Fast-neutron-Activation Analyses of Various Water Sources of East Central Indiana

Diana S. Bennett
Matthew J. Buchkowski
Cheryl A. Bye
David L. Loewenstein
and
David R. Ober
Department of Physics and Astronomy
Ball State University
Muncie, Indiana 47306

Introduction

In recent years, much attention has been focused on the extent of environmental contamination. This problem has grown extensively primarily due to expansions in the industrial sector. Therefore, an adequate means for the detection and monitoring of potential industrial contamination was needed. In response the following methods of analysis have been used successfully for detection of environmental contamination: 1) gas chromatography (organic contents); 2) coulometric titration (dissolved gases); 3) electrochemical techniques (inorganic anions); 4) atomic absorption spectrophotometry (metals); and 5) neutron activation analysis (metals) (1). This study utilized fast neutron activation analysis (NAA) in an effort to determine the trace element composition of various northeastern Indiana water supplies. The source of neutrons for this study was the Ball State University Neutron Generator. This facility has been used previously in studies that searched for trace elements in coal, aspirin, precipitation (snow), and water samples.

The primary purpose of this investigation was to document regional fluctuations in the concentrations of certain trace elements found in the water samples. The study included local sampling sites representing both river and drinking water supplies. At three of the drinking water sites, multiple samples were taken at different times in an effort to study the time dependence of trace elements and to check the reproducibility of results.

Theoretical Considerations

Neutron activation analysis (NAA) takes advantage of the fact that characteristic radioactive isotopes are produced when a sample containing trace elements is bombarded with fast neutrons. The resulting unstable isotopes subsequently decay either by gamma-ray or beta emission. By measuring the gamma-ray emissions with a high resolution Ge detector/multichannel analyzer system, gamma-ray energies and half lives may be determined. This enables one to determine the parent isotope associated with a particular gamma ray, thus providing a means for identifying the trace element present in the original sample (target).

The fast neutrons for this investigation were produced by a Cockcroft-Walton type neutron generator by accelerating dueterium ions through a potential difference of 150 kV and allowing them to strike a stationary tritium target, inducing the following nuclear reaction:

$${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He^{++} + {}^{1}_{0}n + 17.6\ MeV.$$

The neutrons in this reaction have a kinetic energy of 14 MeV with the rest of the energy (3.6 MeV) being carried away by the alpha particle.

The initial disintegration rate A_0 (activity) of the product nuclei is directly proportional to the number (N) of target nuclei present in the sample, the neutron flux (ϕ) in n/(cm²/s), the reaction cross section (σ), and a time-dependent exponential saturation term which is dependent upon the decay constant (λ) and the time of irradiation (t_r):

$$A_o = N\phi\sigma(1 - e^{-\lambda t}r).$$

From this relation it can be seen that activity is directly propotional to the neutron flux. Because the sensitivity of the procedure depends on the activity of the sample, higher fluxes produce greater sensitivities. The flux effect can be visualized by comparing the flux and sensitivities of both fast and thermal neutrons. The thermalized neutron fluxes available in reactors are on the order of 10^{12} - 10^{13} (n/cm²s). The fluxes of fast neutrons from sources such as that used in this investigation are three to four orders of magnitude less (10^9 n/(cm²s) (2). The sensitivities obtained by this method are typically 0.5 ppm, whereas the sensitivities resulting from thermalized neutrons have been reported for selected elements to be on the order of 1 ppb. For example, sensitivities of 0.4 ppb gold, 0.6 ppb cobalt, 3 ppb copper, and 6 ppb zinc are not uncommon (1).

The sensitivities of this investigation were computed by comparing unknown samples with known amounts of standard solutions, taking into account relative flux and time corrections before comparison of the activities.

Experimental Details

The fast (14-MeV) neutrons used in this investigation were produced by the Ball State Neutron Generator facilities which include a 150-kV Cockcroft-Walton accelerator and a borontrifluoride (BF_3) neutron flux monitor system.

The gamma-ray spectrometer system consisted of a high resolution intrinsic germanium (Ge) detector (12.5% efficiency), a multi-channel analyzer, and a printer/plotter. The detector resolution was approximately 2.5 keV full width at half maximum (FWHM) at 1332 keV (^{60}Co).

The following steps were carried out in obtaining and preparing samples for irradiation: 1) sample site selected, 2) sample collected, 3) sample concentrated, and 4) sample transferred to a suitable medium for irradiation.

