

Battery solutions

Determination of tetrafluoroborate, perchlorate, and hexafluorophosphate in an electrolyte sample for lithium-ion battery production

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Keywords

Dionex IonPac AS20 column, suppressed conductivity detection, RFIC

Goal

To update the application that determined tetrafluoroborate, perchlorate, and hexafluorophosphate in an electrolyte sample that was designed to simulate a lithium-ion battery production sample with new equipment and a current generation electrolytic suppressor

Introduction

Rechargeable batteries are an increasing part of our daily life as we use more portable electronic devices, including mobile phones. These batteries are also important for the electric car industry. Lithium-ion batteries are the most commonly used rechargeable batteries because of their high volumetric energy density.¹ The electrolyte in these batteries are lithium salts in non-aqueous solutions. Commonly used lithium salts are lithium hexafluorophosphate (LiPF_6), lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4), lithium hexafluoroarsenate (LiAsF_6), lithium hexafluorosilicate (LiSiF_6), and lithium tetrphenylborate ($\text{LiB}(\text{C}_6\text{H}_5)_4$). Commonly used organic solvents are ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate, propylene carbonate, methyl formate, methyl acrylate, methyl butylate, and ethyl acetate.¹ The electrolyte in lithium batteries may have a mixture of these lithium salts and organic solvents. The electrolyte's concentration in the solvent ranges from 0.1 to 2 M, with an optimal range of 0.8 to 1.2 M. The anions of the added lithium salts can be determined by ion chromatography (IC) to ensure that the solutions have been prepared at the proper

concentrations. Thermo Scientific™ Application Note 258 (AN258)² demonstrated that the anionic content can be determined accurately using a Thermo Scientific™ Reagent-Free™ Ion Chromatography (RFIC™) System with 4 mm versions of Thermo Scientific™ Dionex™ IonPac™ AS20 Columns. Here we demonstrate the same application using updated equipment and suppressor with 2 mm versions of Dionex IonPac AS20 columns and an improved method for the determination of the lithium salt anions in simulated battery electrolyte solutions.

Equipment and consumables

- Thermo Scientific™ Dionex™ ICS-6000 Dual Channel HPIC™ System with RFIC-EG module, Conductivity Detector (CD)*
- Thermo Scientific™ Dionex™ AS-AP Autosampler with 250 µL syringe and tray temperature control
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System (CDS) Software, version 7.2.1

* Equivalent results can be achieved using a single channel Thermo Scientific™ Dionex™ ICS-6000 System, Thermo Scientific™ Dionex™ ICS-5000+ System, or Thermo Scientific™ Dionex™ Integrion™ HPIC™ System with Conductivity Detection.

Consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Potassium Hydroxide Eluent Generator Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ ADRS 600 Dynamically Regenerated Suppressor, 2 mm (P/N 088667)
- Thermo Scientific™ Dionex™ IonPac™ AS20 IC Analytical Column, 2 × 250 mm, (P/N 063065)
- Thermo Scientific™ Dionex™ IonPac™ AG20 IC Guard Column, 2 × 50 mm (P/N 063066)
- Dionex AS-AP Autosampler Vials, 10 mL (P/N 074228)

Reagent and standards

- Degassed deionized (DI) water, 18 MΩ-cm resistance or better
- Lithium tetrafluoroborate (LiBF₄, Sigma-Aldrich™)
- Lithium perchlorate (LiClO₄, Sigma-Aldrich)
- Lithium hexafluorophosphate (LiPF₆, Sigma-Aldrich)
- Ethylene carbonate, 98% (C₃H₄O₃, Sigma-Aldrich)
- Diethyl carbonate, 99% (C₅H₁₀O₃, Sigma-Aldrich)
- Propylene carbonate (C₄H₆O₃, Sigma-Aldrich)

