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Determination of 17 Elements in 20 Canadian Mineral Waters by Evaporation and Systematic Instrumental Neutron Activation Analysis.

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ABSTRACT

Mean concentrations of Ba, Br, Ca, Cl, Co, Cs, Cu, I, K, Mg, Mn, Na, Sb, Sr, V, U and Zn determined in 20 samples of mineral waters from Canada, were equal to 74, 2.7, 23700, 1390, 0.28, 0.22, 39, 2.2, 802, 5430, 18, 2240, 0.14, 123, 0.35, 1.1 and 312 ppm resp. Vanadium, Mn, Co, Br, Sb, I, Cs and U could be detected at better than ppb level.

INTRODUCTION

Neutron activation (NAA) analysis is a very powerful analytical method which is best suited for the analysis of solid samples. This is due to the fact that no dissolution is needed before irradiation and consequently the risk of contamination of samples is minimal. Despite this unique feature, NAA can be also applied to liquid samples as we hope to show in this paper. Knowledge of the concentration of elements in mineral waters is of interest because some ground waters are contaminated by toxic elements either from natural or man-made sources. Also the quality of the drinking water from public water supplies is being questioned by some consumers and for this reason bottled mineral water has become a hot commodity in the marketplace. In order to find out if toxic or beneficial elements are present in mineral waters sold in stores in Montreal, we decided to analyze them by evaporation followed by the systematic instrumental neutron activation.

EXPERIMENTAL

Samples of 20 mineral waters were obtained from different stores in the Montreal area. In order to minimise losses due to splashing, they were evaporated very slowly on stainless steel planchette. It took typically 2 days to evaporate each sample. Then the dry deposits were carefully scraped off with a plastic spatule and transferred to irradiation vials. The planchette were weighed before and after the scrapping so that losses could be accounted for and equivalent volume of water analyzed could be calculated. The vials were irradiated in the SLOWPOKE reactor of Ecole Polytechnique at a neutron flux of $5*10^{11}$n/cm^2/s for 30 seconds, then after waiting at least 1 day the same samples were reirradiated for 300 seconds and finally after waiting at least one week for 3000 seconds. After each irradiation the samples were counted with a Ge detector several times after decay times which varied from 34 s to 122 days for counting times which ranged from 100 and 63000 seconds depending on irradiation time. The decay times were chosen in such a way that all radioisotopes formed could be detected. The resulting gamma ray spectra were analyzed by our computer program (1), which locates the characteristic peaks and calculates the concentrations using K_o method (2). Altogether, 140 spectra were analyzed.

RESULTS AND DISCUSSION

The concentrations of 17 elements found in the mineral waters (or their detection limits) were calculated by using K_o method and they are listed in Table 1. The first number in the table stands for the mean concentration in ppb or for the detection limit (which was calculated using Currie's formula (3) for a well known blank). The number in the parentheses stands for the standard deviation calculated either from the data (if more than 1 result was obtained) or from the statistical counting error (at 95% confidence level).

Table 1. Mean concentrations and standard deviations in ppb of 17 elements in Canadian mineral waters.

Brand	A	B	C	D	E	F	G
V-ml	1634	600	800	518	587	850	630
Na	5010(640)	7330(690)	1710(57)	242(12)	157(16)	2460(130)	1050(130)
Mg	3770(360)	5150(780)	4800(120)	3380(280)	6510(1330)	6300(260)	554(120)
Cl*	1040(190)	12900(1500)	914(76)	160(14)	106(12)	443(15)	1020(120)
K	683(73)	<100	1040(120)	144(7)	511(45)	550(23)	173(61)
Ca	18400(2700)	16600(2200)	46000(4600)	18600(440)	37600(500)	38300(1500)	2490(410)
V	0.36(0.09)	0.53(0.1)	<0.1	0.54(0.06)	0.15(0.02)	<0.1	0.1(0.03)
Mn	10(1)	5.3(0.5)	4.2(0.1)	12(1)	2.1(0.2)	8.9(0.6)	0.9(0.2)
Co	0.44(0.02)	0.67(0.07)	0.15(0.03)	0.21(0.01)	0.05(0.02)	<0.01	0.07(0.02)
Cu	57(11)	91(7)	37(7)	31(4)	16(4)	68(5)	4(1)
Zn	84(3)	<10	75(2)	88(3)	57(3)	<10	19(1)
Br*	6.7(0.5)	<0.5	2.5(0.3)	<0.5	0.5(0.2)	<0.5	1.2(0.2)
Sr	30(4)	<10	317(20)	82(8)	140(5)	463(38)	13(2)
Sb	0.06(0.01)	<0.1	<0.1	<0.1	<0.1	<0.1	0.1(0.04)
I*	1.0(0.2)	4.2(0.8)	2.6(0.7)	2.5(0.3)	0.34(0.13)	0.45(0.1)	2.4(0.6)
Cs	0.06(0.02)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	13(2)	139(11)	30(2)	12(2)	88(21)	41(12)	<5
U	0.6(0.2)	<0.05	0.4(0.1)	0.14(0.05)	1.0(0.3)	<0.05	<0.05

mean concentrations ... (cont'd).

