The Stability of Hexavalent Chromium, Cr(VI), on PVC Filter Media

Anita Hsouna, Zhen Xu, Svetlana Uzunova, Jianguo Li
High-Purity Standards, 7221 Investment Drive, North Charleston SC 29418

A global manufacturer of single and multielement standards for the calibration of analytical instruments.

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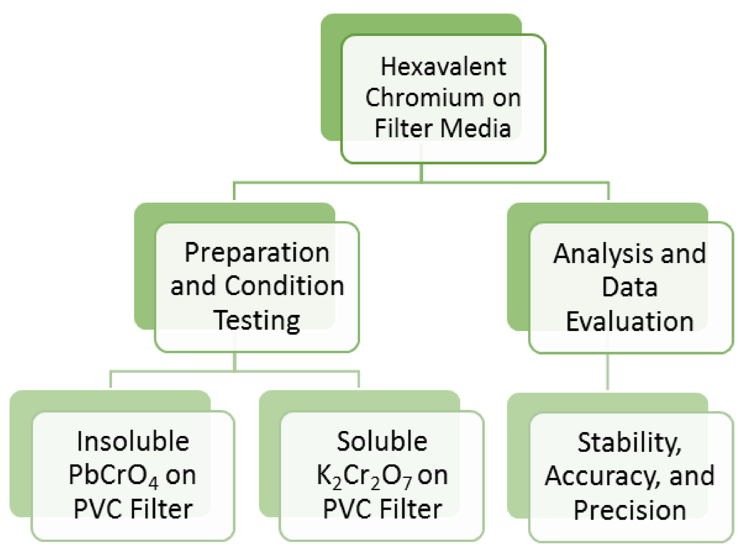
INTRODUCTION

Chromium is a naturally occurring element present in water, rocks, soils, and in biological organisms. Chromium exists in various oxidation states, however, the only biologically and environmentally stable forms are trivalent Cr(III) and hexavalent Cr(VI) chromium. While Cr(III) is an essential nutrient for metabolism, Cr(VI) is toxic and a known carcinogen. Inhalation or ingestion of contaminated air, water, or soil, by Cr(VI) is a major concern for industries using chromate painting, electroplating and welding. Therefore, monitoring Cr(VI) levels to protect workers at various working environments is a priority. Filters commonly used for sampling in industrial hygiene all have some limitations, specifically, stabilizing Cr(VI) for a period of time before analysis. At High-Purity Standards we are investigating how to extend the stability of low levels of Cr(VI) on PVC filter media. A variety of source materials for Cr(VI) are used to deposit onto filter. Various digestion methods and storage conditions are tested. Samples are analyzed by ion chromatography.

OBJECTIVE

- To develop certified reference materials to detect Cr(VI) for industrial hygiene purposes
- To conduct stability study of Cr(VI) on PVC filter media

EXPERIMENTAL DESIGN



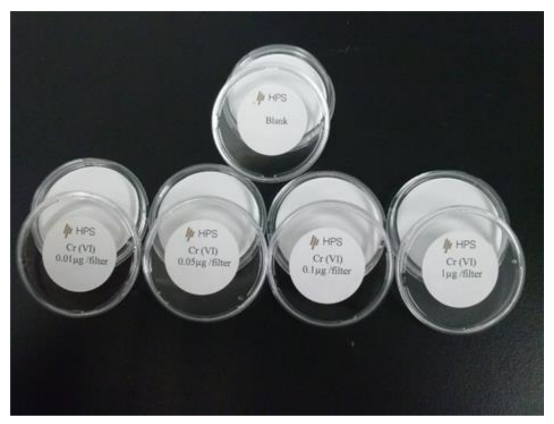


Fig. 1. Cr(VI) on PVC Filter.