Chromatographic condition

Table 1. Chromatographic condition

Columns	Dionex IonPac AS20 IC analytical column, 2 × 250 mm, Dionex IonPac AG20 IC guard column, 2 × 50 mm
Eluent source	Dionex EGC-KOH cartridge with Dionex CR-ATC and Dionex high pressure degasser
Eluent	Potassium hydroxide (KOH) gradient: 0–15 min, 15 mM; 10–13 min, 80 mM; 13–26 min, 80 mM; 26–30 min, 15 mM.
Flow rate	0.3 mL/min
Injection volume	10 µL in push-full mode
Temperature	30°C
Sampler temperature	4.0°C
Detection	Suppressed conductivity, Dionex ADRS 600 Suppressor, 2 mm, recycle mode, 70 mA current
System backpressure	2,800 psi
Background conductance	0.3–1.0 µS/cm
Run time	30 min

Samples

Simulated electrolyte samples:

- 1 M lithium tetrafluoroborate in the mixture of three carbonate solvents
- 1 M lithium perchlorate in the mixture of three carbonate solvents
- 1 M lithium hexafluorophosphate in DI water. Then 1:1 mixed with the mixture of three carbonate solvents

The mixture of three carbonate solvents is a 1:1:1 mixture of ethylene carbonate, diethyl carbonate, and propylene carbonate by weight.

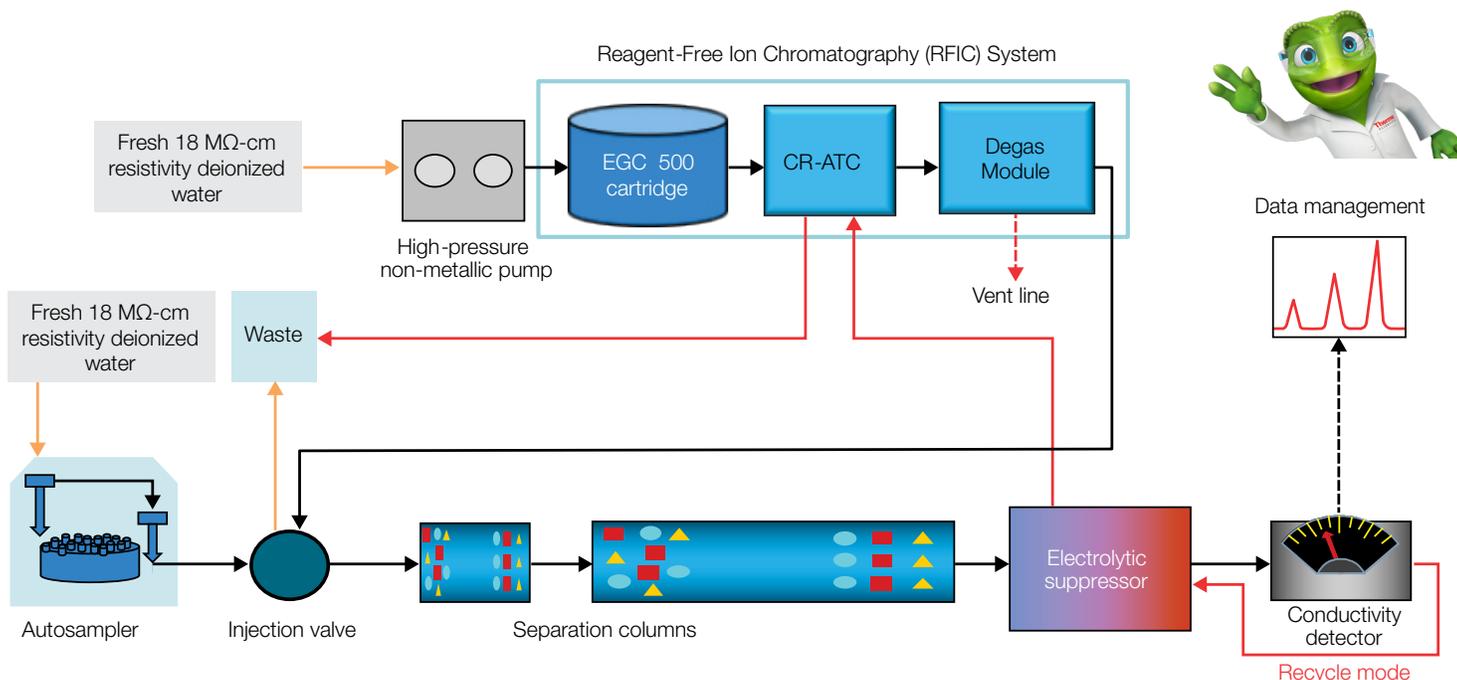


Figure 1. Schematic diagram of a RFIC system

Experimental

A Dionex ICS-6000 HPIC system with RFIC-EG module and CD detector was used here for the determination of tetrafluoroborate, perchlorate, and hexafluorophosphate. Figure 1 shows a schematic diagram of a RFIC system. The updated equipment and suppressor with 2 mm versions of Dionex IonPac AS20 columns were used.

