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Determination of Ca, Mg, Na, K in Precipitation Samples by Inductively Coupled Argon Plasma-Emission Spectrometry

by
P.D. Goulden, D.H.J.Anthony
National Water Research Institute

O. El-Kei and K.D. Austen
Water Quality National Laboratory

ABSTRACT

Precipitation samples can be analyzed directly for Ca, Mg, Na and K using a heated spray chamber with desolvation as the sample introduction system for ICAP. The detection limits are 0.003, 0.015, 0.006, 0.015 mgL^{-1} for Ca, Mg, Na and K respectively.

RÉSUMÉ

On peut doser directement le Ca, le Mg, le Na et le K dans des échantillons de précipitation, en utilisant une enceinte de pulvérisation chauffée munie d'un dispositif de désolvatation comme système d'introduction de l'échantillon dans le plasma d'argon à couplage inductif (ICAP). Les limites de détection sont 0,003, 0,015, 0,006 et 0,015 $mg.L^{-1}$ pour le Ca, le Mg, le Na et le K respectivement.

Management Perspective

This report completes the technology transfer from the Analytical Methods Division to the National Water Quality Laboratory of methodology for the determination of Ca, Mg, Na and K in precipitation samples by inductively coupled argon plasma (ICAP). The data presented in this joint report indicates that there is no significant difference between data generated by ICAP and atomic absorption spectrometry (Ca, Mg) and flame photometry (Na,K). The advantage of the ICAP methodology is that the four elements are determined simultaneously rather than sequentially resulting in increased efficiency and economy for the operational laboratory.

Perspective de la direction

Le présent rapport complète le transfert technologique, de la Division des méthodes analytiques au Laboratoire national de la qualité de l'eau, de méthodes de dosage du Ca, du Mg, du Na et du K dans des échantillons de précipitation, par spectrométrie en plasma d'argon à couplage inductif (ICAP). Selon les données présentées dans ce rapport mixte, il n'y a pas de différence significative entre les données obtenues par spectrométrie ICAP et celles obtenues par spectrométrie d'absorption atomique (Ca, Mg) et par photométrie de flamme (Na, K). Les méthodes ICAP sont plus avantageuses, car les quatre éléments sont dosés simultanément plutôt qu'un à la suite de l'autre; elles permettent donc aux laboratoires qui les utilisent d'être plus efficaces et de diminuer le coût des analyses.

INTRODUCTION

In recent years work has been carried out in these laboratories in developing methodology for the determination of metals in environmental samples by inductively coupled argon plasma-emission spectrometry (ICAP). Much of this work has been directed to the determination of heavy metals at sub microgram per litre levels in natural fresh waters. The approach that has been followed is the development of sample addition systems that deliver large amounts of the sample into the plasma.

Two addition systems that have been developed to date are a heated spray chamber (1)(2) and an ultrasonic nebulizer (3) both using desolvation (see Appendix A and B). The heated spray chamber system has proven to be reliable and reproducible. However, when analyzing surface waters for heavy metals at environmental levels it is necessary to obtain some preconcentration in the 'total metal' digestion step in order to obtain adequate detection limits. With hard waters there is a matrix effect since as the total solids increase the resulting aerosol becomes more difficult to transport into the plasma. The ultrasonic nebulizer system gives better sensitivity and a reduced matrix effect but the necessary equipment is not yet available for routine analysis in the National Water Quality Laboratory (NWQL).

Precipitation samples to date have been analyzed in regional laboratories of the Water Quality Branch (WQB) for the soluble 'major' ions Ca, Mg, Na and K by atomic absorption spectrometry (Ca, Mg) and

flame photometry (Na, K). Extractable heavy metals (Cd, Cu, Fe, Pb, Zn) have been analyzed by atomic absorption spectrometry (AAS). The intention is to carry out these analyses in the NWQL using ICAP.

In the present work the heated spray chamber system has been modified to give about twice the sensitivity previously reported (1) and the procedure has been optimized for the alkali metals Ca, Mg, Na and K. It has been shown that with these changes it is feasible to analyze precipitation samples for these four metals without any preconcentration step.

EXPERIMENTAL SECTION

Apparatus

The equipment is similar to that previously described (1). The modified spray chamber - desolvation equipment is shown in Figure 1. The positioning of the nebulizer in the end of the spray chamber is important. For maximum sensitivity the nebulizer is pointed down and to one side (about 10°) of the centre line of the chamber. This gives a swirling motion to the nebulizer spray.

Procedures

The samples are aspirated directly into the spray chamber. An off-peak measurement is done to establish the zero for each sample,

an on-peak measurement determines the reading for each sample. Each of these measurements is made with an integration time of 30 seconds. The ICAP forward power is 1400 watts, no helium is used in the cooling flow, the observation height is about 3 mm above the top of the R.F. coil. The sample is aspirated for 2 minutes with a 30 second wash between samples.

