Sensitive Determination of Hexavalent Chromium in Drinking Water

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Introduction

Chromates are oxyanions (e.g., CrO_4^{2-}, $Cr_2O_7^{2-}$) of chromium in oxidation state +6. All hexavalent chromium Cr(VI) compounds are strong oxidizing agents and considered toxic and potentially carcinogenic. Hence, chromates are regulated in the environment and are a primary drinking water contaminant in the United States.[1] For example, in 1999, the state of California established a public health goal (PHG) of 0.2 µg/L (ppb) for Cr(VI) and 2.5 µg/L for total chromium.[2] The PHG is based on an estimated one-in-one-million lifetime cancer risk level.

Drinking water standards are regularly re-evaluated by the U.S. Environmental Protection Agency (EPA). In 2008, the agency conducted a comprehensive review of the health effects of chromate based on toxicity studies done by the U.S. National Toxicology Program.[3] In 2009, the Office of Environmental Health Hazard Assessment (OEHHA) at the California EPA proposed to lower the PHG for Cr(VI) to 0.06 ppb.[4] In September 2010, the EPA released the Toxicological Review of Hexavalent Chromium.[5] Based on this review, OEHHA in the state of California recently issued a new PHG for chromate at 0.02 ppb in drinking water.[6]

Currently, dissolved hexavalent chromium is measured as chromate according to a modified version of U.S. EPA Method 218.6.[7–9] This method is based on anion-exchange chromatography on a Thermo Scientific™ Dionex™ IonPac™ AS7 column (4 × 250 mm) and detection after postcolumn reaction with diphenylcarbazide, which yields a compound with visible absorbance at 530 nm. This permits a method detection limit (MDL) for chromate at 0.02 µg/L and can support a reporting limit of 0.06 µg/L.[7]

However, the current method does not allow sufficient sensitivity for routine analysis at the proposed California PHG level of 0.02 µg/L. The work shown here describes modification of the conditions described in EPA Method 218.6, including use of the column in the 2 mm format and a smaller reaction coil to increase method sensitivity. The modified method uses Dionex IonPac AG7 guard (2 × 50 mm) and Dionex IonPac AS7 analytical columns (2 × 250 mm), an eluent of 250 mM ammonium sulfate/100 mM ammonium hydroxide at a flow rate of 0.36 mL/min, a 1000 µL injection volume, and postcolumn reaction with 2 mM diphenylcarbazide/10% methanol/1 N sulfuric acid (using a 125 µL reaction coil) followed by visible absorbance detection at 530 nm. This modified method permits an MDL for chromate of 0.001 µg/L. This results in a quantitation limit of 0.003 µg/L, which is more than sufficient for analysis at the proposed California PHG level.

Equipment

- Thermo Scientific Dionex ICS-2100, ICS-1600, ICS-1100,* ICS-3000, or ICS-5000 system including:
  - SP Single Pump or DP Dual Pump module**
  - DC Detector/Chromatography module**
  - Injection loop, 1000 µL
  - Reaction coil, 125 µL (P/N 053640), 375 µL (P/N 043700)
  - Sample syringe, 5 mL
  - Dionex ICS Series VWD UV-vis Absorbance Detector (P/N 069117, 4 wavelength or P/N 069116, single wavelength) with PEEK™ semi-micro flow cell, 2.5 µL, 7 mm (Victrex P/N 6074-0300) or PEEK standard flow cell, 11 µL, 10 mm (Victrex P/N 6074.0200)

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- Postcolumn Delivery Configuration:
  - DP** or PC10 Postcolumn Pneumatic Delivery Package or the Dionex AXP (P/N 063973) or AXP-MS Metering Pump (P/N 060684)
- AS Autosampler
- Thermo Scientific Dionex Chromeleon™ Chromatography Data System (CDS) software
- Eluent Organizer, including 2 L plastic bottles (P/N 072057) and pressure regulator (P/N 038201)
- Polypropylene injection vials with caps (0.3 mL vial kit, P/N 055428)
- Nalgene™ 125 mL HDPE narrow mouth bottles (VWR P/N 16057-062)
- Nalgene 250 mL HDPE narrow mouth bottles (VWR P/N 16057-109)
- Nalgene 250 mL 0.2 µm nylon filter units (VWR P/N 28199-371)
- Nalgene 1000 mL 0.2 µm nylon filter units (VWR P/N 28198-514)