Preparation of solutions and reagents

Calibration standards

Prepare the stock standard (1,000 mg/L) solutions by dissolving lithium salts in 100 mL (g) of DI water, stored at 4°C (Table 2).

Table 2. Preparation of standard stock solutions

Compound	Weight to prepare 100 mL stock standard (g)	Concentration (mg/L = µg/mL = ppm)
Lithium tetrafluoroborate (LiBF ₄)	0.093	1,000
Lithium perchlorate (LiClO ₄)	0.112	1,000
Lithium hexafluorophosphate (LiPF ₆)	0.105	1,000

Dilute stock standards with water to make mixed calibration standard solutions (Table 3).

Table 3. Calibration standards (mg/L)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
Tetrafluoroborate	1	5	10	20	40
Perchlorate	1	5	10	20	40
Hexafluorophosphate	1	5	10	20	40

Table 4. Preparation of simulated electrolyte samples

Compound	Weight (g)	Solvent	Final V (mL)	Conc. (M)
S1: Lithium tetrafluoroborate (LiBF ₄)	0.938	Organic*	10	1
S2: Lithium perchlorate (LiClO ₄)	1.068	Organic*	10	1
S3: Lithium hexafluorophosphate (LiPF ₆)	1.519	1:1 water: organic**	20	0.5

* Organic solvent: thoroughly mix equal weights of ethylene carbonate, diethyl carbonate, and propylene carbonate.

** LiPF₆ was dissolved in DI water and then mixed 1:1 (V) with the organic solvent before further dilution for analysis.

Sample preparation

Prepare the simulated electrolyte samples by dissolving lithium salts in solvent as shown in Table 4.

The final test samples were prepared by diluting 1–100 twice for S1 and S2, and 1–50 and 1–100 for S3. Spiked sample was prepared by spiking 2 mg/L of the corresponding compound in the final test sample.

Results and discussion

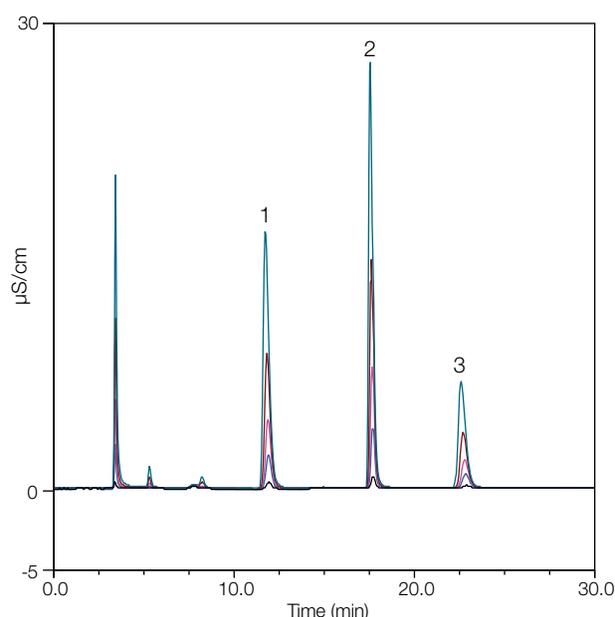
Separation

The Dionex IonPac AS20 column is a hydroxide-selective high-capacity anion-exchange column developed to determine anions that are strongly retained on other anion-exchange columns. With this column, highly retained anions, such as hexafluorophosphate, can be determined with weaker eluents and in less time compared to other anion-exchange columns.^{2,3}

Here we demonstrate the same application first reported in AN258 using an improved method and updated consumables. The improved method to determine tetrafluoroborate, perchlorate and hexafluorophosphate simultaneously in electrolyte samples includes 3 steps: First 15 min of 15 mM KOH to elute tetrafluoroborate; then the KOH concentration increases to

80 mM in 3 min and is held at 80 mM for 13 min to ensure perchlorate, hexafluorophosphate, and other strongly retained anions elute and are resolved. The KOH concentration is then returned to 15 mM for 4 min to prepare the column for the next injection. Figure 2 shows the separation of tetrafluoroborate, perchlorate, and hexafluorophosphate. Tetrafluoroborate elutes at 11.8 min, perchlorate at 17.5 min, and hexafluorophosphate at 22.6 min. Compared to the method in AN258, there is better spacing of peaks, and no peak elutes on the rising baseline that is due to the KOH concentration change, which should result in more reproducible peak integration.