The drinking water sites were selected primarily on the basis of convenience, since they were the drinking water supplies of three of the investigators. The sites were in rural areas adjacent to Muncie — Jay County (northeastern), Union City, and Yorktown. The other sample was taken from the Muncie city water supply. Also chosen for study was the principal source of Muncie's drinking water, the White River. The latter was sampled in three different locations: 1) east of the city at the intake of the Water Treatment Plant, 2) middle of the city near Indiana Steel and Wire, and 3) west of the city near the Sewage Treatment Plant. This selection of sites was designed to detect changes in water composition as a function of location along the river. By choosing these various sites, it was hoped that a comparative water quality study could be obtained.

Soon after collection, the samples were subjected to a rigorous concentration procedure, consisting of evaporation of the water to obtain a more concentrated sample of smaller size. Twenty liters were collected and placed in either 1000-mL or 2000-mL beakers and allowed to boil down until approximately 50-mL was left. During this process precipitates formed. To speed the transfer of the remaining sample to smaller containers, concentrated nitric acid was added to dissolve the precipitates (if soluble). Nitric acid was chosen over other acids, such as hydrochloric and sulfuric, primarily because it does not activate.

To calculate trace element concentrations, it was necessary to prepare and irradiate standard solutions of known concentrations. Such solutions were made for all of the major elements that had been identified or were expected to be found in the water supplies.

Five-minute irradiation times were used. The samples were taped directly onto the end of the accelerator and exposed to a neutron flux for five-minutes. After an irradiation was completed, the activated sample was taken to the Ge detector and placed directly on top, at which time data acquisition was begun. The delay time (typically 60 to 110 seconds) was taken into consideration for computing concentrations. Generally, gamma-ray spectra of the water samples were recorded in five-minute intervals and composite spectra were obtained also for ten-, twenty-, and forty-minute intervals. The standard samples were counted in five-minute intervals for fifteen minutes. Ten-minute composite spectra were obtained also.

Results

A. Analysis of Sample Spectra

The photopeak energies were determined using internal calibration standards such as K-40, Tl-208, and the 511-keV annihilation energy. By comparison of the gamma-ray energies and half lives of the sample and standard spectra, the water-sample photopeaks were identified as to the target element responsible for the associated gamma rays (Figure 1). The concentrations of the detected elements were calculated by using the previously determined empirical sensitivities and normalizing them for flux and delay time associated with each spectrum.

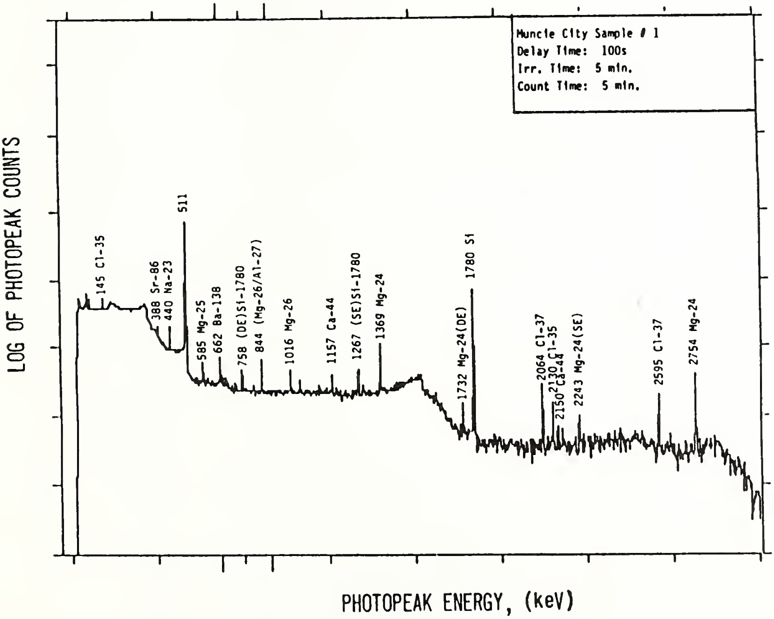

FIGURE 1. A gamma-ray spectrum acquired after a 5-min irradiation of a 20-L concentrated Muncie city drinking water sample. Identified peaks are associated with the trace elements that were activated by the 14-MeV neutrons; gamma-ray energies are expressed in keV.

B. Drinking Water Supplies

Using these methods, nine elements were found to be present in the various drinking water supplies (Table 1). Calcium, chlorine, magnesium, potassium, sodium, and

Table 1. Results of the concentration levels of trace elements detected in the drinking water samples; concentration levels are expressed in parts per million (ppm).

