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The determination of low concentrations of sodium, potassium, magnesium, calcium and strontium in natural waters by graphite furnace AAS

C. A. A. LeGras and B. N. Noller

Supervising Scientist for
the Alligator Rivers Region

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TECHNICAL MEMORANDUM 35

THE DETERMINATION OF LOW CONCENTRATIONS OF SODIUM, POTASSIUM, MAGNESIUM, CALCIUM AND STRONTIUM IN NATURAL WATERS BY GRAPHITE FURNACE AAS

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Methods are described for the determination of low concentrations of sodium, potassium, magnesium, calcium and strontium in rainwater and stream water by Atomic Absorption Spectrophotometry (AAS). The procedures using a graphite furnace are shown to be very precise; comparison of results with waters of known composition, including reference waters, imply good accuracy with detection limits for sodium, potassium, magnesium, calcium and strontium of 6, 3, 1, 4 and 0.1 μg/L respectively. The secondary resonance line was used for all elements except strontium, for which the primary resonance line was used. Caution must be exercised in determinations of potassium and calcium in waters containing a high concentration of sulfate ion compared with analyte concentration.

1 INTRODUCTION

The concentrations of sodium, potassium, magnesium, calcium and strontium in seawater are sufficiently high to be measured easily by flame atomic absorption spectrometry (FAAS) (Millero 1974*a*). The same is usually true for rainwater deposited near the sea (Church 1982). However, the concentrations of these cations progressively decline as rainwater is deposited further from the coast, because seawater-derived aerosols are diluted with continental air, which has no marine influence (Munger & Eisenreich 1983). If there is only a small contribution from land-derived sources to the total cation content in rainwater, the concentrations can be near or below the detection limit for FAAS, even using scale expansion and a long integration time. This is often the case for rainwater from the Alligator Rivers Region.

The major purpose for measuring these metals in rainwater is to calculate their equivalent ratios, called constituent element ratios. Terrestrial contributions to the atmospheric burden of sodium are small (Munger & Eisenreich 1983). Therefore, using established constituent element ratios for marine aerosols (Millero 1974*a*), 'excess' concentrations, that is, land-derived contributions of potassium, magnesium, calcium and strontium to the atmosphere can be calculated. This allows an estimate of wind-borne dust to be made, which may then be correlated with meteorological parameters such as rainfall frequency and intensity, wind direction and atmospheric pressure. Such studies are relevant to the possible mobilisation to the atmosphere of waste materials from the Ranger Uranium Mine (RUM); a uranium mining-milling complex located near Jabiru in the Region.

An additional application of constituent element ratios for these metals is to surface waters, both natural and artificial near RUM. Waste waters released by RUM have Mg:Ca ratios which are much larger than the natural waters into which they flow (Holdway et al. 1988). A change in this ratio may interfere with the metabolic processes of some invertebrates (Allison 1987), particularly those whose body fluids closely reflect ambient water quality (Phillips 1980).

However, if measurements are made which are near the detection limit of FAAS, precision for individual metals will be poor, and ratios derived from these will have even less accuracy. Therefore, the present study was undertaken to develop a graphite furnace atomic absorption spectrophotometric (GFAAS) method for each of sodium, potassium, magnesium, calcium and strontium, applicable to the natural waters of the Alligator Rivers Region (ARR). The authors are not aware of any other report on determining these elements in continental rainwater using GFAAS.

The optimised methods for the individual metal ions were tested using: standard seawater (IAPSO, P92 Institute of Oceanographic Sciences, UK); simulated rainwater (US NBS SRM 2694 I & II) and composite rainwater from the ARR. The methods were then applied to the determination of these metals in rainwater (both local convectional and monsoonal in origin) and creek water collected from Magela Creek in the ARR.