MATERIALS

- Water soluble Cr(VI) from $K_2Cr_2O_7$ – NIST SRM 136d
- Water insoluble Cr(VI) from $PbCrO_4$ – Spectrum ACS Grade
- Filter Media – GLA-5000 PVC (polyvinyl chloride) membrane filter 5 µm pore size, 47 mm

Cr(VI) Filter Preparation:

- Filters were spiked with soluble and insoluble Cr(IV) compounds
- Each filter is packaged in the Petri dish and stored at ambient temperature in the designated room or at 4°C in refrigerator

2.1 Filter Concentration and Storage Condition

Table 1 – Cr(VI) Concentration on Filters

Cr(VI) on Filter (PVC)	Concentration (µg/filter)			
	Trace Level (TL)	Low (L)	Medium (M)	High (H)
	0.01	0.1	0.5	1
Storage Temp (°C)	4°C			
	Ambient (20°C - 25°C)			

ANALYSIS

Instrumentation

- Thermo Scientific Dionex ICS-3000 System with ICS Series VWD UV-vis Absorbance Detector
- Instrument parameters:
- Column: Dionex IonPac AG7 Guard 2x50mm; and IonPac AS7 analytical 2X250mm
- Eluent: 250 mM ammonium sulfate and 100 mM ammonium hydroxide
- Eluent Flow rate: 0.36 mL/min; Inj. Volume: 1000 µL
- Temperature: 30°C; Back pressure: 1700-2000 psi
- Post Column Reagent (PCR): 2 mM diphenylcarbazide in 10% methanol and 1N sulfuric acid
- PCR Flow Rate: 0.12 mL/min
- Detection: Visible absorbance, 530 nm
- Run Time: 10min

Calibration Standards

- Cr(VI) from $K_2Cr_2O_7$ is used in the preparation of calibration standards. The calibration standard curve is shown in Table 2 and Fig 2 and 3.

Table 2 – Calibration Standard

Standard ID	Concentration (µg/L)	Height (mAU)
Blank	0	0
Cr^{+6} 0.1 ppb	0.1	0.5652
Cr^{+6} 0.5 ppb	0.5	2.8966
Cr^{+6} 1 ppb	1	5.6930
Cr^{+6} 5 ppb	5	28.554

Note: 20mM $NaHCO_3$ as matrix for blank and calibrators

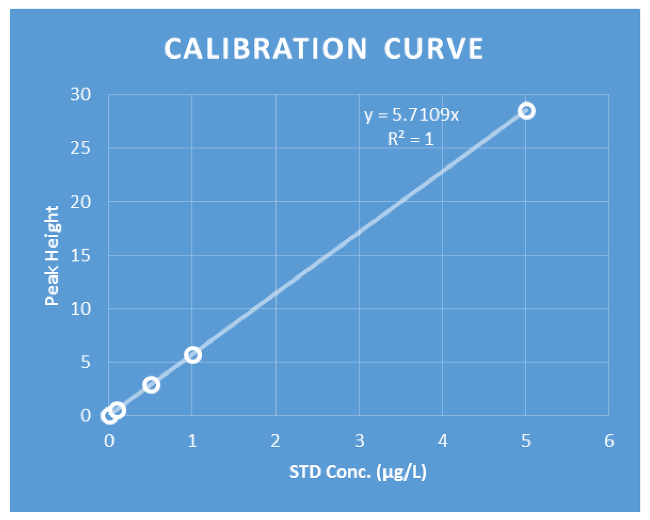


Fig. 2. Calibration curve.

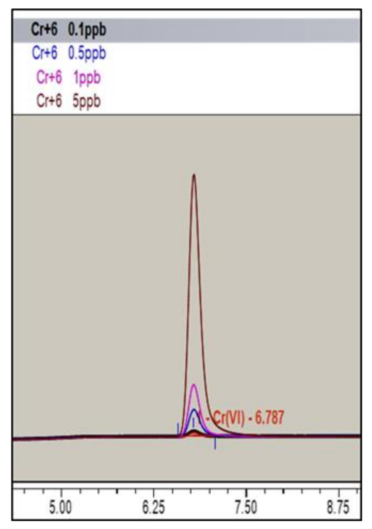


Fig. 3. Cr(VI) calibration standards .

