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## ACKNOWLEDGMENT

The assistance and cooperation of many members of this laboratory are greatly appreciated. Special consideration is given to James Bruce who performed many of these analyses.

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# Multielement Neutron Activation Analysis of Fresh Water Using Ge(Li) Gamma Spectrometry

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**A simple and rapid multielement method for the determination of trace elements in natural fresh water by purely instrumental neutron activation analysis is presented. The method which is based on Ge(Li) gamma spectrometry and computer evaluation of recorded data allows up to 40 elements to be determined without any pre-concentration steps. Data illustrating the precision of the method are given. The determination limit is  $\sim 1 \mu\text{g/l}$ . or less for 30 of the elements concerned, provided "normal" fresh water concentrations of elements giving rise to the most prominent activities, e.g., Al, Cl, and Na are taken into account. Spectral interferences and other possible sources of systematic errors are discussed and shown to be of moderate importance in most cases.**

The investigation of trace elements in natural fresh water resources has become a field of great emphasis in recent years. To facilitate such studies, there is need for simple analytical methods capable of determining elements at very low concentrations with good precision and accuracy. Neutron activation analysis is attractive for this type of work because of its high sensitivity for determination of a great number of elements simultaneously and the freedom of post-irradiation reagent blanks. Applications to natural fresh water have been reported, in most cases, however, using methods which involve radiochemical separation steps (1). The method which covers the most extensive range of elements seems to be that of Landström and Wenner (2) using a radiochemical separation scheme, mainly based on ion exchange techniques, which includes simultaneous determination of up to 30 elements. With the advent of solid-state detectors for gamma spectrometry, the multielement aspect of neutron activation analysis applied to fresh water has become even more evident. Thus several

methods utilizing the combination of Ge(Li) detectors and simple radiochemical group separations have been published in recent years (3, 4).

Less attention, however, has been paid to the simultaneous determination of a great number of elements in fresh water by purely instrumental activation analysis. Reports concerning a small number of elements have been published (5, 6), but no really comprehensive study on the applicability of instrumental neutron activation analysis on fresh water is available. In this connection it has been stressed (4) that the relatively large amount of  $^{24}\text{Na}$  and  $^{42}\text{K}$  present in irradiated natural water, besides preventing the measurement of many elements instrumentally, also limits the sample size and increases the counting times necessary for other elements. In a recent review paper (7), the determination of Ag, Br, Cl, Co, Cr, Cs, Fe, Mn, Na, Rb, Sb, Sc, Se, U, Zn, and occasionally Hg in fresh water by instrumental neutron activation analysis is stated to be possible if several optimal decay times (e.g., 4 hours, 3 and 20 days) before counting are included in the scheme. Schmitz et al. (8) suggest, however, that a higher number of elements may be determined if freeze-drying is introduced as a pre-concentration step.

In the present paper, it is shown that quantitative determination of as many as 40 elements present in natural fresh water can be performed without any pre-concentration steps, using instrumental neutron activation and subsequent gamma spectrometry with Ge(Li) detectors.

## EXPERIMENTAL

**Samples.** Immediately after sampling, the water is transferred to 1-l. polyethylene bottles containing 5 ml suprapure concd nitric acid to prevent loss of trace elements due to sorption effects.

Prior to analysis, the bottles are shaken and then stored for six hours before approximately 5 ml are poured directly, without filtration, into ampoules for irradiation (polyethylene for short, quartz for long irradiation). The sample amount is controlled by weighing, and the ampoules are then immediately heat-sealed.

After irradiation, the ampoules are rinsed with dilute nitric acid

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Table I. Elements Determined by Thermal Neutron Activation of Fresh Water Samples