2 MATERIALS AND METHODS

2.1 Sample collection sites

Rainwater was collected during two consecutive Wet seasons; from 6 November 1984 - 15 April 1985 and 6 November 1985 - 28 April 1986. During the first of these Wet seasons, rainwater was collected from two sites, the roof of the laboratory and from Jabiru Airport (about 100 metres distant), on a total of 53 occasions. During the second Wet season, a total of 38 samples were collected, from the laboratory roof only.

Creek water was sampled from three sites. The first two were in the headwaters of Magela Creek in Arnhem Land; at Bowerbird Billabong and at the outflow of this billabong. The third site, near Jabiru, was approximately 150 m downstream from the outflow of Georgetown Billabong into Magela Creek (see LeGras & Noller 1989).

2.2 Sample collection

Rainwater

Samples were collected in 2 L polyethylene bottles which had been previously acid soaked (Noller et al. 1985) and rinsed with high purity water (Millipore Super-Q Grade) until wash water conductivity was < 1 μS/cm (usually < 0.5 μS/cm). A polyethylene funnel of 150 mm diameter, prepared in a similar fashion, was placed in the top of each bottle and samples collected at the end of each 24-hour period. Sub-samples were decanted into 120 mL acid-soaked, high-purity water-rinsed polyethylene bottles and acidified to 1% v/v HNO_3 with BDH Aristar Grade acid. They, together with blanks of acidified high purity water were stored at 4°C until analysed.

Magela Creek water

Seven 120 mL Nalgene polythylene bottles, 2 for blanks and 5 for samples, were used for each of five sample collections for the Georgetown site. A total of five blank bottles and twenty sample bottles were used for Bowerbird sites. These samples were from an earlier study and their preparation is described elsewhere (LeGras & Noller 1989). Each sample and blank was acidified to 0.1% v/v HNO_3 with BDH Aristar Grade acid; the lower concentration of nitric acid here compared with rainwater samples was to reduce the zinc blank in the earlier study.

2.3 Analytical equipment

All GFAAS determinations were performed using a Perkin-Elmer 5000 spectrophotometer with a HGA 500 graphite furnace and AS 40 autosampler. The optimised methods for potassium, calcium and strontium used wall atomisation of the sample from a pyrolytically-coated graphite tube. Methods for sodium and magnesium used a graphite, stabilised-temperature (L'vov) platform manually fitted into a grooved pyrolytically-coated graphite tube. High purity nitrogen was used as inert gas. Furnace temperature settings are given in Table 1 and instrumental parameters are given in Table 2; Tables 1 and 2 give details for optimised methods including detection limits.

Table 1. Graphite Furnace AAS temperatures (°C) for various cycles in optimised methods for sodium, potassium, magnesium, calcium and strontium

	Cycle			
Element	Dry	Ash	Atomise	Clean-out
Sodium	110	-	2200	2500
Potassium	110	950	2100	2500
Magnesium	110	1000	2400	2600
Calcium	110	1000	2700	2750
Strontium	110	1000	2700	2750

Table 2. Instrumental parameters for the determination of sodium, potassium, magnesium, calcium and strontium in natural waters by graphite furnace AAS

Peak quantitation was by height with an integration time of 5 s for all elements. All measurements were made in concentration mode.

Element	Sodium	Potassium	Magnesium	Calcium	Strontium
Deuterium Background Correction	No	No	Yes	Yes	No
Amplifier Gain	478	474	450	579	349
Hollow Cathode Lamp Current (mA)	10	12	15	30	20
Slit Low (nm)	0.7	0.7	0.7	0.7	0.4
Wavelength (nm)	330.3	404.4	202.5	239.9	460.7
Standards (μg/L)	0,100,500	0,100,500	0,50,100	0,100,500	0,0.5,1.0
Aliquot volume (μL)	40	95	5	95	95
Detection limit (μg/L)	6	3	1	4	0.1

Standard-addition determinations were made using 'Method 3' of the AS 40 autosampler and a standard pyrolytically-coated graphite tube (Cooksey & Barnett 1979). Each determination consists of a three-step process, each step involving determination of the metal:

1. the delivery of a specified aliquot of sample plus a specified ('alternate') aliquot of blank to the graphite tube;

2. the delivery of the same specified volume of sample plus the same alternate volume of standard solution; and

3. the delivery of the combined specified volume plus alternate volume, of blank only.