Detection Limit

- The Cr(VI) Detection Limit was calculated to be 0.0024 ppb and the MDL is 0.012ppb based on analyzing 0.001 ppb standard of Cr(IV) 11 times with 3 times standard deviation.

RESULTS

- See Table 3 and Table 4 for the results of soluble vs. insoluble Cr(VI) on PVC filter media.

Table 3 – Cr(VI) Recovery of Soluble vs. Insoluble at Ambient vs. 4°C

Cr(VI) on PVC Filter	Recovery (%) at Ambient Temperature				Recovery (%) at 4°C			
	Week 5		Week 7	Week 6	Week 5		Week 7	Week 6
	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble
0.01 µg/filter (TL)	105	85	101	52	103	106	98	100
0.1 µg/filter (L)	93	102	97	102	99	113	98	94
0.5µg/filter (M)	97	103	95	100	98	103	98	100
1 µg/filter (H)	97	101	99	98	97	101	100	99

Note: Due to good recovery observed before week 5, only list comparison data on week 5 and week 7

Note: $Recovery = 100 * \frac{C_{coor.sample}}{C_{expected}}$

RESULTS

Table 4 – Cr(VI) Concentration and Precision of Soluble vs. Insoluble

Cr(VI) on PVC Filter	Cr(VI) Conc. at Ambient Temperature				Cr(VI) Conc. at 4°C			
	Mean (µg/filter)		RSD		Mean (µg/filter)		RSD	
	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble
0.01 µg/filter (TL)	0.0104	0.0096*	3%	9%*	0.0102	0.0103	3%	5%
0.1 µg/filter (L)	0.0963	0.1004	5%	3%	0.0982	0.0979	1%	4%
0.5µg/filter (M)	0.4925	0.5002	2%	2%	0.4971	0.5005	2%	1%
1 µg/filter (H)	0.9826	0.9934	1%	1%	0.9868	0.9978	1%	2%

Note: *The insoluble 0.01 µg/filter at ambient condition – the calculated values are based on the testing results of 6 samples through week 1 to week 4; the rest data are based on the results of 8 to 10 samples measured during whole testing period

Stability of 0.01 µg Cr(VI) on PVC Filter

- Below is the stability data of soluble 0.01 µg Cr(VI) on PVC filter. The filter was extracted with 25mL 20mM $NaHCO_3$, and analyzed by IC/LC.

Table 5 – 0.01 µg Cr(VI)/filter on Week 5

Sample ID	Observed Conc. (µg/L)	Conc. Corr. (µg/L)	Dilute (mL)	µg/filter
Cr+6 0.4ppb	0.3885			
S-TL-7 at ambient	0.4093	0.421	25	0.0105
S-TL-17 at 4°C	0.4007	0.412	25	0.0103
Cr+6 0.4ppb	0.3890			

Note: Sample Conc. Corr. $C_{corr.sample} = \frac{C_{STD} * C_{sampleobserved}}{C_{averageSTDobserved}}$

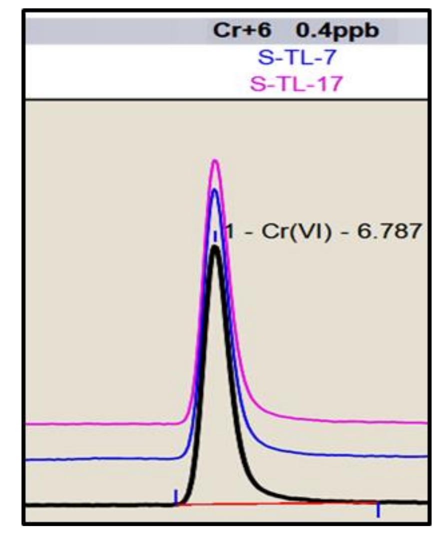


Fig. 4. Trace Level of soluble 0.01 µg Cr(VI) on PVC Filter.