Table 1. Gamma-ray Energies of the Most Abundant Radioisotopes of Fresh Water Samples				
Element	Nuclide formed	Most abundant	Less abundant	Interfering nuclide, (keV)
		gamma ray, keV	gamma ray, keV	
10-min irr. - 3-min decay - 10-min counting				
Mg	<sup>27</sup> Mg	844	1015	<sup>56</sup> Mn (847)
Al	<sup>28</sup> Al	1779		
Cl	<sup>38</sup> Cl	2168		
Ca	<sup>48</sup> Ca	3084		
Ti	<sup>51</sup> Ti	320		
V	<sup>52</sup> V	1434		
Mn	<sup>56</sup> Mn	847	1811	<sup>27</sup> Mg (844)
Cu	<sup>66</sup> Cu	1039		
I	<sup>128</sup> I	443		
Dy	<sup>165</sup> Dy	94	546	
3-day irr. - 3-day decay - 15-min counting				
Na	<sup>24</sup> Na	1368		
K	<sup>42</sup> K	1525		
Ga	<sup>72</sup> Ga	834		<sup>82</sup> Br (827)
As	<sup>76</sup> As	559		<sup>82</sup> Br (554), <sup>122</sup> Sb (564)
Br	<sup>82</sup> Br	777		
Mo	<sup>99m</sup> Tc	140		
Cd	<sup>115m</sup> In	336		<sup>24</sup> Na-double escape (346)
La	<sup>140</sup> La	1597	487	
Sm	<sup>153</sup> Sm	103		<sup>238</sup> Np (106)
Yb	<sup>175</sup> Yb	396	282	
W	<sup>187</sup> W	686	480	
Au	<sup>198</sup> Au	412		
U	<sup>238</sup> Np	106	99	<sup>153</sup> Sm (103)
3-day irr. - 17-day decay - 60-min counting				
Sc	<sup>46</sup> Sc	889	1121	<sup>110m</sup> Ag (885)
Cr	<sup>51</sup> Cr	320		
Fe	<sup>59</sup> Fe	1099	1291	
Co	<sup>60</sup> Co	1333	1173	
Zn	<sup>65</sup> Zn	1115		<sup>46</sup> Sc (1121)
Se	<sup>75</sup> Se	265	136	
Sr	<sup>85</sup> Sr	514		$\beta^+$ (511)
Rb	<sup>86</sup> Rb	1079		
Ag	<sup>110m</sup> Ag	658	885	
Sb	<sup>124</sup> Sb	603	1691	<sup>134</sup> Cs (605)
Ba	<sup>131</sup> Ba	124	496	<sup>152</sup> Eu (122)
Cs	<sup>134</sup> Cs	605	797	<sup>124</sup> Sb (603)
Ce	<sup>141</sup> Ce	145		
Eu	<sup>152</sup> Eu	122	344	<sup>131</sup> Ba (124)
Hf	<sup>181</sup> Hf	482	133	
Hg	<sup>203</sup> Hg	279		<sup>75</sup> Se (279)
Th	<sup>233</sup> Pa	312		

to remove surface contamination. Quartz ampoules used for long irradiations are frozen to avoid loss of volatile radiolytic compounds on opening. After melting, the samples are filtered through glass filter G2 to remove quartz grains.

A comparison of this procedure with the commonly recommended method (4, 7, 9, 10) using a 0.45-micron filter when analyzing fresh water samples for trace elements was carried out. Filtering experiments on water samples, shaken and then stored six hours as mentioned above, showed that mercury was the only element significantly affected by filtration. As additional experiments showed that  $\text{Hg}^{2+}$  ions were only slightly sorbed on the filters, part of the mercury seems to be carried by suspended material (greater than 0.45 micron) present in fresh water.

**Multistandards.** Standard solutions, prepared from analytical grade reagents, are controlled by neutron activation for the content of elements which can give rise to interfering activities.

Depending on half-life and gamma-ray energies of the nuclides produced and the chemical properties of the elements in question, the standards are mixed together into an appropriate number of multistandard solutions. The elements studied, the corresponding radionuclides and the gamma energies used in the measurements are given in Table I.

**Irradiation.** All irradiations were carried out in the JEEP-II D<sub>2</sub>O-moderated reactor (Kjeller, Norway).

Elements giving nuclides with a half-life shorter than about 3 hours are determined after 10-min irradiations (thermal neutron flux of  $1.5 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$ ) using a pneumatic tube facility. The remaining elements are determined after 3 days' irradiation at a fixed position (thermal neutron flux of  $1.4 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$ ).

**Counting.** In the present work, two Ge(Li)-detector systems interfaced to a Nord-1, 12 K computer, were used for activity measurements. The efficiency and resolution were 3.4%, 3.0 keV and 5.4%, 2.1 keV, respectively, defined in the usual manner by means of <sup>60</sup>Co. The counting was carried out at 1 keV/channel.

Dead time corrections which were always less than 15%, were performed by means of a pulse generator as described by Anders (11). The counting geometry was standardized and thus reproducible. Paper tape was used as output and data were transferred to magnetic tape for storage. The different decay and counting times used are given in Table I (footnotes). Typical gama spectra are shown in Figures 1 and 2.

