, but the large detector does not.

A special problem arises when a sample contains an appreciable amount of phosphorus. Phosphorus-32 emits high energy beta particles, which in turn create a continuum of x-rays called bremsstrahlung when the beta particles are decelerated in the Coulombic field of atomic nuclei. Bovine liver and, to a lesser extent, fish had appreciable quantities of phosphorus. The half-life of phosphorus is significantly longer (14.28 days) than that of mercury-197 (65 hours) precluding waiting for it to decay to measure the mercury. The bremsstrahlung prevented the analysis of mercury in bovine liver but was not sufficient to prevent the analysis for mercury in the fish samples.

SECTION V

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16. Abstract

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17a. Descriptors

*Neutron activation analysis, *mercury, analytical techniques,

17b. Identifiers

*INAA, gamma ray detectors, germanium detectors

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