

## Preparing samples and standards for cation analysis

### Analytical information

The Dionex CS16 column has a stationary phase containing negatively charged carboxylic acid functional groups, and uses dilute methylsulfonic acid as the eluant. The eluant is made by the eluant generator, usually using a concentration gradient program that gradually increases the eluant concentration as the run progresses. This system can separate a wide variety of cations.

The procedure here is for seven inorganic anions in natural waters:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$ . It turns out that  $\text{NH}_4^+$  is quite common in natural waters, though usually at very low concentrations. Ba can also be analyzed, but it is almost always at or below the detection limit in most waters using the standard instrument setup. It also takes a long time to elute. Other cationic components can also be analyzed with modified procedures, such as  $\text{Mn}^{2+}$ , hydrazine, and methylamine.

### Sample preparation

All samples should be kept refrigerated and in the dark until they are analyzed, which should be done as quickly as possible. Samples must be free of high molecular weight organics (tannins, humic acids, hydrocarbons, etc.), high concentrations of transition metals, and particulates. Sample pH should be between 1 and 10.

All natural samples need to be filtered for particulates, preferably through a 0.2  $\mu\text{m}$  filter, and some samples must be filtered to remove high-molecular weight organics. The organics will damage the column, and particulate damage is irreversible. Refer to the following table:

### Sample filtration requirements

Sample content	0.2 $\mu\text{m}$ particle filter \$2.00 each*	OnGuard P filter \$4.50 each**
Normal, colorless, dilute samples.	Yes	No
Brown samples having dissolved tannins or other high molecular weight organic compounds.	Yes	Yes
* Unless already filtered, in the field, for example.		
** Removes high molecular weight organics.		

Follow the instructions with the filters. Filters can be stacked on the end of the syringe and filtered in one step, with the particulate filter being the last. The filters are expensive so do not waste them.

### Standard preparation

In general, standards should be similar in composition to the samples being analyzed. Because samples vary enormously, you may want to design your own. For many natural waters the following set of standards is a good place to start. It has 4 standards with seven inorganic components.

**Standard 1, other standards are diluted from this.**

Component	Stock concentrate, ppm	ml added to a 250 ml volumetric flask	Final concentration in 250 ml volumetric flask	Units
Li <sup>+</sup>	1000	0.1	0.4	ppm
NH <sub>4</sub> <sup>+</sup>	1000	0.25	1	ppm
Sr <sup>2+</sup>	1000	0.5	2	ppm
K <sup>+</sup>	1000	1	4	ppm
Mg <sup>2+</sup>	1000	12	48	ppm
Na <sup>+</sup>	1000	25	100	ppm
Ca <sup>2+</sup>	1000	25	100	ppm

Transfer **Standard 1** to a clean 250 ml plastic bottle. Transfer appropriate numbers of 13.9 ml aliquots of DI water and **Standard 1** to three other 250 ml bottles, as follows (we have an adjustable 20 ml pipette):

**Diluting to make the other standards.**

	Standard 1	Standard 2	Standard 3	Standard 4
DI water	-	5	8	9
Standard/1	-	5	2	1
Li <sup>+</sup>	0.4	0.2	0.08	0.04
NH <sub>4</sub> <sup>+</sup>	1	0.5	0.2	0.1
Sr <sup>2+</sup>	2	1	0.4	0.2
K <sup>+</sup>	4	2	0.8	0.4
Mg <sup>2+</sup>	48	24	9.6	4.8
Na <sup>+</sup>	100	50	20	10
Ca <sup>2+</sup>	100	50	20	10
Aliquots are 13.9 ml. 139 ml of each are left in the end.				

Pour ~5 ml of each standard into Dionex autosampler tubes, and press a black filter cap down into the top of each using the filter cap tool. You should run standards at least at the beginning of the run and perhaps also within the run. Alternatively, you can periodically run a check sample and do corrections off line.