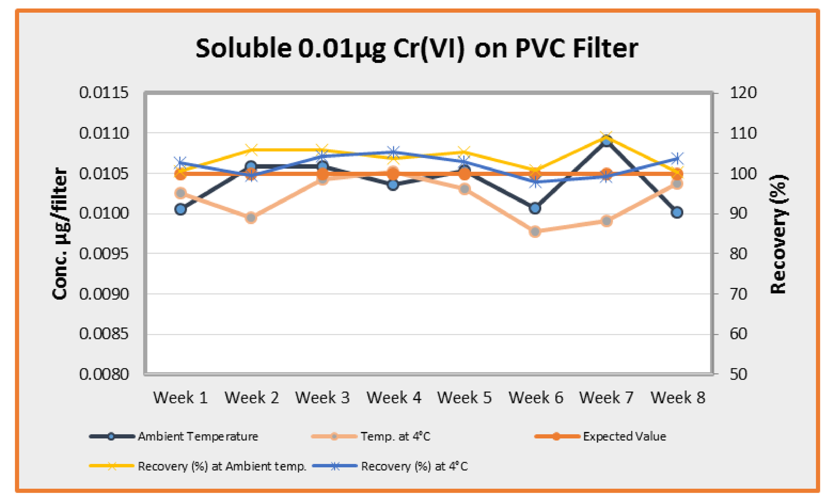


Fig. 5. Trace Level of soluble 0.01 µg Cr(VI) on PVC Filter – Conc. and Recovery vs. Time vs. Storage Condition.

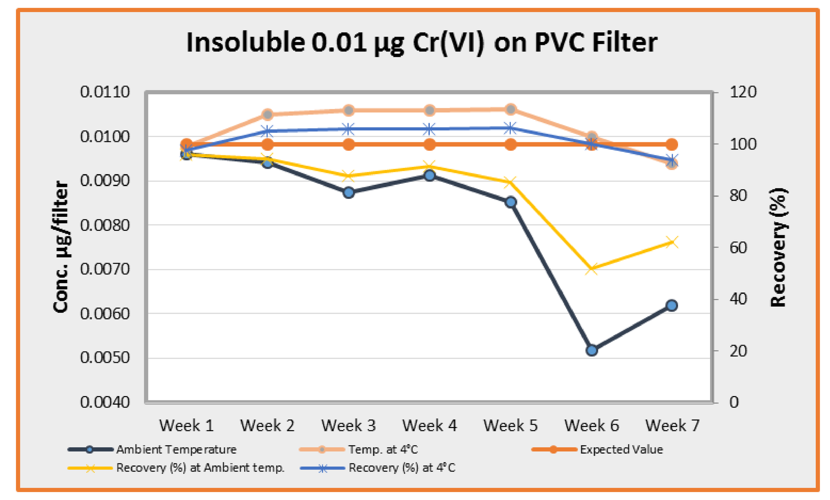


Fig. 6. Trace Level of insoluble 0.01 µg Cr(VI) on PVC Filter – Conc. and Recovery vs. Time vs. Storage Condition.

CONCLUSION

Accuracy and Precision

- IC with UV-Vis detector provides high sensitivity, precision and low detection limit in the determination of trace levels of Cr(VI). Filters spiked with dissolved Cr(VI) have better recovery than filters spiked with an insoluble form of Cr(VI)

Stability

- The PVC filters spiked with soluble Cr(VI) demonstrated stability over a 2-month period when the spiked solutions were prepared in a $NaHCO_3$ solution, which aids Cr(VI) stabilization. The PVC filters spiked with insoluble Cr(VI) were stable for 6 weeks, when stored at 4°C.
- Storage temperature has an effect on the stability of Cr(VI) filter media. Fig. 6 shows that the recovery of trace level of insoluble Cr(VI) is decreased due to the conversion of Cr(VI) to Cr(III) when stored at ambient temperature.

*Additional testing is needed to determine if the matrix has any effect on the stability of insoluble Cr(IV).

High-Purity Standards manufactures hexavalent chromium spiked-PVC filter reference materials from two different sources of Cr(IV). Spiked filters are available in concentrations ranging from 0.01µg/filter to 1µg/filter with a 10% uncertainty and an expiration date of two months when the filters are stored at 4°C.

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