RESULTS AND DISCUSSION

Method Optimization

The heated spray chamber system as originally developed (1) used a laminar carrier flow through the drying chamber. More recently it was realized that there was better mass transfer and heat transfer in this chamber with tangential carrier flow. This flow pattern is achieved by inducing swirl in the spray chamber by positioning the nebulizer off-centre. With this minor change the amount of sample reaching the plasma is approximately doubled. The desolvation condenser used in the present method is similar to that developed for the ultrasonic nebulizer system (3). This is more robust than the two separate condensers previously used (1) and the reduced dead volume gives a somewhat reduced wash-out time.

ICAP Operation

When determining trace metals such as lead and cadmium we have found it preferable to use a small very 'hot' plasma and it is partly to achieve this type of plasma that the helium is added to the cooling argon flow (1). For alkali metals, however, the greatest sensitivity is achieved with a cool plasma, the signals increase going up the plasma from the RF coil. Hence, in the present method, the RF power is 1400 watts and helium is not used in the cooling flow. The viewing height used is a compromise between a higher position for the maximum potassium emission and a lower position for increased emission by magnesium.

Detection Limits

The detection limits are calculated as previously described (1). With a 30 second integration the detection limits are 3, 15, 6 and 15 μgL^{-1} respectively for Ca, Mg, Na and K.

Matrix Effects

The dissolved solids in the precipitation samples are sufficiently low that there are no observed matrix effects. The samples are aspirated as-is to the nebulizer and calibration of the system is done with standard solutions of the four metals of interest.

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Method Comparison

Thirty-five precipitation samples were analyzed for Ca, Mg, Na and K by the present method. The same samples were analyzed by AAS for Ca and Mg and by flame photometry for Na and K. Each of these analyses was repeated on another day. The results of these paired analyses are shown in Tables 1 and 2. The mean differences and the standard deviations of these paired determinations for each element and method are shown in Table 3. From these it is concluded that there are no significant differences between the results obtained by ICAP and the current AAS and flame photometer methods.

It should be noted that, although these analyses are described as being 'soluble' determinations, it has not been the practice in the AAS and FP determinations to filter the samples, but rather to decant the liquid from a settled sample. For the sake of continuity this has also been done in the ICAP measurements.

LITERATURE CITED

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3. Goulden, P.D. and D.H.J. Anthony, Anal. Chem. 1984. 56:2327-2329.

TABLE 1. Ca, Mg Analysis by ICAP and AAS

Sample	Calcium mg L^{-1}				Magnesium mg L^{-1}			
	ICAP		AAS		ICAP		AAS	
	1	2	1	2	1	2	1	2
1	0.040	0.040	N.D.*	0.03	0.001	0.001	N.D.	0.01
2	0.062	0.063	N.D.	0.03	0.062	0.071	0.05	0.05
3	0.15	0.15	N.D.	0.08	0.024	0.021	0.01	0.02
4	0.051	0.064	N.D.	0.03	0.002	0.006	N.D.	0.01
5	0.050	0.046	0.05	0.45	0.046	0.039	0.01	0.05
6	0.067	0.069	N.D	0.02	0.009	0.001	N.D.	0.01
7	0.22	0.23	0.06	0.18	0.023	0.030	0.02	0.03
8	0.48	0.53	0.36	0.40	0.077	0.076	0.06	0.06
9	0.89	0.86	0.71	0.74	0.085	0.073	0.09	0.07
10	0.31	0.33	0.16	0.23	0.032	0.051	0.03	0.04
11	0.13	0.13	N.D.	0.13	0.001	0.002	N.D.	0.02
12	0.52	0.53	0.52	0.52	0.087	0.089	0.09	0.08
13	0.13	0.12	N.D.	0.07	0.038	0.014	0.01	0.02
14	0.27	0.25	0.13	0.20	0.040	0.029	0.03	0.03
15	0.18	0.18	0.03	0.12	0.035	0.021	0.01	0.03
16	0.21	0.22	0.14	0.19	0.011	0.011	0.01	0.02
17	0.12	0.17	0.01	0.10	0.015	0.012	N.D.	0.01
18	0.13	0.12	N.D.	0.10	0.026	0.023	0.01	0.03
19	0.23	0.24	0.15	0.21	0.41	0.39	0.39	0.33
20	0.21	0.20	0.19	0.21	0.050	0.059	0.06	0.06
21	0.062	0.063	0.04	0.04	0.003	0.009	0.01	0.02
22	0.37	0.35	0.44	0.44	0.72	0.70	0.86	0.91
23	0.70	0.72	0.96	1.03	1.7	1.7	2.26	2.45
24	0.23	0.20	0.22	0.23	0.12	0.10	0.13	0.14
25	0.18	0.25	N.D.	0.01	0.001	0.002	N.D.	0.01
26	0.033	0.036	0.02	0.01	0.029	0.016	0.02	0.03
27	1.15	0.18	0.13	0.12	0.12	0.10	0.13	0.12
28	0.056	0.066	0.06	0.04	0.046	0.047	0.05	0.05
29	0.27	0.27	0.42	0.43	0.039	0.041	0.07	0.06
30	0.49	0.50	0.73	0.74	0.066	0.074	0.13	0.12
31	0.13	0.11	0.15	0.09	0.012	0.028	0.02	0.02
32	0.28	0.29	0.32	0.29	0.031	0.039	0.05	0.05
33	0.050	0.087	0.05	0.01	0.001	0.001	N.D.	N.D.
34	0.036	0.039	0.06	0.02	0.002	0.002	N.D.	N.D.
35	0.043	0.052	0.05	0.03	0.002	0.002	0.01	0.01