The addition of a matrix modifier to the sample was accomplished by the delivery of a specified volume of sample to the graphite tube followed by an alternate volume of the modifying reagent, using Method 1 of the AS 40 autosampler. All solutions were contained in 2 mL polystyrene cups except for the blank used in standard-addition experiments and the matrix modifier in direct-calibration experiments. These were both contained in a polypropylene receptacle of approximate volume 50 mL, which was placed in a well constructed in the housing of the autosampler.

3 METHOD DEVELOPMENT

For each element the objective was to develop a GFAAS method using a direct calibration technique. Direct calibration is less time-consuming and more precise than the alternative method of standard additions. Each method was developed by examining: i) a direct determination of sodium, potassium, magnesium, calcium and strontium in a sample of composite rainwater prepared from samples collected in the Alligator Rivers Region, and in individual samples of 1985-86 rainwater; and ii) by a standard-additions technique, which was compared with the results of each direct-calibration method.

The criteria used to assess the accuracy of the direct-calibration methods were conformity of the results for these metals to certified or accepted values in:

(a) a commercially-available simulated rainwater (NBS SRM 2694, I & II);

(b) diluted standard seawater (IAPSO P92); and

(c) diluted USEPA Mineral Quality Control Samples 2, 3 and 4 (for sodium, potassium, calcium and magnesium) and NBS SRM 1643b (for strontium).

Scans for the atomisation peaks of all metals were recorded for the alternative direct-calibration methods developed, to ensure that the absorption profiles were symmetric with an acceptably low noise level. Absorption profiles were determined using a standard solution of the metal; NBS SRM 2694 I & II; US EPA Mineral Reference 4 and the composite rainwater sample described earlier.

3.1 Preliminary investigations

For all metals, replicate (n = 10) determinations were performed on a single sample of serially diluted (1:10000) IAPSO P92 seawater and on the composite rainwater sample using both the standard-additions and direct calibration technique on the same aliquots. Wall atomisation from a pyrolytically-coated tube was used. These results are presented in Table 3. For at least one of these matrices, the signal was depressed for sodium, potassium and magnesium with direct calibration whereas for calcium and strontium, an enhanced signal was obtained using direct calibration, particularly for seawater. The origin of this enhanced signal for these metals cannot be explained with certainty, but may be due to stoichiometric rather than proportional interference. For the standard-additions method, this would give a proportionately greater suppression of the signal for the sample aliquot than for the signal of the standard solution aliquot. The interference effects must be small, however, because direct calibration yields results which agree well with certified or known results, except for calcium and potassium in NBS SRM 2694 I & II (Table 6), as discussed later.

3.2 Optimisation of methods

Signal suppression using direct calibration and wall atomisation from a pyrolytically coated tube was most pronounced with sodium (Table 4). This suppression could be due to:

(a) ionisation of sodium at the atomisation temperature;

(b) volatilisation during the ashing step; or

(c) chemical interference during atomisation.

The first possibility was tested by adding a 10 μL aliquot of 100 mg/L caesium solution (caesium chloride Merck Suprapur) to a 20 μL aliquot of sample, using the alternate volume facility of the autosampler. Each of the 38 samples from the 1985-86 Wet season was determined individually. The mean ± standard deviations were 340 ± 390 μg/L for the matrix modified direct method compared with 470 ± 510 μg/L for standard additions. Clearly ionisation of sodium was not responsible for the reduced signal obtained using direct calibration, because matrix modification afforded no improvement.

