*ELEMENTAL ANALYSIS OF WATER AND AIR SOLIDS
BY NEUTRON ACTIVATION ANALYSIS*

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Abstract

Instrumental neutron activation analysis was used to determine the elemental concentrations in water and air solids samples collected on Nucleopore and Whatman filters from the Walker Branch Watershed. The results from this study show that the trace element concentrations removed by water from the watershed vary seasonally, as well as geographically. The data point up the usefulness and versatility of absolute neutron activation analysis.

The NBS Standard Orchard Leaves was assayed in a similar manner, and good agreement was obtained between results here and standard values.

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INTRODUCTION

This study is to measure the elemental output via the solids in the stream runoff from the Walker Branch Watershed and the elemental input from the aerosols. The Walker Branch Watershed (WBW) has been described in detail elsewhere (1). The study site (Fig. 1) is 97.5 hectare catchment, located on the Oak Ridge Reservation in Oak Ridge, Tennessee. It consists of two gaged sub-catchments: the east and the west branches, which contain 59.1 and 38.4 hectare, respectively. Both catchments are drained by small, perennial spring-fed streams. Discharge is maximum during the winter months and lowest in late summer.

Stream water sampled, collected at each of the spring and weir (basin) sites indicated in Fig. 1, were filtered through 0.4-micron Nucleopore filters immediately upon collection, and suspended sediments were then analyzed.

Aerosol samples were collected at the weir sites (See Fig. 1) using both Whatman 41 filter papers and Nucleopore filters.

Blank filters for the water samples were washed with a liter of distilled water to remove any soluble trace elements they contained. Blanks for the air filter were used as they came from the box.

The sample filters were sealed in polyethylene inserts after they were reweighed to determine the weight of solids collected.

To detect and determine quantitatively the maximum number of trace elements in each sample of filtered water or air, the samples were irradiated in the ORNL High Flux Isotope Reactor (HFIR) pneumatic system, which has a thermal flux of 5.5×10^{14} n/cm²/sec. The γ rays from the induced radioactive nuclides were counted on a Ge(Li) detector coupled to a computer-based multichannel analyzer. The study reported here uses the optimum irradiation and decay times to achieve the maximum useful data from the minimum number of gamma measurements and irradiations. The procedure was evaluated using NBS Standard Orchard Leaves. The data were processed by MONSTR computer program written by J. F. Emery (2).

EXPERIMENTAL

NBS Orchard Leaves Samples

The NBS Orchard Leaves samples of 100 to 150 milligrams were weighed and sealed in polyethylene inserts for irradiation. The samples were irradiated for 11 seconds in the HFIR, the induced radioactivity measured on Ge(Li) detectors, and the resulting spectral data processed by program MONSTR (2) for the trace element concentration. Several measurements were made to select the decay time to detect and measure the most short-lived radionuclides. After a week's delay to allow the induced radioactivity to decay, the samples were re-irradiated for 600 seconds. The induced radioactivities in the samples were measured after one day's decay and for several days thereafter until only long-lived radionuclides remained.

The results of the analysis of NBS Orchard Leaves with NBS values are in Table I. These values by absolute neutron activation analysis agree closely with the NBS values. The methods used by NBS to obtain their data on the Orchard Leaves include (1) atomic absorption spectroscopy, (2) flame emission spectrometry, (3) neutron activation, and (4) optical emission spectroscopy.

The decay time chosen to follow the short irradiation is usually several minutes so as to allow the ^{28}Al to decay until it is not the predominate radioactivity. This decay time depends upon the composition of the sample but usually ^{28}Al is the major radioactivity. By allowing the ^{28}Al to decay a few minutes, the precision and standard deviation of the minor peaks are improved as the ratio of the radioactivity in the respective γ -ray peak can be more accurately analyzed. After the long irradiation, a decay time of about two days (three if the sodium is very high) allows for the detection and measurement of the medium half-lived trace elements in the presence of the ^{24}Na radioactivity. If the measurement is made too soon, the only gamma photo peaks observed are those of ^{24}Na . The long-lived radionuclides are measured after two weeks of decay, or when the ^{24}Na has decayed out and the samples can then be counted near the detector. This measurement usually requires overnight counting to obtain good counting statistics and/or limits of detection for the long-lived radionuclides.