*With addition of the optional column heater
**For the Dionex ICS-3000 or ICS-5000

Reagents and Standards

Reagents

- Prepare all solutions from analytical reagent-grade chemicals (when commercially available). Note: There is a possibility of the presence of trace levels of chromate in some commercially available chemicals.
- Deionized (DI) water, 18 MΩ or better
- Ammonium sulfate (Mallinckrodt General P/N AR 7725)
- Ammonium hydroxide (Sigma P/N A6899)
- Sulfuric acid, 95-98% (J.T. Baker® Instra-Analyzed® P/N 9673)
- Methanol, HPLC grade (Fisher Optima P/N A454-4)
- Potassium dichromate (J.T. Baker P/N 4765-01)
- Sodium and potassium salts, A.C.S. reagent grade, for preparing the anion standards

Conditions	
Method	
Columns:	Dionex IonPac AG7 Guard, 2 × 50 mm (PN 063099), Dionex IonPac AS7 Analytical, 2 × 250 mm (PN 063097)
Eluent:	250 mM Ammonium sulfate and 100 mM ammonium hydroxide
Eluent Flow Rate:	0.36 mL/min
Inj. Volume:	1000 µL (Full loop)
Temperature:	30 °C
Back Pressure:	1700–2000 psi
Postcolumn Reagent (PCR):	
	2 mM diphenylcarbazide, 10 % methanol, 1 N sulfuric acid
PCR Flow Rate:	0.12 mL/min
Detection:	Visible absorbance, 530 nm
Noise:	6–8 µAU
Run Time:	10 min

Preparation of Solutions and Reagents

Eluent

- 250 mM Ammonium sulfate
- 100 mM Ammonium hydroxide
- Dissolve 66 g of ammonium sulfate in ~1 L of DI water and add 13 mL of 29% ammonium hydroxide solution. Dilute to 2.0 L with DI water.

Sample Adjustment Buffer

- 250 mM Ammonium sulfate
- 1000 mM Ammonium hydroxide
- Dissolve 3.3 g of ammonium sulfate in ~75 mL of DI water and add 6.5 mL of 29% ammonium hydroxide. Dilute to 100 mL with DI water.

Postcolumn Reagent

- 2 mM Diphenylcarbazide
- 10% Methanol
- 1 N Sulfuric acid

Add 28 mL of 98% sulfuric acid to ~500 mL of DI water in a 1.0 L volumetric flask (caution: this mixture may get hot). Mix and allow to cool. Add 0.5 g of 1,5-diphenylcarbazide to ~75 mL of HPLC-grade methanol in a 100 mL volumetric flask and sonicate to dissolve. Bring to volume with methanol, mix, and add to the cooled sulfuric acid solution. Dilute to 1.0 L with DI water, mix, and transfer to the pressurized PCR container. The PCR is stable for 3–4 days. Prepare fresh as needed.

Standard Solutions

Add 0.283 g of potassium dichromate (dried at 100 °C to a constant weight) to ~50 mL of DI water in a 100 mL volumetric flask. Dissolve and bring to volume with DI water. Store the stock standard at 4 °C. Prepare working standards fresh daily. Adjust the pH to 9.0–9.5 by adding 1 mL of sample adjustment buffer per 100 mL of final volume before bringing to final volume.

High-Ionic-Strength Water

High-ionic-strength water (HIW) is defined in EPA Method 300.1[10] as simulated drinking water prepared from DI water fortified with chloride (100 mg/L), nitrate (10 mg/L as N), phosphate (10 mg/L as P), sulfate (100 mg/L), and carbonate (100 mg/L). In the current work, HIW was prepared from DI water and fortified with fluoride (1 mg/L), nitrite (0.1 mg/L), and bromide (0.02 mg/L), in addition to the ions mentioned in EPA Method 300.1. This HIW was prepared by diluting appropriate volumes of the 1000 mg/L stock standards with DI water.