Table 3. A preliminary assessment of direct calibration vs standard additions for sodium, potassium, magnesium, calcium and strontium in standard seawater and composite rainwater (n = 10) using wall atomisation from pyrolytically-coated graphite tubes

Element	IAPSO seawater (mg/L) (mean ± sd)		Composite rainwater (μg/L) (mean ± sd)	
	Direct calibration	Standard additions	Direct calibration	Standard additions
Sodium	10400 ± 410	12100 ± 710	120 ± 1	150 ± 6
Potassium	420 ± 8	450 ± 31	45 ± 1	50 ± 4
Magnesium	1050 ± 13	1260 ± 70	23 ± 1	20 ± 1
Calcium	440 ± 12	360 ± 29	24 ± 2	23 ± 6
Strontium	7.4 ± 0.2	5.5 ± 0.4	0.17 ± 0.01	0.15 ± 0.02

Table 4. Summary of comparisons of determinations for 38 individual 1985-86 rainwater samples between direct calibration and standard additions (n = 1) for sodium, potassium, magnesium, calcium and strontium (μg/L)

Element	Direct calibration (mean ± sd)	Standard additions[c] (mean ± sd)
Sodium[a]	420 ± 470	470 ± 510
Potassium[b]	56 ± 63	55 ± 68
Magnesium[a,d]	49 ± 45	48 ± 44
Calcium[b,d]	51 ± 74	55 ± 87
Strontium[b]	0.63 ± 0.39	0.57 ± 0.55

a direct calibration method used atomisation from L'vov platform;
b direct calibration method used atomisation from the wall;
c standard additions method used atomisation from the wall; and
d background correction used for these determinations; absorption profiles for other metals with all matrices used showed background correction to be unnecessary.

The second possibility was tested by eliminating the ashing step from each determination of the 1985-86 samples. The resulting mean and standard deviation was 350 ± 380 μg/L. This mean concentration is not sufficiently greater than that of the matrix-modified experiment to be certain of a volatilisation effect; however, Na_2O, expected to be one of the products of the ashing step, (L'vov et al. 1984) sublimes at 1275°C and could have significant volatility at the ashing temperature (900°C). An examination of absorption profiles with and without an ashing step gave atomisation peaks which were symmetric, sharp and free from observable background. So an ashing step was omitted for subsequent sodium determinations in these solutions, to avoid the possibility that some sodium was volatilised during an ashing step.

The third possibility was tested by performing determinations on individual samples using a stabilised-temperature L'vov platform (Koirtyohann & Giddings 1984; Chakrabarti et al. 1984). The mean and standard deviation was 420 ± 470 μg/L (n = 38) and was judged to be in satisfactory agreement with the standard additions result. A stabilised-temperature L'vov platform was also used for the determination of individual samples for magnesium. The results (Table 4) were: 49 ± 45 μg/L for direct calibration with a L'vov platform and 48 ± 44 μg/L for standard additions.

A stabilised-temperature L'vov platform could not be used for determinations of potassium, calcium and strontium because of insufficient sensitivity. For potassium and calcium this could be overcome by using the more sensitive wavelength for these metals and dilution of samples. However, this approach would introduce a strong possibility of environmental contamination at sub-μg/L concentrations. A stabilised-temperature L'vov platform was not required for these three elements for the rainwater matrix (see Table 4).

4 EVALUATION OF OPTIMISED METHODS

4.1 Analysis of reference waters

Seven reference waters were determined to test the accuracy of the optimised direct-calibration techniques. These were: NBS SRM 2694 I & II; NBS SRM 1643b; USEPA Mineral Quality Control Samples 2, 3 and 4 and IAPSO P92 seawater. The results are presented in Table 5.