**Data Processing.** Peak location and calculation of peak areas was performed by means of GAMANL, a computer program developed by Gunnink et al. (12) and adjusted to the CD 3300 computer at the University of Oslo by Scheidemann (13). According to this program, a peak is located when the tangent drawn to the spectrum curve changes in sign. This is accomplished by taking the first derivative of parabolas fitted to successive three-channel

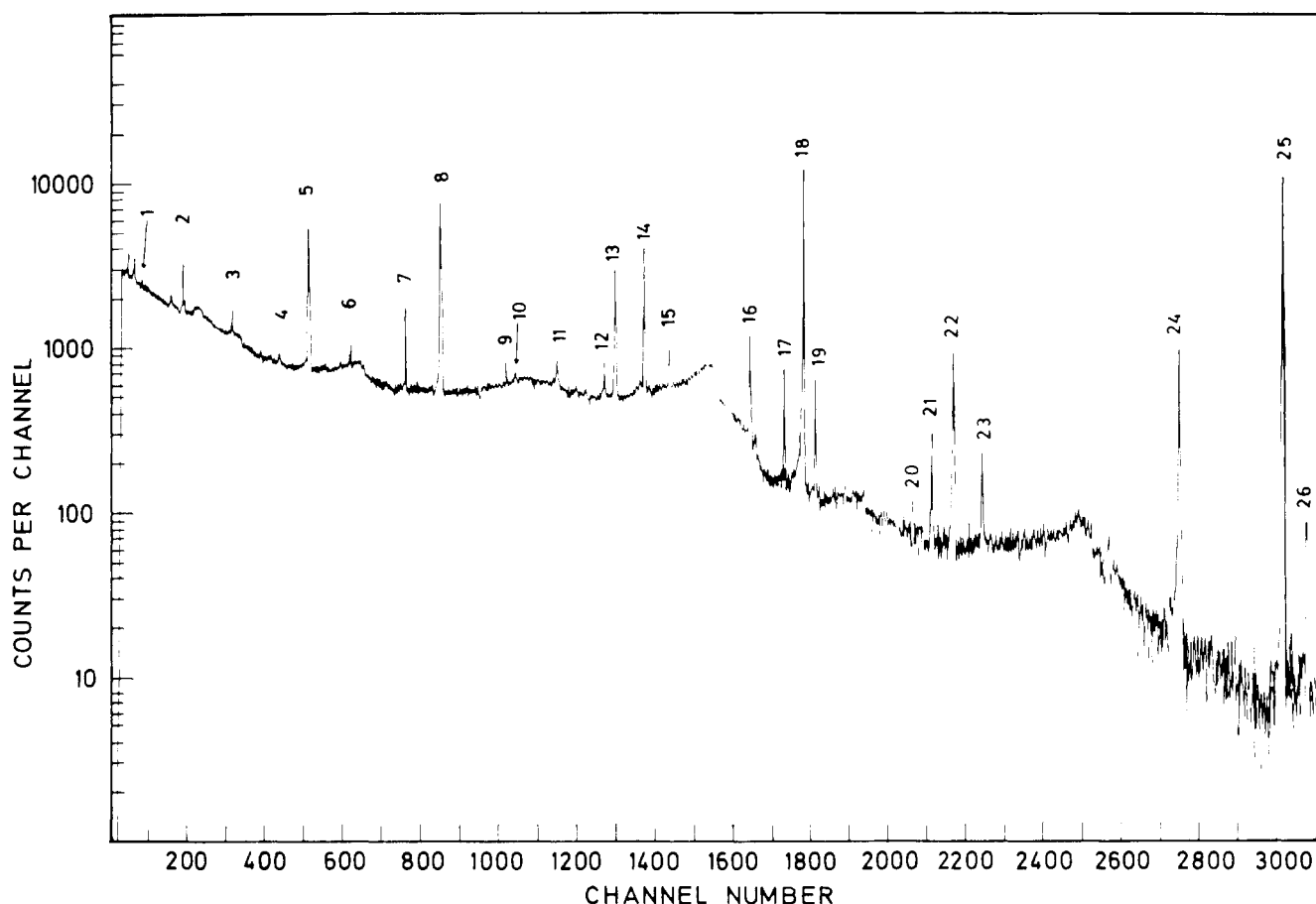


Figure 1. Gamma spectrum of 5-ml water sample.