Sample Preparation

Clean all sample collection equipment and containers with concentrated HNO_3 diluted 1:1 with DI water and rinse well with DI water before use. Collect samples in amber glass bottles with plastic lined caps. Do not filter the samples at the time of collection, but immediately add the sample adjustment buffer dropwise until the sample pH falls in the range of 9.0–9.5. Be careful not to contaminate the sample while measuring the pH. Most drinking water samples can be adjusted to pH 9.0–9.5 by adding 1 mL or less of the adjustment buffer per 100 mL of sample, which introduces an acceptable 1% dilution error.

For more difficult samples, start with a known amount of sample and accurately measure the amount of buffer added so that the amount of Cr(VI) as CrO_4^{2-} determined by ion chromatography (IC) can be corrected for dilution. Cool to 4 °C and hold at 4 °C during transport and storage. Analyze samples within 24 h of collection to minimize the potential loss of Cr(VI) through chemical reduction.

System Preparation and Configuration

The VWD UV-vis absorbance detector can be equipped with either a standard (PEEK) or a semi-micro (PEEK) flow cell when the DP or AXP pumps are used to deliver the postcolumn reagent. If the PC10 module is used for postcolumn reagent delivery, the standard (PEEK) flow cell must be used. An end line filter (P/N 045987) can be used for the eluent and postcolumn reagent lines to reduce noise, though none were used for the data shown in this application update.

Alternatives for Postcolumn Delivery

DP Pump Module

The postcolumn reagent can be delivered via the second pump of the DP module, the PC10, or the AXP pump. Operate the DP pump at a backpressure of 1400–1600 psi. Use green PEEK tubing (P/N 044777) between the pump and backpressure tubing (connect using union P/N 042627) to reduce pump noise.

AXP Pump

Configure the AXP pump as described in the AXP/AXP-MS Manual and operate at a typical backpressure of 1400–1600 psi.[11] Use green PEEK tubing (P/N 044777) between the AXP pump and backpressure tubing (connect using union P/N 042627) to reduce pump noise. An equilibrated system has peak-to-peak noise of less than 10 µAU.

PC10

Configure the IC and the PCR system as shown in Figure 3 of Dionex Technical Note 26,[9] and as described in the PC10 Postcolumn Delivery System installation instructions.[12] A standard (PEEK) UV cell is recommended with the PC10. Pump the eluent at 0.36 mL/min and set the PC10 pneumatic pressure to ~40 psi.

To measure the PCR flow rate, collect the effluent from the detector (i.e., the total flow from the IC pump and the PCR module) in a 10 mL graduated cylinder for 10 min. The PCR flow rate is the difference between the total flow rate and that of the IC pump. Adjust the air pressure of the postcolumn delivery module (PC10) and remeasure the flow rate until the correct PCR flow rate of 0.12 mL/min is established. Variations in the PCR flow rate affect the postcolumn reaction time, pH, dilution, mixing rate, and ratio of the reactants. Stable day-to-day results depend on a well-controlled PCR flow rate.

Confirm this flow rate on a daily basis or whenever detector response for a calibration check standard deviates beyond quality control acceptance criteria. Once the flow rate has been established, the PCR flow rate can be monitored by observing the absorbance at 280 nm (obtained from a 4-channel VWD). The absorbance at 280 nm should remain at the same level during the full series of injections.

Column Equilibration

The storage solution that the Dionex IonPac AS7 column is shipped with is 30 mM nitric acid. After equilibrating the column with eluent for 60 min, analyze a system blank of 1000 µL of DI water. An equilibrated system has a background signal of less than 200 mAU and peak-to-peak noise of less than 10 µAU. No peaks should elute within the retention time window of the chromate peak. The column is equilibrated when two consecutive injections of a standard produce the same retention time for chromate.

Instrument Operational Considerations

After running a sequence of injections, if the system will not be running this application for a few days, it is recommended to run the pumps used for eluent and PCR delivery with DI water for >2 h. The UV-vis lamps should be turned off to extend their life. When the system is idle for short periods (1–2 weeks), the pump can be run with DI water at a reduced flow rate to achieve rapid startup.

Results and Discussion

Dionex ICS-3000 System

Figure 1 shows a chromatogram of a 0.1 µg/L Cr(VI) as CrO_4^{2-} standard in DI water and in HIW using a DP pump for PCR delivery and a semi-micro flow cell. The elution time for chromate was about 7 min. A slight shift (0.05 min) in the retention time for chromate in the HIW matrix was observed. However, the peak shape and the peak area response are similar to standards in DI water. In the concentration range 0.005–1 µg/L, the peak response recovery ranges from 89–103% in the presence of 100 mg/L chloride, sulfate, and carbonate.