Results conform satisfactorily to expected values except for potassium and calcium in the two samples of NBS SRM 2694. The main apparent matrix difference between this simulated rainwater and other samples analysed is the relative concentration of sulfate ion. For the other sample matrices the sulfate/potassium ratios (on a mg/L basis) varied between 1:1 and 7.5:1. For NBS SRM 2694 I the ratio is 56:1 and for NBS SRM 2694 II it is 110:1 (these ratios are a consequence of the intended purpose of the SRM; to analyse 'acid rain'). However, this matrix interference supposition was not confirmed by experiment; samples of composite rainwater spiked with 10 μL of 50 mg/L sulfate ion using the alternate volume facility of the AS 40 autosampler yielded the same concentration for potassium (17.5 ± 3.1 μg/L; n = 10) as unspiked samples (17.3 ± 1.7 μg/L; n = 10). Similarly, raising the atomisation temperature for potassium from 2100° to 2450°C, the temperature of 'maximum furnace efficiency' for potassium (Sturgeon & Berman 1983), had no effect on the concentration obtained for composite rainwater, IAPSO P92 seawater or NBS SRM 2694 I & II (Table 6). We attribute the low apparent concentrations obtained for potassium and calcium in NBS SRM 2694 to a specific matrix effect of unknown origin but possibly connected with the relatively high concentrations of sulfate ion in these solutions. It may be possible to overcome this matrix effect by use of a L'vov platform and the most sensitive absorption wavelength for potassium and calcium, but this would necessitate dilution of the solution, with consequent risk of gross contamination of ultratrace concentrations of these metals.

Table 5. Results of determinations for sodium, potassium, magnesium, calcium and strontium in reference waters by optimised direct-calibration techniques (μg/L)

		Sodium		Potassium		Magnesium		Calcium		Strontium	
Reference Water	n	Found	Expected	Found	Expected	Found	Expected	Found	Expected	Found	Expected
IAPSO P92[a]	10	11100±100	11200[b]	418±8	414[b]	1460±20	1350[b]	440±12	429[b]	7.7±0.3	8.4[b]
NBS SRM 2694I	15	190±13	205±9	36±7	52±7	25±3	24±2	10±2	14±3	-	-
NBS SRM 2694II	15	410±34	419±15	77±13	106±8	54±6	51±3	35±2	49±11	-	-
USEPA MQ 2[a]	3	8.9±0.2	8.2±1	2.3±0.1	2.1±0.4	1.9±0.1	1.8±0.4	5.2±0.1	5.3±0.8	-	-
USEPA MQ 3[a]	15	6.7±0.5	7.0±0.4	1.7±0.2	1.7±0.2	2.6±0.3	2.4±0.3	6.0±0.8	6.7±0.6	-	-
USEPA MQ 4[a]	6	43±1	40±4	7.7±0.1	7.2±1.3	7.1±0.2	7.1±1.1	31±2	32±3	-	-
NBS SRM 1643[b]	15	-	-	-	-	-	-	-	-	240±8	231±6

[a] mg/L;

[b] data from Millero (1974b)

Table 6. The effect of atomisation temperature on the measured concentration of potassium in various water matrices

Sample	n	Potassium (mean ± sd)	
		2100°C	2450°C
Composite rainwater (µg/L)	10	17 ± 2	16 ± 2
IAPSO P92 seawater (mg/L)	10	340 ± 40	340 ± 30
NBS SRM 2694 I (µg/L)	5	34 ± 1	35 ± 1
NBS SRM 2694 II (µg/L)	5	71 ± 2	69 ± 1

Table 7. Means (standard deviations) for five determinations of each metal in 38 samples of rainwater collected in 1985-86, (µg/L)