Element	Jay Co. Well # 1	Jay Co. Well # 2	Jay Co. Well # 3	Muncie City # 1	Muncie City #2	Muncie City # 3	Yorktown Well # 1	Yorktown Well # 2	Yorktown Well # 3	Union City # 1
Aluminum	.06 ppm	.05 ppm	.04 ppm	.88 ppm	.88 ppm	.45 ppm	.36 ppm	.38 ppm	.40 ppm	.29 ppm
Barium	.04 ppm	.03 ppm	.03 ppm	.15 ppm	.27 ppm	.17 ppm	.24 ppm	.23 ppm	.20 ppm	.40 ppm
Calcium	77 ppm	82 ppm	55 ppm	146 ppm	154 ppm	150 ppm	88 ppm	106 ppm	101 ppm	89 ppm
Chlorine	—	—	—	15 ppm	45 ppm	43 ppm	37 ppm	31 ppm	22 ppm	6.7 ppm
Iron	1.1 ppm	1.8 ppm	1.5 ppm	3.0 ppm	3.6 ppm	1.5 ppm	1.0 ppm	1.5 ppm	1.1 ppm	1.8 ppm
Magnesium	56 ppm	57 ppm	55 ppm	27 ppm	27 ppm	24 ppm	37 ppm	36 ppm	36 ppm	23 ppm
Potassium	2.4 ppm	2.6 ppm	2.7 ppm	5.3 ppm	4.9 ppm	4.9 ppm	2.7 ppm	2.6 ppm	2.5 ppm	.4 ppm
Sodium	47 ppm	40 ppm	32 ppm	13 ppm	22 pm	17 ppm	15 ppm	16 ppm	20 ppm	16 ppm
Strontium	18 ppm	20 ppm	16 ppm	3.9 ppm	4.1 ppm	5.5 ppm	1.6 ppm	1.0 ppm	.95 ppm	5.6 ppm

strontium were found in gross amounts, whereas, aluminum, barium, and iron were found in trace quantities. The concentrations of the detected elements were independent of sampling time except for the following: the aluminum, potassium, and chlorine concenrations of the Muncie City water supply. Since chlorine, alum, and potassium permanganate are some of the common substances added for water purification, fluctuations in these concentrations were expected (3). The iron concentrations were found to be approximately 1.0 ppm, which is a normal background level for this area based upon an atomic absorption study performed on these same samples (4).

Regional differences in several trace element concentrations were observed among the various drinking water samples. The Delaware County area has a larger barium concentration than the Jay County area. Barium is commonly found in water supplies in the form of carbonates and sulfates. Due to the insoluble nature of these salts, it is normally found in trace amounts, under the 1.0 ppm standard for safe drinking water (5). The aluminum concentrations seemed to follow the same trend as the barium. Because aluminum is one of the most abundant elements found in nature, its presence in the water supplies was not unexpected. One of the more interesting regional differences in trace element concentrations can be found in the strontium concentration levels (Table 1); the Jay Conty samples have significantly more strontium than those from Delaware County. Strontium is normally found in nature as a slightly soluble sulfate salt; however, its presence in such high levels was unexpected (5). It can also be seen that the city water supplies were lower in magnesium content than were the county well sites. For a more complete graphical presentation of concentration results (Figures 2 and 3).

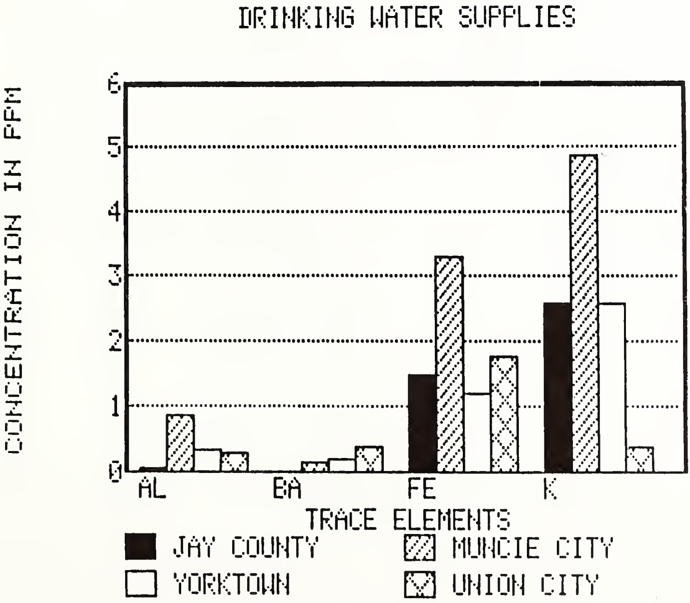

FIGURE 2. A graphical comparison of the concentration levels for aluminum, barium, iron, and potassium in parts per million (ppm), for the drinking water samples.