Irradiation time: 10 min; decay time: 3 min; counting time: 10 min. Peak identification, nuclide ( $\gamma$ -energy, keV): 1)  $^{165}\text{Dy}$  (94), 2)  $^{19}\text{O}$  (197), 3)  $^{51}\text{Ti}$  (320), 4)  $^{128}\text{I}$  (443), 5)  $\beta^+$  (511), 6)  $^{80}\text{Br}$  (616), 7)  $^{28}\text{Al}$  d.e., 8)  $^{27}\text{Mg}$  &  $^{56}\text{Mn}$  (846), 9)  $^{27}\text{Mg}$  (1014), 10)  $^{66}\text{Cu}$  (1039), 11)  $^{38}\text{Cl}$  s.e., 12)  $^{28}\text{Al}$  s.e., 13)  $^{41}\text{Ar}$  (1293), 14)  $^{24}\text{Na}$  (1368), 15)  $^{52}\text{V}$  (1434), 16)  $^{36}\text{Cl}$  (1642), 17)  $^{24}\text{Na}$  d.e., 18)  $^{28}\text{Al}$  (1778), 19)  $^{56}\text{Mn}$  (1811), 20)  $^{38}\text{Cl}$  d.e., 21)  $^{56}\text{Mn}$  (2112), 22)  $^{38}\text{Cl}$  (2167), 23)  $^{24}\text{Na}$  s.e., 24)  $^{24}\text{Na}$  (2754), 25) pulse generator, 26)  $^{49}\text{Ca}$  (3084). d.e.: Double escape peak. s.e.: Single escape peak

groupings. When  $Y(i)$  is the number of counts in channel  $i$ , the slope of the tangent is given by

$$\text{BTST}(i) = \frac{Y(i+1) - Y(i-1)}{[Y(i+1) + Y(i-1)]^{1/2}} \quad (1)$$

In order to define a peak as significant, the statistical variation in the background must be considered. In the present work, the minimum detectable signal  $N = T - B$  is assumed to be  $2\sqrt{B}$ . Setting  $T = Y(i+1)$  and  $B = Y(i-1)$ , this yields

$$\text{BTST}(i) > 1.4 \quad (2)$$

The tangent then searches for start and end channel of the peak (shift of sign or constancy). The base line is constructed by searching seven channels on both sides of the peak to find the least mean value calculated from three successive channels.

The net area is the difference between the total area and background area, the latter defined through the base line. Its standard deviation is given by

$$\text{SIGPNT} = (\text{PKGROS} + \text{BKGD}(\text{END}-\text{START})/3)^{1/2} \quad (3)$$

where  $\text{PKGROS}$  = total peak area =  $\text{NET} + \text{BKGD}$ ,  $\text{NET}$  = net peak area,  $\text{BKGD}$  = background area =  $BA$ ,  $B$  = mean counts in background, and  $A = (\text{END}-\text{START})$  = width of peak.

In the present work, a peak is accepted for quantitative determination if the net area exceeds twice its standard deviation.

Calculations yield

$$\text{NET} > 2\sqrt{B} \sqrt{A + \frac{A^2}{3}} \quad (4)$$

According to the program, the exact peak position is decided by fit of a Gaussian function. In this process, more than 3 and less than

30 points are required, i.e., the minimum total width of a peak (at the base line) is three channels ( $A = 3$ ). Thus, the calculation of the determination limit ( $n_Q$ ) is based on

$$\text{NET} > 2\sqrt{6B} \quad (5)$$

Finally, the element concentrations are calculated by means of a simple program similar to that of Slavic et al. (5).

## DISCUSSION

The procedure described in the present paper has been applied to a study of water samples from 11 Norwegian rivers, the results of which will be published elsewhere. The experience, however, from this work with regard to information necessary in order to judge the applicability of the method i.e., precision, accuracy, and sensitivity, is discussed below.