*N.D. - Not Detected, these are values less than 0.05 mg L^{-1} for Ca and 0.01 mg L^{-1} for Mg. All ICAP values are reported even if they are less than the detection limit.

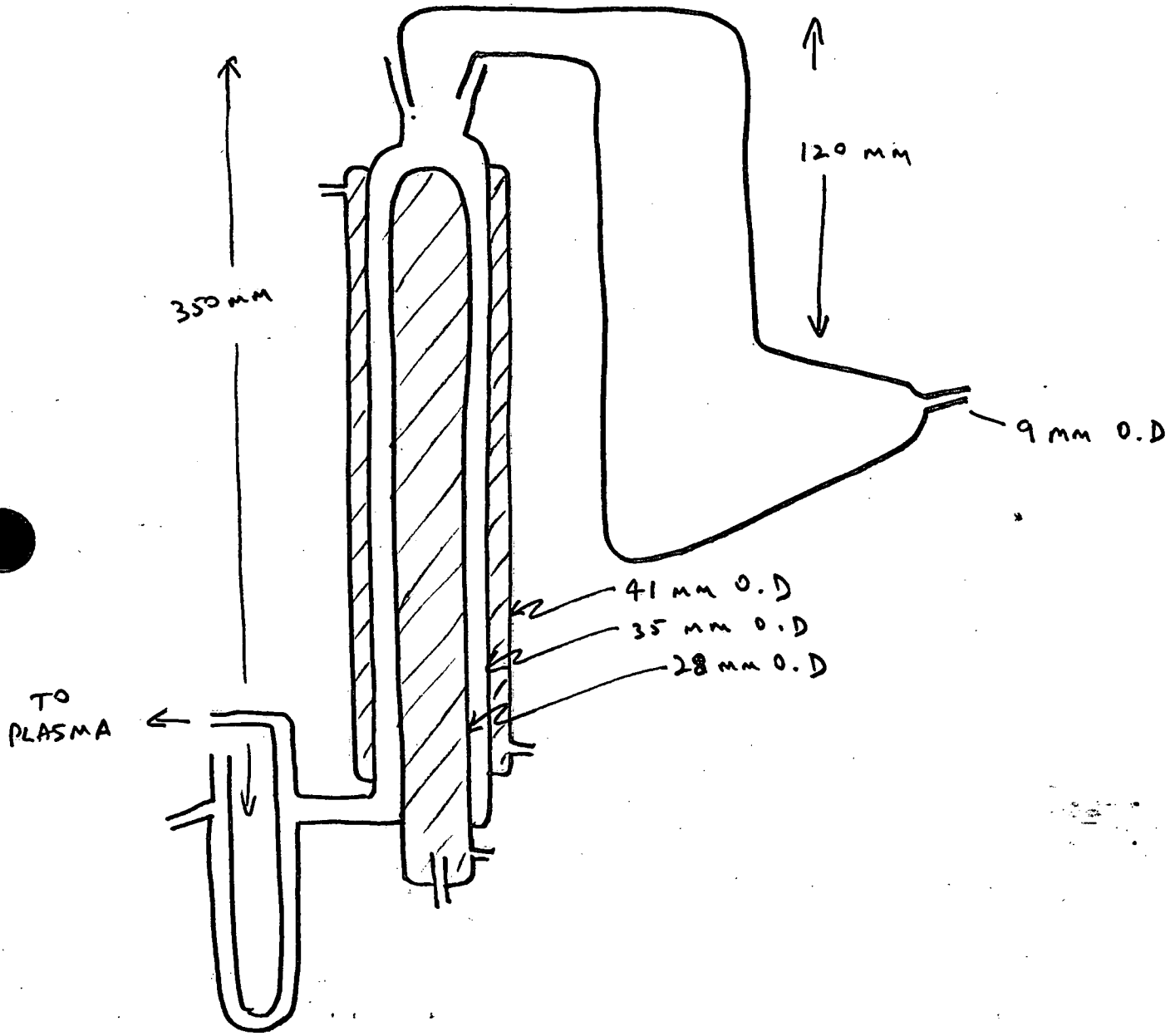
TABLE 2. Na, K. Analysis by ICAP and Flame Photometry