C. *River Water Supplies*

Nine elements were also identified in the river water samples (Table 2). However,

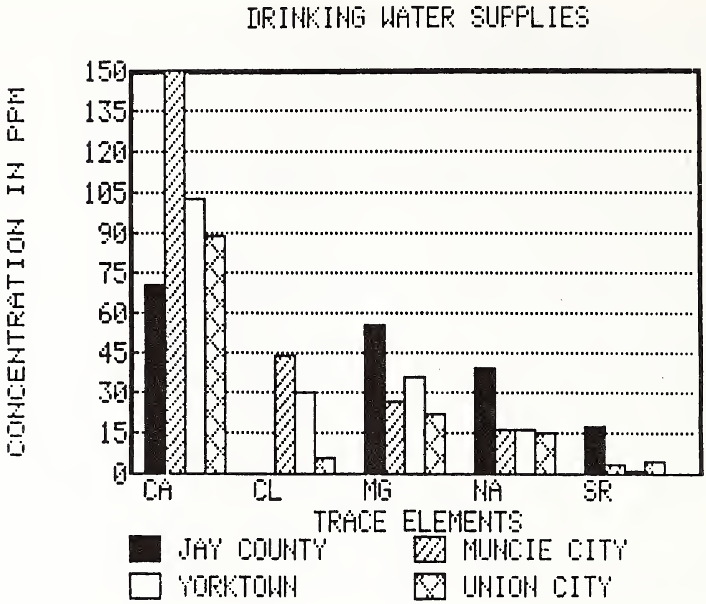

FIGURE 3. A graphical comparison of the concentration levels by sample for calcium, chlorine, magnesium, sodium, and strontium in parts per million (ppm).

TABLE 2. Results of the concentration levels of trace elements detected at three sampling sites along the White River at Muncie, Indiana; sampling sites were chosen where the river entered the city (Water Treatment Plant), a site within the city (near Indiana Steel and Wire), and a site beyond the city (Sewage Treatment Plant). Sample concentrations are expressed for elements detected in ionic and particulate (filtered) form. Concentration levels are expressed in parts per million (ppm).

Element	Water Treatment Plant Intake	Water Treatment Plant (Filter)	Indiana Steel And Wire	Indiana Steel & Wire (Filter)	Sewage Treatment Plant	Sewage Treatment (Filter)
Aluminum	.41 ppm	5.0 ppm	.81 ppm	5.1 ppm	.91 ppm	5.8 ppm
Barium	.04 ppm	.15 ppm	.08 ppm	.09 ppm	.12 ppm	.12 ppm
Calcium	43 ppm	45 ppm	48 ppm	35 ppm	65 ppm	34 ppm
Chlorine	5.8 ppm	—	3.2 ppm	—	20 ppm	—
Iron	.21 ppm	.71 ppm	—	4.1 ppm	.98 ppm	3.0 ppm
Magnesium	20 ppm	7.7 ppm	22 ppm	8.0 ppm	34 ppm	—
Potassium	2.7 ppm	2.6 ppm	2.9 ppm	2.4 ppm	4.3 ppm	1.69 ppm
Sodium	20 ppm	—	26 ppm	—	31 ppm	—
Strontium	.33 ppm	1.07 ppm	.48 ppm	.56 ppm	.75 ppm	1.6 ppm

as one would expect, these elements were detected in much higher concentrations than for the drinking water samples. Concentrations were seen to vary as a function of location along the river. The farthest upstream site was the water treatment plant, the next was the river near Indiana Steel and Wire, and the last sample was taken approximately one mile downstream from the sewage treatment plant. In most instances, the concentrations increased as one moved farther downstream. Alum, an aluminum salt, and potassium permanganate were being added as purifiers to the river water at the water treatment plant. This could account for the higher levels of aluminum and potassium observed further downstream. Figures 4 and 5 are graphical representations of concentration levels at various sites along the White River.