**Precision.** In order to investigate the reproducibility of this instrumental multielement approach for the elements concerned, 4 aliquots of a river water sample (Skien river) were analyzed. This sample was assumed to represent a typical fresh water sample as far as the bulk element composition is concerned. The results obtained for 31 different elements, together with the average counting error and the maximum deviation from the mean value for each element, are listed in Table II. Factors contributing to the random error are flux gradients within the irradiation can and variable counting geometry. The composite error due to such factors probably did not exceed 5% in the present experiments. For a major number of elements, however, the main factor affecting the reproducibility seems to be counting

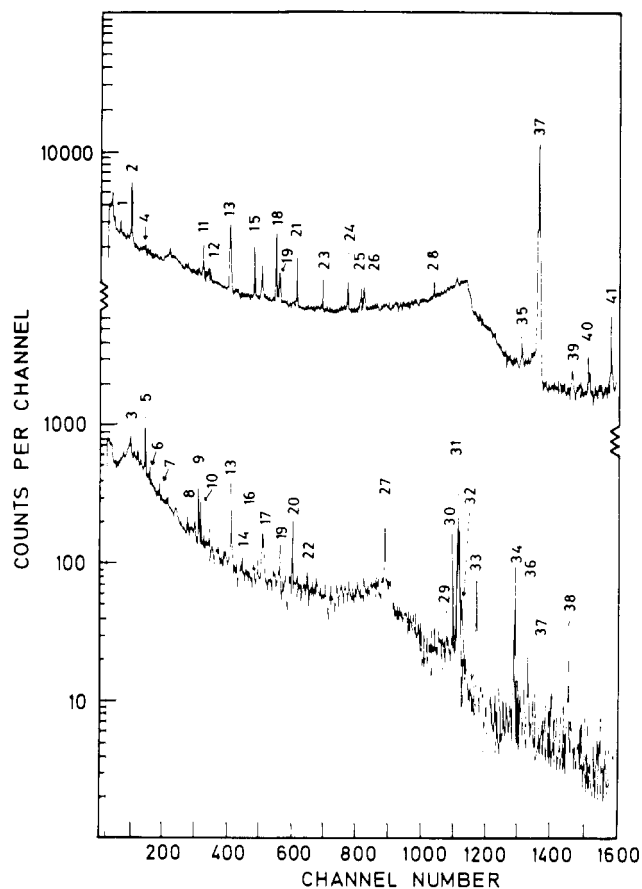
statistics, as indicated from the correspondence between the observed counting errors and the spread of single values (Table II). The counting error is influenced by the counting time employed and the ratio of net area to background area of the peak in question. Generally speaking, the precision is dependent on the sample composition and will be lowered as the detection limit is approached.

**Accuracy.** The accuracy of the results may be affected by systematic errors associated with sampling, storage, or analysis. Discussion of possible sampling errors is not considered to be within the scope of this paper. The following sources of error associated with storage or analysis may be significant.

**Blank Contribution.** Possible contamination due to the polyethylene storage bottles and the added acid was studied by comparing analyses of distilled water stored in Pyrex

**Figure 2.** Gamma spectrum of 5-ml water sample (Same batch as in Figure 1)

Irradiation time: 3 days. Upper half: decay time: 3 days; counting time: 15 min. Lower half: decay time: 17 days; counting time: 60 min. Peak identification, nuclide ( $\gamma$ -energy, keV): 1)  $^{197}\text{Hg}$  (77), 2)  $^{153}\text{Sm}$  &  $^{239}\text{Np}$  (104, 106), 3)  $^{152}\text{Eu}$  &  $^{131}\text{Ba}$  (122, 124), 4)  $^{99\text{m}}\text{Tc}$  (140), 5)  $^{141}\text{Ce}$  (145), 6)  $^{47}\text{Sc}$  (160), 7)  $^{59}\text{Fe}$  (192), 8)  $^{203}\text{Hg}$  (279), 9)  $^{233}\text{Pa}$  (312), 10)  $^{51}\text{Cr}$  (320), 11)  $^{140}\text{La}$  (328), 12)  $^{115\text{m}}\text{In}$  (336), 13)  $^{198}\text{Au}$  (412), 14)  $^{181}\text{Hf}$  (482), 15)  $^{140}\text{La}$  (487), 16)  $^{131}\text{Ba}$  (496), 17)  $\beta^+$  &  $^{85}\text{Sr}$  (511, 514), 18)  $^{82}\text{Br}$  &  $^{76}\text{As}$  (555, 559), 19)  $^{122}\text{Sb}$  (564), 20)  $^{124}\text{Sb}$  &  $^{134}\text{Cs}$  (603, 605), 21)  $^{82}\text{Br}$  (619), 22)  $^{110\text{m}}\text{Ag}$  (658), 23)  $^{82}\text{Br}$  (698), 24)  $^{82}\text{Br}$  (776), 25)  $^{140}\text{La}$  (816), 26)  $^{82}\text{Br}$  (828), 27)  $^{46}\text{Sc}$  (889), 28)  $^{82}\text{Br}$  (1044), 29)  $^{86}\text{Rb}$  (1078), 30)  $^{59}\text{Fe}$  (1099), 31)  $^{65}\text{Zn}$  (1115), 32)  $^{46}\text{Sc}$  (1121), 33)  $^{60}\text{Co}$  (1173), 34)  $^{59}\text{Fe}$  (1291), 35)  $^{82}\text{Br}$  (1317), 36)  $^{60}\text{Co}$  (1332), 37)  $^{24}\text{Na}$  (1368), 38)  $^{40}\text{K}$  (1460), 39)  $^{82}\text{Br}$  (1475), 40)  $^{42}\text{K}$  (1525), 41)  $^{140}\text{La}$  (1596)