Filter Blanks

The choice of filters in air and water particulate sampling depends on flow characteristics and elemental impurities of the filters. Recent studies (3) have shown that Whatman #41 has a low level of trace element impurities. This filter was used for part of the air particulate studies.

The Nucleopore filter has a similar level of trace element impurities per filter and was used in most of the sampling for water and air solids. Several blank filters were irradiated, their radioactivity measured after appropriate decay times, and the trace element concentration determined.

The trace element values from these data were used after air filtration. Another set of four filters was used to filter one liter of distilled water to determine any leaching effects on the trace elements in the filters. These were then irradiated and the radioactivity assayed as above. The comparative data on washed and unwashed filters are reported in Table II. The data for the washed filter are very similar to the unwashed except for zinc and cobalt, which were removed by the washing. The iron concentration varied widely from filter to filter, but the averages obtained for washed and unwashed were nearly equal.

Another set of filters was washed in another lab, but apparently the same precautions were not used (Table III). The potassium and bromine in these filters were considerably higher than the unwashed or other washed filters.

Later, a new batch of larger Nucleopore filters was received and used for sampling. Then the used and new filters were irradiated for the trace elements. It was immediately evident that the new batch of filters contained uranium. The uranium content ranged from 16 micrograms per filter to less than 2 micrograms per filter as compared to none for original filters. Hence, they were not used as the induced radioactivity from the uranium was much greater than the induced radioactivity from the collected sample. Thus all new batches of filters should be analyzed prior to use to ensure that their trace element content is satisfactory.

Element Grouping

The radionuclides to be determined were grouped according to their half-lives; where two or more radioisotopes of the same elements were produced, the sensitivity and interferences dictated the choice. Due to the presence

of ^{56}Mn , ^{38}Cl , ^{24}Na , ^{82}Br , and ^{140}La in varying concentrations in all irradiated samples, the detection and measurements were made on the longer lived isotope (with asterik) in the following elements: $^{65}\text{Zn}^*$, ^{69}mZn ; ^{87}mSr , $^{85}\text{Sr}^*$; ^{139}Ba , $^{137}\text{Ba}^*$; ^{122}Sb , $^{124}\text{Sb}^*$; $^{60\text{m}}\text{Co}$, $^{60}\text{Co}^*$; ^{66}Cu , $^{64}\text{Cu}^*$ and ^{108}Ag , $^{110\text{m}}\text{Ag}^*$.

The elements—Mg, Al, Cl, Ti, Mn, V, and I—were determined after the 11-second irradiation and 10-minute decay. Following the 600-second irradiation and 48 hours decay, the elements—Na, K, Cu, As, Br, Mo, La, W, Au—were measured. Then, after a decay of at least 14 days, the long-lived radionuclides ($t_{1/2} > 3.0$) were counted overnight to accurately determine the concentration or a lower limit of detection.

DATA

The particulate solids were filtered from a liter of water each month immediately after sampling through 0.4 microns Nucleopore filter paper. The trace elements in the solids were determined by the established neutron activation procedures developed with standard samples and blank filters. The spectral data were processed with program MONSTR for the trace element concentrations. The major trace elements measured in West Spring water solids over a period of one year are presented in Table IV. The other sampling stations (See Fig. 1) had a similar variation in the trace element concentration during the year. The trace element data from the Walker Branch Watershed for the 2 February 1975 sampling are presented in Table V. This table shows all the trace elements determined each month in the suspended solids, and this month's data are typical for the other months.

The aerosol samples were collected at the weir sites using 5 l/minute vacuum pumps with Nucleopore filters as collection surface. Also, Hi-Vol air samplers were used with Whatman 41 filter paper. The aerosol samples had a total volume of 224 and 202 m^3 , respectively. The results of the aerosol samples are given in Table VI. The Hi-Vol aerosol sampler was used to collect aerosols for one set of experiments, and our data show the copper contamination in these samples to average 40 micrograms per 200 m^3 of air and range from 36 to 60 micrograms per filter. This copper contamination of aerosol samples when using Hi-Vol samplers has also been reported by Hoffman and Duce (4).

CONCLUSIONS

The absolute neutron activation analysis method of determining the trace elements in samples has been evaluated with NBS Standard Orchard Leaves, and acceptable data were obtained. The sensitivity and accuracy for this number of elements in a single sample using the HFIR as a neutron source and absolute neutron activation analysis methods cannot be duplicated by other analytical methods. By using absolute neutron activation analysis, considerable time is saved with the elimination of standards for all elements found in the samples. Thus, the cost per analysis is comparable or lower than other analytical methods for the same number of elements per sample.