As in AN258, hydroxide eluent is generated using a RFIC system. However, the current RFIC system uses a the Dionex EGC 500 KOH eluent generator cartridge (EGC) that is operational up to 5,000 psi backpressure, a new CR-ATC 600 continuously regenerated anion trap column, and a new Dionex high pressure degasser. This setup did not use a Thermo Scientific™ Dionex™ CRD 200 Carbonate Removal Device as in AN258. To improve the method by reducing EGC consumption and waste generation, we used 2 mm versions of the Dionex IonPac AS20 columns instead of 4 mm versions. This reduces the flow rate 4-fold and thus there is a 4-fold reduction in EGC consumption and waste generation.



Columns:	Dionex IonPac AG20, 2 × 50 mm and Dionex IonPac AS20, 2 × 250 mm
Eluent:	Potassium hydroxide (KOH) gradient
Gradient:	0–15 min, 15 mM; 10–13 min, 80 mM; 13–26 min, 80 mM; 26–30 min, 15 mM
Eluent source:	Dionex EGC KOH cartridge with Dionex CR-ATC and Dionex high pressure degasser
Flow rate:	0.30 mL/min
Inj. volume:	10 μL (Full loop)
Column temp.:	30°C
Sampler temp.:	4°C
Detection:	Suppressed conductivity, Dionex ADRS 600 suppressor, 2 mm, 30°C, 70 mA, recycle mode
Samples:	Mixed standards at 1, 5, 10, 20, and 40 mg/L
Peaks:	
	min
1-Tetrafluoroborate	11.8
2-Perchlorate	17.5
3-Hexafluorophosphate	22.6

Figure 2. Chromatograms of calibration standards

Linearity

The method linearity was determined by triplicate injections of five levels of calibration standards from 1 to 40 mg/L (Table 3).

The study shows that peak area responses are linear over the concentration range with $r^2 = 1.000$ for tetrafluoroborate, perchlorate, and hexafluorophosphate (Table 5, Figures 3–5).

Table 5. Linearity for the determination of tetrafluoroborate, perchlorate, and hexafluorophosphate

Analyte	RT (min)	Range (mg/L)	Coefficient of determination * (r^2)	Slope
Tetrafluoroborate	11.8	1–40	1.000	0.161
Perchlorate	17.5	1–40	1.000	0.174
Hexafluorophosphate	22.6	1–40	1.000	0.082

* Calibration type is linear with offset.