Figure 2 shows the chromatograms obtained for DI water, HIW, and Sunnyvale, CA, tap water spiked with Cr(VI) at 0.1 µg/L using an AXP pump for the PCR delivery and a standard flow cell. The baseline (2–6 min) signal in the tap water sample did not affect the chromate peak eluting at ~7 min. The tap water blank has a background level of 0.05 µg/L chromate (Figure 3, C). The calibration curve is linear over the calibration range 0.01–0.2 µg/L for Cr(VI) as CrO_4^{2-}, with a coefficient of determination of 0.994.

The MDLs for Cr(VI) as CrO_4^{2-} are summarized in Table 1. MDL is a measure of the precision of replicate injections of a low-level standard and is defined as the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

In this application, the MDL for chromate Cr(VI) as CrO_4^{2-} was determined by analyzing seven replicate injections of HIW fortified with Cr(VI) as CrO_4^{2-} at two concentration levels of 0.001 and 0.005 µg/L (i.e., approximately 3–5× the estimated instrument detection limit). Both levels produced a calculated MDL value of 0.001 µg/L. This will enable a minimum quantitation limit of 0.003 µg/L for Cr(VI) as CrO_4^{2-}, which will be adequate for routine analysis at the proposed California PHG of 0.02 µg/L.

Table 1. Method detection limits for chromate in HIW based on a 1000 µL injection.

Chromate Conc. (µg/L)	Std. Dev. (µg/L)	RSD (%)	MDL (µg/L)
0.001	0.0003	10.03	0.0009
0.005	0.0004	6.62	0.0013

MDL for chromate for 1000 µL n = 7 injections

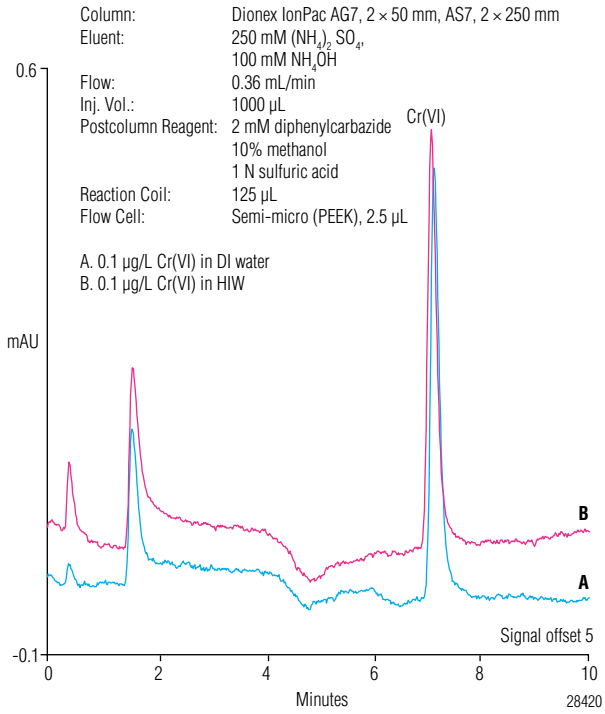

Figure 1. Determination of chromate (0.1 µg/L) in A) DI water and B) HIW on a Dionex ICS-3000 system. Postcolumn reagent delivered by a DP pump. Flow cell: semi-micro (PEEK).