**Table II.** Data Obtained by Analysis of 4 Aliquots of a Fresh Water Sample from the Skien River

Element	Single values, $\mu\text{g/l}$				Average counting error, %	Mean value, $\mu\text{g/l}$	Maximum deviation from mean, %
	1	2	3	4			
Ag <sup>a</sup>	0.34	0.49	0.41	0.43	19	0.43	22
Al	0.118 <sup>b</sup>	0.113 <sup>b</sup>	0.115 <sup>b</sup>	0.118 <sup>b</sup>	2.6	0.116 <sup>b</sup>	3
As	0.29	0.21	0.25	0.29	16	0.26	20
Au	0.015	0.017	0.012	0.016	8.3	0.015	20
Ba	10.8	13.5	11.0	13.1	8.1	12.1	11
Br	5.1	5.6	5.5	5.4	7.3	5.4	6
Ca	2.0 <sup>b</sup>	2.5 <sup>b</sup>	2.1 <sup>b</sup>	2.6 <sup>b</sup>	9.5	2.3 <sup>b</sup>	13
Ce	0.14	0.21	0.12	0.21	33	0.17	30
Cl	0.88 <sup>b</sup>	0.92 <sup>b</sup>	0.90 <sup>b</sup>	0.90 <sup>b</sup>	1.1	0.90 <sup>b</sup>	3
Co	0.08	0.11	0.09	0.08	33	0.09	22
Cr	1.53	1.11	1.44	1.52	33	1.4	21
Cs <sup>a</sup>	0.090	0.107	0.102	0.093	4.0	0.098	10
Eu <sup>a</sup>	0.007	0.010	0.008	0.011	13	0.009	23
Fe	0.079 <sup>b</sup>	0.070 <sup>b</sup>	0.059 <sup>b</sup>	0.076 <sup>b</sup>	33	0.071 <sup>b</sup>	17
Hf	0.10	0.16	0.11	0.15	27	0.13	23
Hg	0.09	0.12	0.09	0.10	22	0.10	20
I	0.41	0.44	0.52	0.47	38	0.46	13
K	0.55 <sup>b</sup>	0.50 <sup>b</sup>	0.50 <sup>b</sup>	0.57 <sup>b</sup>	32	0.53 <sup>b</sup>	9
La	0.30	0.39	0.31	0.32	22	0.33	8
Mg	0.33 <sup>b</sup>	0.38 <sup>b</sup>	0.36 <sup>b</sup>	0.41 <sup>b</sup>	19	0.37 <sup>b</sup>	12
Mn	33.7	36.1	35.4	33.6	3.1	34.7	4
Na	0.67 <sup>b</sup>	0.67 <sup>b</sup>	0.71 <sup>b</sup>	0.71 <sup>b</sup>	1.4	0.69 <sup>b</sup>	4
Rb	0.99	1.27	1.05	1.09	19	1.10	16
Sb	0.20	0.21	0.28	0.23	18	0.23	22
Sc	0.014	0.017	0.015	0.014	20	0.015	11
Sm	0.13	0.13	0.10	0.12	20	0.12	17
Sr	17.6	21.1	19.2	16.1	14	18.5	14
Th	0.07	0.10	0.08	0.07	25	0.08	22
V	0.26	0.30	0.27	0.31	29	0.29	9
Yb	0.13	>0.11	0.22	0.25	41	0.20	37
Zn	6.1	7.1	6.3	6.1	9.5	6.4	11

<sup>a</sup> Six months' decay. <sup>b</sup> mg/l.