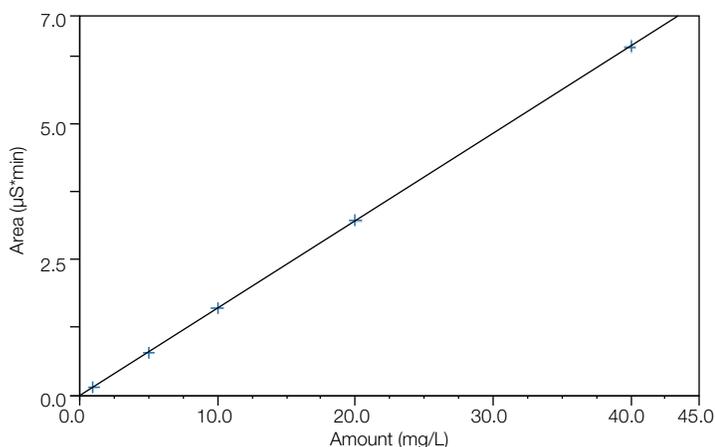


Figure 3. Calibration plot for tetrafluoroborate

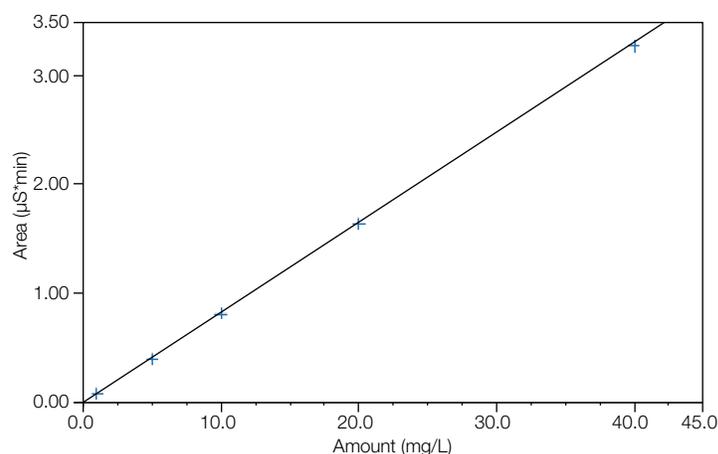


Figure 5. Calibration plot for hexafluorophosphate

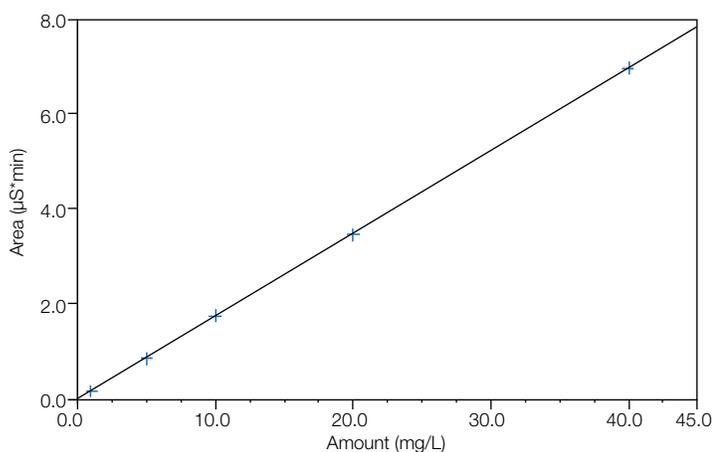
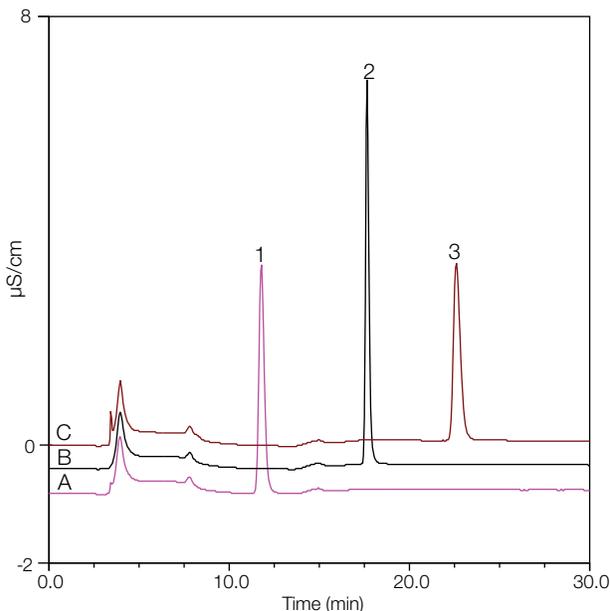


Figure 4. Calibration plot for perchlorate

Sample analysis

Three simulated lithium-ion battery electrolyte samples were prepared. One-molar solutions of lithium tetrafluoroborate and lithium perchlorate were prepared in an organic solvent (1 to 1 to 1 mixture of ethylene carbonate, diethyl carbonate, and propylene carbonate), then were diluted 1 to 10,000 (1 to 100 twice) with DI water prior to analysis by IC. One-molar lithium hexafluorophosphate was prepared in DI water and then diluted 1 to 1 with the mixture of three carbonate solvents. This sample was diluted 1 to 5,000 (1 to 50, then 1 to 100) with DI water prior to analysis by IC. Figure 6 shows the chromatography of each sample.