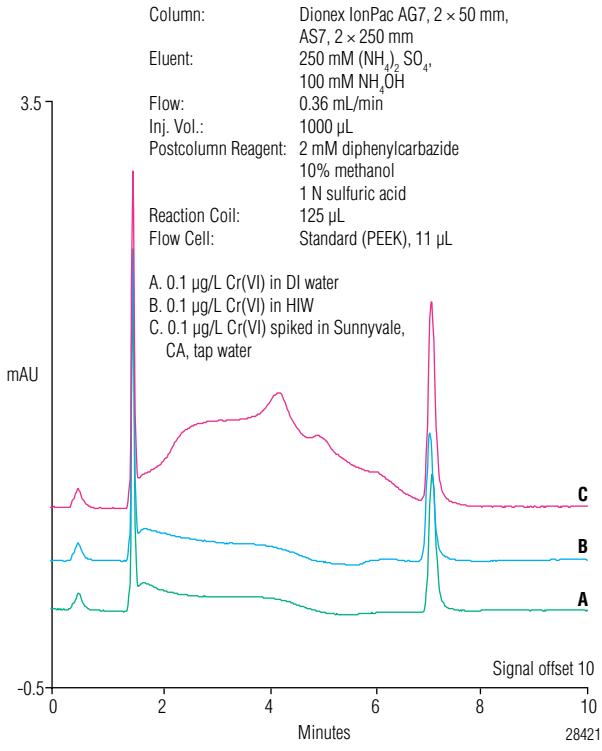

Figure 2. Determination of chromate in A) DI water, B) HIW, and C) Sunnyvale, CA, tap water using a Dionex ICS-3000 system. Sunnyvale, CA, tap water blank has a background Cr(VI) level of 0.05 µg/L chromate. Postcolumn reagent delivered by an AXP pump. Flow cell: standard (PEEK).

Comparable results were obtained for seven replicate injections of DI water fortified with Cr(VI) as CrO_4^{2-}. Figure 3 shows a 0.007 µg/L Cr(VI) as CrO_4^{2-} standard in a DI water blank A), DI water B), and a Sunnyvale, CA, tap water sample C) with a measured concentration of 0.05 µg/L Cr(VI).

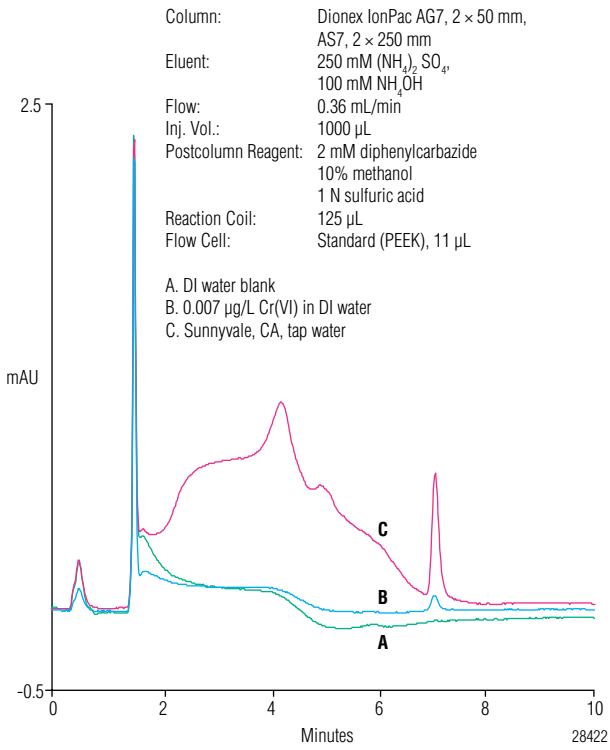

Figure 3. Determination of chromate in A) DI water blank, B) 0.007 µg/L, and C) Sunnyvale, CA, tap water blank on a Dionex ICS-3000 system. Postcolumn reagent delivered by the second pump of DP. Flow cell: standard (PEEK).

Lowest Concentration Minimum Reporting Limit

Lowest concentration minimum reporting limit (LCMRL) is defined as the lowest spiking concentration such that the probability of spike recovery in the 50–150% range is at least 99%. The LCMRL calculated using the EPA's LCMRL calculator for chromate in HIW was 0.019 µg/L (Figure 4).[13]

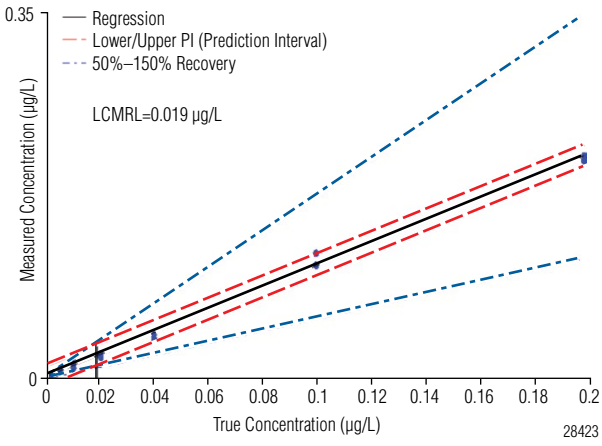

Figure 4. Determination of the LCMRL using LCMRL calculator.