**Table III. Necessary Corrections for Blank Contribution**

Element	Contribution from container and acid range (mean) $\mu\text{g/l.}$	Contribution from quartz ampoules range (mean) $\mu\text{g/l.}$	Necessary corrections, $\mu\text{g/l.}$
Ag	< 0.058–0.082 (0.07)		0.07
Au	0.0012–0.0031 (0.002)	0.0012–0.0026 (0.002)	0.004
Br	0.18–0.34 (0.26)	0.18–0.45 (0.30)	0.56
Co		< 0.03–0.05 (0.04)	0.04
Hg	0.038–0.067 (0.05)	< 0.008–0.011 (0.01)	0.06
Na	4.8–6.2 (5.6)	23.7–28.5 (26.7)	31.8
Sb	0.014–0.022 (0.02)	< 0.11–0.35 (0.21)	0.23
Sc	< 0.002–0.007 (0.005)		0.005
Sm	< 0.014–0.031 (0.02)		0.02
Zn	0.33–0.90 (0.60)		0.60

**Table IV. Detection and Determination Limits of the Present Method Based on 5-ml Sample**

Element	Detection limit, $m_D$ , $\mu\text{g/l.}^b$	Determination limit, $m_Q$ , $\mu\text{g/l.}^b$	Determination limit, $n_Q$ , $\mu\text{g/l.}^c$	Background level counts/channel
Ag <sup>a</sup>	0.009	0.06	0.08	10
Al	0.2	0.8	1.1	250
As	0.06	0.22	0.16	800
Au	0.0004	0.0016	0.002	900
Ba	1.8	8.9	5.7	40
Br	0.05	0.17	0.19	400
Ca	4.6	32.2	36.8	20
Cd	0.18	0.62	0.50	900
Ce	0.01	0.04	0.06	300
Cl	0.7	3.1	4.6	200
Co	0.007	0.05	0.04	15
Cr	0.12	0.52	0.40	80
Cs <sup>a</sup>	0.006	0.033	0.028	10
Cu	1.2	4.4	4.1	400
Dy	0.0003	0.017	0.010	3000
Eu <sup>a</sup>	0.001	0.005	0.003	20
Fe	7.8	51.1	38.6	20
Ga	0.18	0.58	0.50	800
Hf	0.006	0.03	0.04	60
Hg	0.01	0.08	0.06	100
I	0.05	0.20	0.18	800
K	22	56	68	200
La	0.007	0.03	0.05	200
Mg	14.6	45.3	50.9	400
Mn	0.07	0.48	0.60	250
Mo	0.2	0.6	0.4	1000
Na	0.2	0.8	1.1	400
Rb	0.2	1.6	0.9	30
Sb	0.02	0.18	0.14	10
Sc	0.0008	0.005	0.004	40
Se	0.13	0.58	0.34	100
Sm	0.007	0.022	0.017	1500
Sr	1.4	6.8	8.9	40
Ti	2.0	7.1	6.1	1000
Th	0.002	0.012	0.020	200
U	0.11	0.36	0.23	1500
V	0.01	0.04	0.05	400
W	0.03	0.15	0.12	800
Yb	0.05	0.16	0.10	900
Zn	0.6	4.6	3.1	20

<sup>a</sup> Decay time of six months. <sup>b</sup> Based on definitions given by Currie (15). <sup>c</sup> Based on the GAMANL program criterion.

bottles with the same water quality stored in polyethylene bottles containing 5 ml concd nitric acid. Contribution due to the irradiation containers was studied by activating six empty ampoules of each type, assuming the difference in recoil effects in water and in air to be nonsignificant. The results of this blank contribution study are given in Table III, and the necessary corrections are listed. No contribution from the polyethylene ampoules has to be taken into

account while minor corrections are necessary for some elements when quartz ampoules are used. The high and variable contribution of Sb from the quartz makes the determination of this element uncertain.

*Effects of Nitric Acid Addition.* During examination of the water samples, the loss of iodine was evident. Model experiments with 0.1M nitric acid and 0.1M ammonia solutions each containing known amounts of <sup>131</sup>I<sup>-</sup> ions showed

that the loss of iodine in acid solution increased with the initial amount of iodine and with the time of storage in the polyethylene bottles. A reasonable explanation seems to be oxidation to  $I_2$  which has a tendency to diffuse through walls of the polyethylene bottles (14). Additional losses are likely to occur during the irradiation. The sum of these effects necessitates a fairly large correction (~50%) to the determined iodine concentrations.

Similar studies with Cl and Br show that no such losses are observed for these elements.