Columns: Dionex IonPac AG20, 2 × 50 mm and Dionex IonPac AS20, 2 × 250 mm
 Eluent: Potassium hydroxide (KOH) gradient
 Gradient: 0–15 min, 15 mM; 10–13 min, 80 mM; 13–26 min, 80 mM; 26–30 min, 15 mM
 Eluent source: Dionex EGC KOH cartridge with Dionex CR-ATC and Dionex high pressure degasser
 Flow rate: 0.30 mL/min
 Inj. volume: 10 μL (Full loop)
 Column temp.: 30°C
 Sampler temp.: 4°C
 Detection: Suppressed conductivity, Dionex ADRS 600 suppressor, 2 mm, 30°C, 70 mA, recycle mode

Samples: A – 10000× of 1 M Lithium Tetrafluoroborate*
 B – 10000× of 1 M Lithium Perchlorate*
 C – 5000× of 0.5 M Lithium Hexafluorophosphate**

* In 1:1:1 mixture of ethylene carbonate, diethyl carbonate, and propylene carbonate.
 ** In 1:1 DI water /mixed carbonate solvents

Peaks:	min
1-Tetrafluoroborate	11.8
2-Perchlorate	17.5
3-Hexafluorophosphate	22.6

Figure 6. Chromatograms of samples

The method precision was evaluated by measuring samples prepared on two days with a new sample preparation for each salt on each day. Each prepared salt sample was diluted in triplicate to create three samples for each salt. The relative standard deviations (RSD) of the results from the six samples for each salt were used to judge precision (Table 6). Interday precision was evaluated by comparing the results from the two days. The method is precise with interday precision less than 1.8% for tetrafluoroborate, 0.8% for perchlorate, and 4.5% for

hexafluorophosphate. The higher RSD for hexafluorophosphate may be due to hexafluorophosphate instability in the mixed organic/DI-water. This suggests that hexafluorophosphate should be measured as soon as possible after sample preparation.

To judge accuracy the simulated samples were spiked with 2 mg/L of the same anion prior to dilution. The spiked recoveries of 99% for tetrafluoroborate, 97% for perchlorate, and 111% for hexafluorophosphate suggesting that the method is accurate.

Table 6. Assay results for the samples and spiked samples

Day	Amount (mg/L)					
	Tetrafluoroborate		Perchlorate		Hexafluorophosphate	
	Sample	Spiked sample	Sample	Spiked sample	Sample	Spiked sample
Day 1	9.81	11.8	9.34	11.3	15.1	17.7
	9.90	11.8	9.38	11.2	15.6	17.5
	9.92	11.8	9.43	11.3	15.2	17.5
Day 2	9.63	11.6	9.23	11.3	14.1	16.2
	9.54	11.5	9.28	11.3	14.1	16.2
	9.54	11.6	9.28	11.3	14.1	16.3
Average (mg/L)	9.72	11.7	9.32	11.3	14.7	16.9
RSD	1.8	1.2	0.8	0.2	4.5	4.3
Spiked recovery (%)		99		97		111

The method accuracy was also evaluated by comparing measured concentrations to the calculated concentrations (Table 7) and found that the measured concentrations are 112, 94, and 101% of the calculated concentration for perchlorate, tetrafluoroborate, and hexafluorophosphate. This also suggests the method is accurate.

Table 7. Assay results for the samples and spiked samples compared to calculated concentrations

Analyte	Calculated concentration (mg/L)	Average measured concentration (mg/L)	Recovery (%)	Spiked concentration (mg/L)	Average measured concentration (mg/L)	Recovery (%)
Tetrafluoroborate	8.70	9.72	112	2	11.7	109
Perchlorate	9.95	9.32	94	2	11.3	94
Hexafluorophosphate	14.5	14.7	101	2	16.9	102

Conclusion

This application demonstrated an improved method for the determination of tetrafluoroborate, perchlorate, and hexafluorophosphate in simulated lithium-ion battery production samples using a RFIC system with suppressed conductivity detection, and 2 mm versions of Dionex IonPac AS20 columns. This method significantly reduces eluent consumption and thus prolongs the life of the EGC as flow rate is reduced from 1.2 to 0.3 mL/min. The method has a linear calibration over the concentration range of 1 to 40 mg/L and was shown to be precise and accurate.

References

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