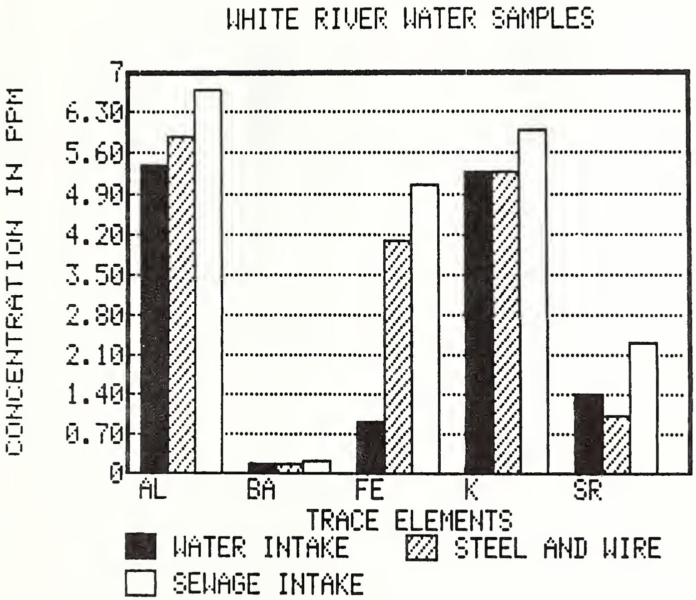

FIGURE 4. A graphical comparison of the concentration levels of aluminum, barium, iron, potassium, and strontium in parts per million (ppm) for three sampling sites along the White River at Muncie, Indiana.

D. Comparisons and Contrasts

The water samples in this investigation were found to have trace-element concentration levels similar to those of comparable sites. As one would expect, the river sample concentration levels were typically higher than those of the drinking water supplies.

Perhaps the most interesting comparison can be made between the Muncie City water samples and the White River samples. Both supplies showed similar levels of barium, iron, magnesium, potassium, and strontium, which was expected, since the White River is the source of Muncie's water (Tables 1 and 2).

Conclusions

The methods of fast neutron activation analysis (NAA) proved to be successful in identifying and determining the concentrations of nine elements commonly found in water

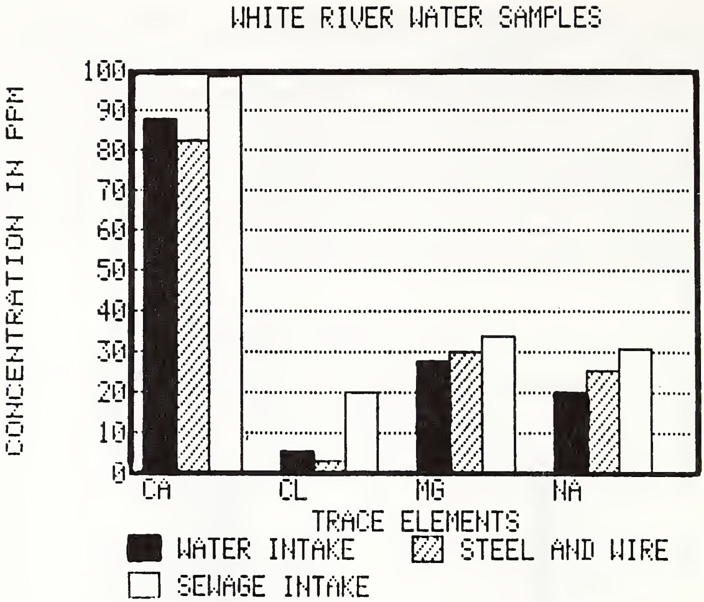

FIGURE 5. A graphical comparison of the concentration levels of calcium, chlorine, magnesium, and sodium, in parts per million (ppm) for three sampling sites along the White River at Muncie, Indiana.

supplies. The following elements were identified both qualitatively and quantitatively by this method: aluminum, barium, calcium, chlorine, iron, magnesium, potassium, sodium, and strontium. Silicon was also detected but only qualitative comparisons were done since silicon is found in all water samples. For the most part, calcium, magnesium, potassium, and sodium were found in gross amounts, whereas, aluminum, barium, iron, and strontium were found in trace quantities. It was estimated that the overall sensitivity of NAA was in the ppm range; this estimate was substantiated by the fact that results by the NAA were in excellent agreement with atomic absorption spectroscopy measurements to within specified uncertainties (4).

The strontium levels in the Jay County samples were considerably higher than the levels found in other similar water supplies. This could imply that there are strontium deposits located in the Jay County area. It was also noted that the aluminum concentrations for Muncie's drinking water were higher than normal; however, the addition of alum (aluminum sulfate) is quite common when drinking water is taken from a river supply. Overall the trace element concentration levels were consistent among samples and independent of sampling time. All of the concentrations for drinking water samples were within the USPHS Drinking Water Standards (3).

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