Brand	H	I	J	K	L	M	N
V-ml	370	900	900	525	1665	1600	2000
Na	3720(360)	329(50)	656(28)	1400(204)	1410(15)	1980(57)	963(64)
Mg	1730(150)	1250(71)	2280(800)	9330(620)	3190(230)	4130(260)	792(47)
Cl*	2420(230)	90(2)	385(33)	1642(190)	2150(14)	959(130)	1040(140)
K	770(70)	171(9)	343(41)	<90	298(12)	594(23)	180(10)
Ca	9170(2200)	19000(1400)	38300(6100)	9320(740)	36400(4500)	27800(3900)	6130(170)
V	0.2(0.02)	0.1(0.05)	0.47(0.1)	0.15(0.05)	1.1(0.2)	0.2(0.04)	<0.1
Mn	9.2(0.7)	29(2)	0.9(0.2)	<1	5.0(0.2)	57(2)	1.6(0.3)
Co	0.27(0.04)	0.02(0.01)	0.12(0.02)	<0.02	0.92(0.05)	0.11(0.02)	0.04(0.01)
Cu	31(5)	13(6)	94(23)	13(2)	15(4)	48(10)	46(7)
Zn	96(5)	21(2)	258(8)	<10	45(5)	421(9)	52(3)
Br*	3.1(0.3)	<1	1.3(0.1)	<1	<1	1.7(0.2)	1.7(0.2)
Sr	50(8)	170(20)	277(9)	<10	62(12)	29(3)	13(2)
Sb	0.07(0.02)	0.01(0.004)	0.01(0.004)	<0.02	<0.03	<0.05	0.14(0.01)
I*	5.7(0.9)	0.17(0.05)	0.17(0.06)	<0.2	1.6(0.3)	1.5(0.4)	0.28(0.03)
Cs	0.8(0.01)	0.02(0.01)	0.02(0.01)	<0.1	<0.05	<0.05	0.13(0.03)
Ba	<5	8.9(2.8)	89(3)	139(30)	87(12)	50(5)	<10
U	<0.05	<0.05	<0.05	<0.1	0.1	0.2(0.04)	0.3(0.05)

mean concentrations ... (end).

Brand	O	P	Q	R	S	T
V-ml	1325	724	920	457	1680	1737
Na	3220(180)	5560(840)	5410(1300)	1370(200)	364(25)	609(46)
Mg	20500(1400)	30000(4200)	18500(4100)	2080(490)	2010(200)	1380(64)
Cl*	479(28)	906(220)	80(13)	159(15)	55(2)	176(14)
K	1050(28)	2440(28)	4990(470)	239(24)	316(64)	187(16)
Ca	40000(2800)	15300(900)	36100(9500)	34000(2600)	14000(350)	13000(1600)
V	0.13(0.03)	<0.1	0.28(0.03)	<0.05	0.21(0.02)	0.4(0.1)
Mn	55(2)	12(1)	81(1)	57(6)	23(1)	0.72(0.05)
Co	0.57(0.02)	0.2(0.01)	1.1(0.1)	<0.02	0.02(0.01)	0.06(0.01)
Cu	41(3)	42(8)		21(6)	34(4)	44(7)
Zn	112(3)	59(2)	3230(100)	51(7)	21(2)	161(8)
Br*	2.4(0.5)	11(2)	<0.5	1.0(0.4)	0.6(0.1)	0.5(0.1)
Sr	77(5)	29(3)	<20	250(50)	42(1)	48(2)
Sb	0.17(0.03)	0.16(0.12)	0.6(0.2)	0.55(0.25)	0.06(0.01)	<0.05
I*	2.0(0.3)	3.3(0.5)	7.6(0.2)	3.5(0.5)	0.4(.02)	0.22(0.7)
Cs	0.2(0.03)	0.08(0.02)	0.5(0.2)	<0.1	0.02(0.01)	<0.04
Ba	146(29)	107(9)	387(27)	<10	28(5)	11(1)
U	3.8(1)	0.9(0.3)	0.6(0.3)	1.0(0.1)	4(2)	0.5(0.2)