**Nuclear Effects.** Contributions from interfering nuclear reactions induced by fast neutrons depend on the fast neutron flux component in the actual irradiation positions. In the present study, this component was only about 5% of the thermal neutron flux, thus negligible. Systematical errors due to neutron shielding effects can in general be disregarded as no elements of high absorption cross section are present in significant concentrations either in fresh water samples or standards.

Because of contribution from fission of U, a minor correction may have to be applied. In the present case, however, only the Mo content had to be corrected.

**Counting Errors.** If the dead time loss is kept below 15%, as in our case, no significant errors associated with high counting rates are likely to occur.

**Spectral Interferences.** Depending on the sample composition, interferences and high background level caused by some few elements may lower the sensitivity of some others.

If short irradiation times are used, the nuclides  $^{24}\text{Na}$ ,  $^{28}\text{Al}$ , and  $^{38}\text{Cl}$  may, in some cases, contribute to a background level which makes the determination of  $^{51}\text{Ti}$  and  $^{66}\text{Cu}$  difficult. When using 3 days' irradiation, the background level due to  $^{24}\text{Na}$  and the numerous gamma peaks from  $^{82}\text{Br}$  will complicate determinations of other elements yielding nuclides with comparable half-lives (i.e., As, Ga). In most cases, interferences can be avoided by using gamma peaks other than those commonly used (Table I).

The preceding discussion indicates that post-sampling systematic errors may in most cases be fairly small. This implies that statistical counting errors will contribute most to the total experimental error, especially for elements present in low concentrations. In this case, the accuracy will be comparable to the precision of the method.

Parallel to the present work, water samples taken simultaneously with those investigated in this work were analyzed in another research laboratory by atomic absorption spectrometry with respect to Na, K, and Ca. The atomic absorption results did not show any bias with respect to the neutron activation values. This observation seems to support the assumption that post-sampling systematic errors are relatively low.

**Limits of Detection and Determination.** The present method has a sensitivity for the different elements which depends on matrix composition and counting statistics.

Using definitions of "minimum detectable mass" ( $m_D$ ) and "determinable mass" ( $m_Q$ ) as given by Currie (15) and assuming normal distributions (number of counts are sufficiently large), constancy of the variance, a confidence level of 95% ( $\alpha = \beta = 0.05$  and  $k = 1.645$ ) (Currie notation) and quantitative determinations with a relative standard deviation of 10% ( $k_Q = 10$ ) (Currie notation) the detection and determination limits of 40 elements are calculated and given in Table IV. The calibration factors involved in these calculations are related to the activation and detection procedures used and include nuclear properties of the investigated elements and the nuclides formed. The calculations

are based on a 5-ml water sample with a typical level of elements giving rise to the most prominent activities. The corresponding background level for each element, expressed as counts/channel, is given in Table IV.

Determination limits  $n_D$  may also be calculated using the GAMANL criterion of the least possible registerable peak area as the present method is based on automatic calculation of peak areas. In this case, determination and detection limits coincide. Data obtained by this method are also given in Table IV. It is seen that the theoretical and the empirical approaches yield good agreement for the large majority of elements concerned. The determination limit by instrumental neutron activation analysis as applied in the present work is  $\sim 1 \mu\text{g/l.}$  or below for 30 of the 40 elements concerned. All the limits are, however, far below the maximum permissible concentrations for drinking water set by the U.S. Public Health Service (16).

## CONCLUSION

The present study confirms that instrumental neutron activation analysis using Ge(Li) detectors is a very useful tool for the simultaneous determination of a great number of elements in natural fresh water samples without any pre-concentration or pre-separation steps. Using a standard computer program for automatic analysis of spectra and further evaluation of data, a great number of samples can be analyzed with reasonable precision and accuracy within a short time. For a major number of the elements concerned, the determination limits will be well below the concentration levels found in most of the common river waters. Our experience from analysis of fresh water samples shows that the following 22 elements are easily determined: Al, Au, Br, Ca, Ce, Cl, Co, Cs, Eu, Fe, Hg, I, K, La, Mg, Mn, Na, Sb, Sc, Sm, Sr, Zn. An additional 12 elements: Ag, Ba, Cr, Cu, Dy, Hf, Rb, Ti, Th, U, V, Yb can be determined, but depend to a greater extent on sample composition. The remaining elements under investigation: As, Cd, Ga, Mo, Se, W are more difficult to determine quantitatively.

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