This study confirms that instrumental absolute neutron activation analysis using Ge(Li) detector greatly enhances the simultaneous determination of a large number of trace elements in small quantities of water solids and aerosols.

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Table I

Trace Element Concentration in NBS Orchard Leaves
by Absolute Neutron Activation Analysis

<u>Element</u>	<u>Concentration, $\mu\text{g/gm}$</u>	
	<u>This Work</u>	<u>NBS*</u>
Al	333	340
Cl	739	700
Ca	2.13%	2.09%
V	0.58	0.58
Mg	0.70%	0.62%
K	1.50%	1.47%
Mn	89.9	91.4
Na	84.4	82

*See text for methods used for standardization.

Table II

Trace Elements in Washed and Unwashed
47-mm Nucleopore Filters

<u>Element</u>	<u>Concentration,* μg per Filter</u>			
	<u>Unwashed</u>	<u>Standard Deviation</u>	<u>Washed</u>	<u>Standard Deviation</u>
Al	0.81	0.027	0.72	0.12
Cl	1.96	0.45	1.60	0.15
Mn	0.014	0.006	0.015	0.009
V	0.006	0.001	0.001	0.000
Na	1.15	0.05	0.57	0.19
Br	0.012	0.001	0.027	0.004
Co	0.021	0.028	≤ 0.001	0.001
Zn	0.61	0.02	$< 0.02^{**}$	-
Cr	0.34	0.04	0.35	0.00
Fe	1.58	1.40	1.57	1.49

*Average of 4 filters each.

**< = limit of detection for condition used in analysis.

Table III

Selected Trace Elements in Nucleopore Filter Blanks
Before and After Washing

<u>Treatment</u>	<u>Concentration,* $\mu\text{g}/\text{filter}$</u>				
	<u>Zn</u>	<u>Na</u>	<u>K</u>	<u>As</u>	<u>Br</u>
Unwashed	0.61	1.15	≤ 0.20	$< 6.0\text{E}-4$	0.012
Washed ^a	$< 0.03^{**}$	0.57	0.31	$2.5\text{E}-3$	0.12
Washed ^b	$< 0.03^{**}$	0.57	$\leq 0.2^{**}$	$< 8.7\text{E}-5$	0.027

*Average of 4 determinations.

**< = limit of detection for conditions used in analysis.

^aLaboratory 1.

^bLaboratory 2.

Table IV

Trace Element Variation in West Spring Water
Solids during 1974

<u>Element</u>	<u>Concentration, $\mu\text{g/liter}$</u>				
	<u>February</u>	<u>April</u>	<u>June</u>	<u>August</u>	<u>December</u>
Al	236	182	118	70.8	107
Br	0.43	0.10	0.11	0.17	0.048
Ce	0.17	0.22	0.22	0.17	0.12
Cr	0.80	0.14	0.22	0.25	0.42
Cs	0.028	0.013	8.0E-3	6.1E-3	5.5E-3
Fe	68.2	57.5	47.8	28.8	40.6
Hg	0.10	6.0E-3	0.021	0.059	1.E-4
K	29.3	23.4	18.6	14.3	13.5
La	0.080	0.11	0.12	0.083	0.057
Mn	0.61	2.18	7.05	5.97	0.66
Na	0.38	0.67	0.74	0.36	0.78
Ti	8.50	7.74	8.40	9.81	3.60
Th	0.031	0.026	7.0E-3	0.013	0.014
V	0.27	0.22	0.16	0.091	0.13
Zn	4.91	1.40	2.29	0.75	1.13
Total Solids	2.9 mg	2.4 mg	3.3 mg	2.9 mg	1.1 mg