Dionex ICS-2100 System

Figure 5 shows a 0.1 µg/L Cr(VI) as CrO_4^{2-} standard in DI water A) and in HIW B) by using the AXP pump for PCR delivery and a semi-micro flow cell. The two configurations (Dionex ICS-3000 and ICS-2100) provided similar results (Figures 2 and 5).

The reaction coil is not temperature controlled in an ICS-2100 system. This may result in nonsystematic baseline noise. This will not interfere with chromate detection because the nonsystematic noise is less than 5% of the chromate signal at 0.005 µg/L.

Reaction Coil

The current method can be configured with a 125 µL or a 375 µL reaction coil. The data shown here was generated with a 125 µL reaction coil. Increased peak area response was obtained with a 375 µL reaction coil in the concentration range 0.02–0.2 µg/L. However, there was no significant difference in the MDL when measured using either the 125 µL or the 375 µL reaction coil. Although the 375 µL reaction coil ensures greater reaction efficiency, it also causes greater peak dilution. At lower concentrations (<0.02 µg/L), there is less difference in reaction efficiency and any gain from the 375 µL reaction coil is lost due to peak dilution. Hence, both coils yield the same lower detection limits.

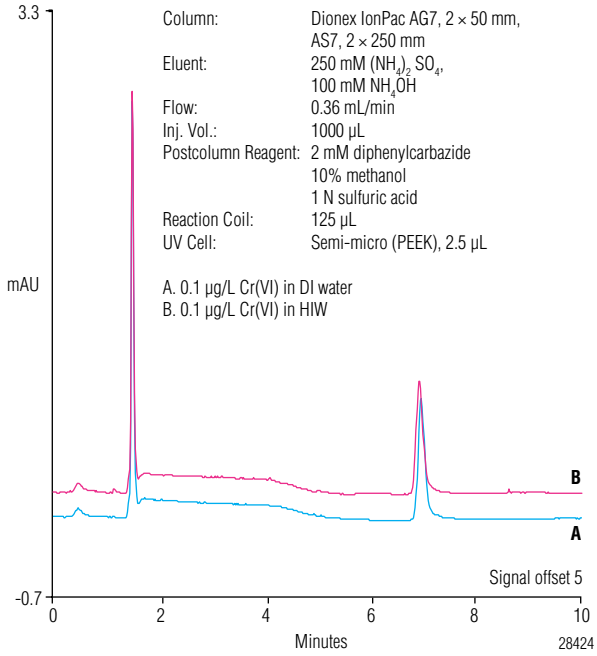

Figure 5. Determination of chromate (0.1 µg/L) in A) DI water and B) HIW on an ICS-2100 system. Postcolumn reagent delivered by an AXP pump. Flow cell: semi-micro (PEEK).

Conclusion

This testing presents modifications to the existing U.S. EPA Method 218.6 to allow sufficient sensitivity for determining hexavalent chromium (i.e., Cr(VI) as CrO_4^{2-}) at the proposed California PHG level of 0.02 µg/L. This includes the use of a Dionex IonPac AG7 guard, 2 × 50 mm, and Dionex IonPac AS7 analytical, 2 × 250 mm, columns while appropriately reducing the flow rates and reaction coil volume. Postcolumn reagent delivery can be configured three ways. The resulting MDL for Cr(VI) as CrO_4^{2-} at 0.001 µg/L will allow a minimum quantitation limit of 0.003 µg/L, which is more than sufficient for the proposed California PHG of 0.02 µg/L.

Suppliers

- VWR, 1310 Goshen Parkway, West Chester, PA 19380, U.S.A. Tel: 800-932-5000.
- Sigma-Aldrich Chemical Co., P.O. Box 2060, Milwaukee, WI 53201, U.S.A. Tel: 800-558-9160.
- Fisher Scientific, 711 Forbes Avenue, Pittsburgh, PA 15219, U.S.A. Tel: 800-766-7000
- Mallinckrodt Baker, 222 Red School Lane, Phillipsburg, NJ 08665, U.S.A. Tel: 800-582-2537

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