Date	Sodium	Potassium	Magnesium	Calcium	Strontium x 100
06.11.85	190(20)	20(3)	32(3)	21(3)	14(7)
11.11.85	230(16)	64(7)	110(7)	46(2)	42(7)
11.11.85	160(18)	30(4)	37(5)	29(3)	21(7)
12.11.85	100(10)	14(3)	17(2)	11(5)	8.5(3)
22.11.85	1100(58)	190(29)	140(5)	130(5)	110(4)
26.11.85	66(5)	14(1)	16(2)	17(5)	8.5(5)
02.12.85	440(25)	84(10)	73(6)	70(5)	54(3)
09.12.85	120(8)	51(6)	18(1)	11(3)	12(5)
11.12.85	150(12)	19(2)	27(3)	18(2)	12(7)
12.12.85	65(6)	11(3)	13(2)	12(2)	7.0(3)
20.12.85	620(36)	130(19)	100(11)	90(7)	80(2)
24.12.85	120(13)	16(3)	19(3)	10(3)	9.6(5)
31.12.85	540(11)	45(5)	57(6)	35(4)	37(4)
02.01.86	58(8)	20(2)	9.0(1)	10(3)	6.0(2)
10.01.86	98(8)	21(2)	18(2)	19(4)	6.8(3)
13.01.86	660(26)	110(18)	80(11)	54(8)	39(1)
15.01.86	160(38)	16(3)	30(5)	24(4)	13(2)
17.01.86	35(5)	13(2)	9.5(2)	8(5)	5(-)[a]
20.01.86	1400(45)	110(26)	160(13)	52(3)	77(4)
21.01.86	410(58)	15(3)	57(7)	11(2)	20(1)
23.01.86	700(4)	66(7)	94(5)	34(2)	51(2)
24.01.86	500(94)	41(4)	69(4)	23(3)	31(1)
29.01.86	470(73)	34(4)	70(6)	36(4)	44(1)
05.02.86	710(25)	100(18)	110(14)	170(16)	130(8)
10.02.86	210(51)	19(2)	36(3)	29(5)	26(2)
20.02.86	290(42)	170(11)	42(5)	60(8)	30(3)
28.02.86	290(32)	130(17)	78(9)	230(13)	69(7)
03.03.86	82(17)	17(2)	13(2)	10(3)	5(-)[a]
04.03.86	150(24)	25(3)	25(2)	21(2)	9.6(2)
07.03.86	56(12)	35(7)	17(2)	21(4)	7.0(2)
10.03.86	37(7)	8.1(0.8)	6.2(0.6)	6.1(2)	5(-)[a]
19.03.88	600(22)	210(19)	89(5)	140(7)	57(4)
25.03.86	360(47)	55(3)	55(5)	41(3)	30(4)
26.03.88	260(21)	25(3)	42(7)	24(3)	20(3)
01.04.88	54(7)	6.7(2)	11(1)	15(4)	5(-)[a]
10.04.88	120(17)	10(1)	20(3)	27(5)	10(3)
14.04.88	140(28)	9.6(1)	19(2)	15(2)	10(3)
28.04.88	1200(45)	300(25)	180(15)	430(35)	160(7)

[a] Figure quoted is half the detection limit; all strontium determinations for this sample were below the detection limit.

Table 8. Means (standard deviations) of each of five runs of 1985-86 rainwater samples (n = 38) (μg/L)

	Sodium	Potassium	Magnesium	Calcium	Strontium x 100
Run 1	340(330)	56(63)	49(45)	51(74)	31(36)
Run 2	330(330)	61(69)	54(46)	54(79)	36(36)
Run 3	340(360)	65(73)	58(46)	52(76)	34(39)
Run 4	350(350)	54(62)	52(45)	54(85)	35(38)
Run 5	340(340)	60(71)	52(43)	52(84)	34(35)

4.2 Precision data for 1985-86 rainwater

Each metal was determined a total of five times in each of the 38 samples using the optimised method. The sequence used was to determine the five metals in each sample (a total of 190 determinations) then return to the beginning of the protocol, giving 950 individual metal determinations.

From the data summarised in Tables 7 and 8 it is clear that the GFAAS method yields reproducible results for the five metals determined.