Table V
Walker Branch Watershed Suspended Sediment
of February 2, 1975

<u>Element</u>	<u>Trace Element Concentration, $\mu\text{g/liter}$</u>			
	<u>West Basin</u>	<u>West Spring</u>	<u>East Basin</u>	<u>East Spring</u>
Mg	22.3	9.40	28.5	33.2
✓ Al	174	107	268	292
✓ Cl	0.97	1.06	1.20	1.30
✓ Ca	<5.0	3.12	≤7.8	4.79
✓ Ti	7.24	3.60	7.73	8.38
✓ V	0.22	0.13	0.32	0.33
✓ Mn	3.93	0.66	3.77	1.75
✓ Cu	≤0.25	≤.16	≤.48	≤0.20
✓ Sr	≤2.04	<0.8	<1.5	≤0.86
✓ I	0.047	0.035	≤.069	0.035
✓ Ba	1.08	0.52	1.00	0.84
✓ Na	0.99	0.78	1.39	1.01
✓ K	24.4	13.5	35.2	45.4
✓ As	0.037	0.018	0.047	0.046
✓ Br	0.15	0.048	0.056	0.045
✓ Mo	<0.04	<0.05	<0.05	<0.04
✓ Cd	<0.1	<0.07	<0.1	<0.10
✓ La	0.14	0.057	0.15	0.18
✓ W	1.8E-3	8.0E-4	≤1.6E-3	≤2.3E-3
✓ Au	5.0E-3	7.1E-4	2.9E-3	5.6E-3
✓ U	<.01	<7.0E-3	0.015	0.013
✓ Sc	0.041	0.022	0.058	0.068
✓ Cr	0.67	0.42	0.29	0.66
✓ Fe	65.2	40.6	102	126
✓ Ni	<3.1	<1.4	<2.5	<2.6
✓ Co	0.050	0.020	0.059	0.041
✓ Zn	2.66	1.13	2.02	<0.2
✓ Se	<0.02	<8.2E-3	<0.01	≤.014

Table V (continued)

<u>Element</u>	<u>Trace Element Concentration, $\mu\text{g/liter}$</u>			
	<u>West Basin</u>	<u>West Spring</u>	<u>East Basin</u>	<u>East Spring</u>
Rb	0.14	0.065	0.21	0.27
Zr	<1.3	<0.6	<1.0	<1.1
Sb	0.043	0.14	0.16	0.16
Cs	0.012	5.5E-3	0.017	0.020
Ce	0.27	0.12	0.35	0.31
Nd	<0.1	<0.06	0.14	0.25
Eu	4.2E-3	1.9E-3	4.0E-3	5.0E-3
Tb	3.5E-3	1.5E-3	2.8E-3	4.9E-3
Yb	0.010	5.3E-3	0.012	0.013
Lu	4.2E-3	1.9E-3	4.3E-3	5.1E-3
Hf	0.019	5.1E-3	0.011	9.0E-3
Ta	$\leq 1.8\text{E-}3$	$\leq 1.5\text{E-}3$	$\leq 2.1\text{E-}3$	$\leq 1.9\text{E-}3$
Hg	0.010	1.E-4	3.3E-3	1.9E-3
Ag	<0.01	<6.2E-3	<0.01	<0.01
Th	0.024	0.014	0.035	0.039

Table VI

Trace Elements in Aerosols

<u>Element</u>	<u>Nanogram per m³</u>	
	<u>A</u> 224 cu meter air flow, m ³ /mn	<u>B</u> 202 cu meter air flow, m ³ /mn
Mg	<92	<105
✓ Al	714	713
✓ Cl	11	6.4
✓ Ca	<93	<110
✓ Ti	36	< 29
✓ V	2.41	2.30
✓ Mn	14	11.8
✓ Cu	<9	<9
✓ Sr	<7	<7
I	0.49	0.34
Na	125	122
K	208	205
As	1.52	1.89
Br	8.35	8.61
Mo	4.33	3.71
Cd	4.29	4.21
La	0.49	0.54
W	<0.1	<0.1
Au	<0.003	<0.003
U	<0.62	<0.49
Sc	0.13	0.12
Cr	2.1	2.2
Fe	274	246
Ni	<9.4	<10
Co	0.14	0.13
Zn	14.6	15.5
Se	0.98	0.94
Rb	0.80	1.44
Zr	28.7	23.6
Ag	<0.04	<0.04
Sb	0.31	0.30
Cs	0.058	0.059
Ba	29.8	27.1
Ce	1.56	1.49
Nd	0.85	1.14
Eu	0.012	0.011
Tb	<0.009	<0.007
Yb	0.004	0.004
Lu	0.012	0.011
Hf	0.041	0.044
Ta	0.012	0.010
Hg	0.067	0.074
Th	0.12	0.11