Sample	Sodium mg L^{-1}				Potassium mg L^{-1}			
	ICAP		Flame Phot.		ICAP		Flame Phot.	
1	0.10	0.099	0.09	0.10	0.031	0.014	N.D.*	0.03
2	0.57	0.57	0.47	0.49	0.081	0.090	0.02	0.04
3	0.18	0.14	0.09	0.11	0.14	0.094	0.05	0.07
4	0.086	0.078	0.07	0.09	0.027	0.014	0.01	0.02
5	0.30	0.28	0.18	0.35	0.079	0.071	0.05	0.08
6	0.24	0.22	0.14	0.21	0.031	0.017	N.D.	0.02
7	0.055	0.056	0.06	0.07	0.020	0.021	0.02	0.03
8	0.069	0.066	0.05	0.07	0.039	0.035	0.02	0.04
9	0.085	0.088	0.09	0.09	0.078	0.077	0.10	0.10
10	0.044	0.070	0.04	0.06	0.005	0.010	0.01	0.02
11	0.21	0.24	0.23	0.29	0.032	0.060	0.04	0.06
12	0.17	0.16	0.14	0.14	0.039	0.050	0.06	0.06
13	0.22	0.21	0.13	0.13	0.033	0.017	0.01	0.02
14	0.073	0.075	0.07	0.07	0.049	0.029	0.03	0.03
15	0.34	0.39	0.11	0.23	0.029	0.025	0.04	0.03
16	0.13	0.14	0.14	0.13	0.030	0.042	0.06	0.05
17	0.088	0.13	0.07	0.09	0.005	0.010	0.02	0.02
18	0.17	0.17	0.17	0.17	0.021	0.005	0.03	0.03
19	2.9	2.7	2.94	3.07	0.019	0.021	0.11	0.13
20	0.48	0.49	0.48	0.54	0.060	0.060	0.06	0.08
21	0.38	0.35	0.27	0.32	0.006	0.004	0.01	0.02
22	7.7	7.5	7.77	7.71	0.30	0.33	0.30	0.29
23	21.3	18.5	19.64	20.13	0.85	0.67	0.76	0.75
24	0.86	0.81	0.96	1.02	0.072	0.072	0.08	0.10
25	0.12	0.15	0.07	0.08	0.020	0.005	0.01	0.01
26	0.38	0.35	0.28	0.28	0.031	0.005	0.02	0.02
27	1.0	1.1	1.10	1.12	0.085	0.082	0.06	0.06
28	0.52	0.53	0.53	0.54	0.026	0.035	0.02	0.02
29	0.20	0.25	0.25	0.27	0.064	0.083	0.06	0.10
30	0.16	0.17	0.26	0.29	0.063	0.071	0.09	0.12
31	0.35	0.17	0.11	0.12	0.039	0.071	0.02	0.04
32	0.20	0.21	0.24	0.22	0.034	0.052	0.06	0.06
33	0.79	0.80	0.10	0.07	0.007	0.010	0.01	0.01
34	0.20	0.25	0.19	0.21	0.022	0.057	0.01	0.02
35	0.23	0.24	0.19	0.19	0.005	0.014	0.01	0.01

*N.D. - Not Detected, these are values less than 0.02 mg L^{-1} for Na and K.

TABLE 3. Standard Deviations and Mean Differences for Replicate Analyses

	Calcium	Magnesium	Sodium	Potassium
		mg L^{-1}		
AAS-FP Replicates				
Standard Deviation	0.0624	0.0259	0.0685	0.0122
Mean Difference	0.0547	0.0168	0.0454	0.0132
ICAP Replicates				
Standard Deviation	0.022	0.0107	0.0476	0.0340
Mean Difference	0.0186	0.0101	0.0362	0.0236
ICAP/AAS-FP Pairs				
Standard Deviation	0.0602	0.0187	0.0313	0.0147
Mean Difference	0.0487	0.0108	0.0279	0.0113



SPRAY CHAMBER - DESOLVATION EQUIPMENT

FIGURE 1