* non volatile species only

Volatile elements such as Br and I are lost during the evaporation. Consequently, the concentrations of these elements shown in Table 1 represent only their non-volatile forms (p.e bromides and iodides) and not their total concentrations. Iron, chromium and titanium were sometimes detected in our samples. We analyzed one of our evaporation planchettes and it contains these elements in high concentrations. Because they may originate from them, their concentrations are not listed. The evaporation increases the analyzed sample size up to 2000 times and because of this, V, Mn, Co, Br, Sb, I, Cs and U could be detected at better than ppb level, even when low-flux reactor such as SLOWPOKE is used.

Then, the mean and median concentrations were calculated for the Canadian mineral waters analyzed in this work (Table 2). They are compared with the current Quebec's maximum permissible concentrations (MPC) for the bottled water (4). The main radioisotope (RI) and the principal gamma ray energy (E) used for the identifications of these elements are also listed in Table 2.

Table 2. Mean and median concentrations (in ppb) of 17 elements in 20 Canadian mineral waters and their standard deviations (SD).

	RI	E - keV	Mean	SD	Median	CS	MPC
Na	Na-24	1368	2240	2140	493	6300	
Mg	Mg-27	1014	5430	7130	1770	5000	150 000
Cl	Cl-38	2167	1390	2870	238	100	250 000
K	K-42	1524	802	1180	343	14000	
Ca	Ca-49	3084	23700	128000	28700	13700	200 000
V	V-52	1434	0.35	0.25	0.092	100	
Mn	Mn-56	1811	17.7	22.8	6.4	850	50
Co	Co-60	1333	0.28	0.33	0.07		
Cu	Cu-66	1039	39	25	36	20	1000
Zn	Zn-65	1115	312	787	161	50	5000
Br	Br-82	777	2.7	3.0	1.5	5	
Sr	Sr-87m	388	123	130	56	300	
Sb	Sb-122	564	0.14	0.18	0.06	10	
I	I-128	443	2.2	2.2	0.17	5	
Cs	Cs-134	605	0.22	0.29	0.13	6	
Ba	Ba-131	1238	74	105	87	500	1000
U	Np-239	106	1.1	1.3	0.2	1	5000

CS = Typical concentration in soil in ppm (8)

The elements in Table 2 can be divided into 3 categories :

1) elements essential (5) for the human health (Ca, Cl, Co, Cu, I, K, Na, Mg, Mn and Zn),
2) toxic elements (6,7) (Ba, Mn, Sb, Sr and U),
3) and the elements of uncertain biological effect (Br, Cs, V).

This categorisation is somewhat arbitrary because some elements such as Mn are considered to be toxic by some researchers and to be essential by others. The elements of interest in this study were those in the first and the second category. As far as toxicity is concerned, the concentrations of toxic elements found by us are well bellow the current standards for drinking water. As the contributor to the intake of minerals essential for human health the mineral waters analyzed are of little value, except when consumed in large amounts. Most of the elements found in our mineral waters samples are those which are normally present in soil. This is quite comprehensible considering that soils are the most important source of elements in mineral waters. This relationship becomes quite obvious, when the median concentrations of elements in mineral waters are compared with their concentrations in soils

(sixth and seventh columns in Table 2). When the concentration in soil is high the concentration in water is also high.

Finally, sequential linear regression analysis was performed on our data in order to find out if the concentrations of elements are related. Stepwise, the linear regression coefficients for all possible combinations of couples of elements were calculated and when greater than 0.9, they are indicated in Table 3. For example, the concentrations of Ba, Cs, Cu and K seem to be correlated.

Table 3. Linear regression coefficients between concentrations of elements in Canadian mineral water.

Ba						
0.99	Cs					
0.94		Cu				
0.93			K			
		0.96	0.93	Sb		
		0.99	0.91	0.93	Sr	
0.93		0.99		0.95	0.99	Zn

CONCLUSIONS

Systematic instrumental neutron activation analysis can be successfully applied to the determination of elements in mineral waters. In conjunction with evaporation, results can be obtained with very high sensitivity. Using this method, many trace and minor elements can be determined. Among the elements found were some essential (Ca, Cl, Co, Cu, I, K, Na, Mg, Mn and Zn) and some toxic elements (Ba, Sb, Sr and U) but the concentrations measured were very low.

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