5 APPLICATION OF METHODS

5.1 Magela Creek water

Table 9 gives data for all five metals at all three sites. The most interesting aspect of these values is the decline in concentration of all metals at the Georgetown site as the flood peak approaches, and the progressive increase in all concentrations after the peak. This phenomenon corresponds to an observed decrease in the conductivity of the creek water on the rising arm of the hydrograph and an increase in conductivity after the peak (Hart et al. 1987). This effect is interpreted by these authors as a dominant contribution by runoff water during the rising flood, followed by a period dominated by interflow and baseflow. A comparison of data from the Bowerbird Billabong sites with that from just before the flood peak at the Georgetown site suggests that flood-event runoff contributes mainly potassium and calcium to the water; sodium, magnesium and strontium concentrations are similar to those at the headwater sites.

5.2 Constituent element ratios in natural waters

The GFAAS methods may be applied to give better quality data for constituent ratios when the elements are present at concentrations below or near the detection limits by FAAS. The results in Tables 8 and 9 show that rainwater and sometimes Magela Creek water have concentrations of potassium, calcium and magnesium which are below or near the detection limits of FAAS.

The Table 10 data show that calcium to magnesium ratios in rainwater and in Magela Creek water at the Georgetown site, near the Ranger release pipe, are similar. In contrast, the calcium to magnesium ratios in Retention Pond 2 and Retention Pond 4 waters at Ranger were 0.15 ± 0.08 (n = 3) and 0.10 ± 0.07 (n = 3) respectively during the period January-April 1987. These comparisons may be relevant in assessing safe dilution ratios applicable to authorised releases of Ranger waste water. The GFAAS methods provide relatively simple techniques for measuring low calcium and magnesium concentrations and subsequent calculation of reliable ratios.

Table 9. Mean concentrations (standard deviations) of sodium, potassium, magnesium, calcium and strontium in Magela Creek water at three locations (μg/L)

Location	n	Sodium	Potassium	Magnesium	Calcium	Strontium
Bowerbird Billabong	10	820(10)	130(4)	330(5)	99(2)	1.7(0.02)
Bowerbird Billabong Outflow	10	800(10)	130(5)	330(10)	93(7)	1.7(0.03)
Georgetown site before and after flood peak						
-12 hours	5	950(20)	310(20)	380(10)	270(4)	2.2(0.1)
-5 hours	5	870(20)	240(10)	310(10)	190(10)	1.7(0.1)
+12 hours	5	1200(50)	330(40)	440(30)	280(20)	2.0(0.1)
+20 hours	5	1400(30)	470(20)	550(10)	360(10)	2.3(0.1)

\- indicates before a flood peak
\+ indicates after a flood peak

Table 10. Calcium to magnesium ratios in Magela Creek and rainwater

Sample	n	Calcium:magnesium (mean ± sd)
Bowerbird Billabong (all samples)	20	0.3 (0.03)
Georgetown site before and after flood peak		
-12 hours	5	0.7 (0.04)
-5 hours	5	0.6 (0.05)
+12 hours	5	0.6 (0.09)
+20 hours	5	0.7 (0.03)
Rainwater (1986 only)		
Jabiru East	38	0.5 (0.3)
Ja Ja Camp	4	0.7 (0.9)

6 CONCLUSIONS

The GFAAS methods described are suitable for the determination of very low concentrations of sodium, potassium, magnesium, calcium and strontium in several natural-water matrices including diluted sea water, rainwater and stream water.

The methods developed allow calculation of reliable constituent element ratios. The results are reproducible, and comparisons with solutions of known composition indicate that the methods provide accurate data. The only results which did not conform to certified concentrations were for potassium and calcium in NBS SRM 2694. This could possibly be due to the relatively high concentrations of sulfate ion in this SRM although this was not conclusively demonstrated. The methods for potassium and calcium should therefore be used with caution if a high concentration of this anion compared with analyte is known or suspected. This presumed chemical interference could possibly be reduced by the use of a L'vov platform, but this would require determinations to be performed at the most sensitive absorption wavelength and dilution of sample to a concentration range where gross contamination could be expected without rigorous care during analysis.

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