Determination of Trace Levels of Hexavalent Chromium on Filter Media

INTRODUCTION

The toxicity of chromium metal ions depends primarily on its chemical forms. For example, whilst the reduced form of chromium (i.e. Cr (III)) is an essential micronutrient, its oxidized form (i.e. Cr (VI)) is a well known carcinogen. Therefore, relying entirely on total chromium levels may be misleading. As a result, the more toxic form should be monitored in order to limit exposure of individuals to this species.

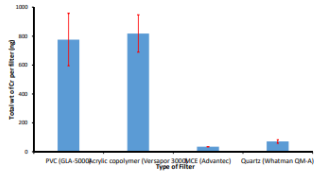
Sampling air using filters is a common method of sampling chromium. The challenges are associated with the inherent nature of the chemistry and the oxidation/reduction processes that occur in certain environments with chromium. These processes can alter the sample that is collected, affecting both the accuracy and stability of the measurement. This poster takes a look at the extensive research conducted on this topic by High-Purity Standards and our collaborating partners.

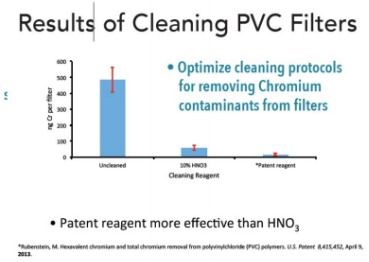
OBJECTIVE

- Comparison of filter media
- Comparison of spiked source material
- Effect of storage methods
- Analytical methods

FILTER MEDIA

Question: Are filter media free of Chromium contaminants[1]?





Answer: Different media have different levels of contaminants, but Chromium contamination can be accommodated by a proper cleaning process. High-Purity Standards is licensed for the use of a patented[2] reagent used to receive superior cleaning levels.

SPIKING MATERIAL AND STORAGE CONDITIONS

Question: Does the source material of the Chromium spike on the filter matter? How will the storage conditions affect the standard?

The results of these questions were presented at a poster session at the 2016 Winter Conference on Plasma Spectrochemistry[3] and are shown below. After 7-week test for soluble Cr(VI) and 6-week test for insoluble Cr(VI), the comparison results of soluble vs. insoluble Cr(VI) on PVC filter media under designated storage conditions are listed in the Table 3 and Table 4.

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 6	Week 7	Week 5		Week 6	Week 7
	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble
0.01 µg/filter (TL)	105	85	101	52	103	106	100	98
0.1 µg/filter (L)	93	102	97	102	99	113	94	98
0.5 µg/filter (M)	97	103	95	100	98	103	100	98
1 µg/filter (H)	97	101	99	98	97	101	99	100

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

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%
0.5 µg/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 are based on the results of 8-10 samples measured during whole testing period

Note: All filters were pre-treated with NaHCO3 following a modification of EPA Method "Standard Operating Procedure for the Determination of Hexavalent Chromium in Ambient Air Analyzed by Ion Chromatography (IC)"4

Answer: At low concentrations, the use of insoluble hexavalent chromium forms resulted in loss of recovery. But if the standard was maintained at 4°C, stability was regained. Note that this study did not definitively address the question if there was interconversion between Cr(III) and Cr(VI). That will be addressed in the next section.

Spiking Cr onto Filters

ANALYTICAL METHODS

Question: What are the best methods for analyzing the total and speciated Chromium coming from the filters?

The results of these questions were presented in a 2016 Pittcon poster[5] and are summarized below:

Methods reviewed

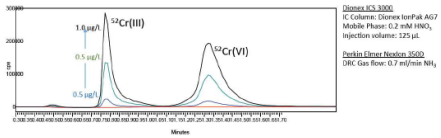
1. OSHA ID215 Method for Cr(VI) determination by IC
2. Direct IDMS for total Chromium
3. EPA Method 6800 Direct SIDMS
   a. Samples spiked with Cr-53 enriched Cr(VI) or Cr-50 enriched Cr(III)6
   b. Digested following Modified EPA Method 3060A

Table 2. IDMS Results. Listed and measured concentrations of total chromium on mixed cellulose ester (MCE) filters. These determinations are not blank corrected.

Filter ID	Description	Cr-total (µg/filter)	Total Cr found (µg/filter)
1600633	MCE filter, Blank	0	0.042 ± 0.008
1600620	MCE filter, ^{nat} Cr(III)	0.1	0.14 ± 0.05
1600622	MCE filter, ^{nat} Cr(VI)	0.1	0.12 ± 0.01
1600623	MCE filter, ^{nat} Cr(VI) + ^{nat} Cr(III)	0.2	0.215 ± 0.006

- There is agreement between the amount spiked on the filters and the total Cr found by IDMS suggesting that IDMS can successfully be applied to determine Cr in filters.
- Filters still contained residual Cr that was not removed during the cleaning of filters.

IC/ICP MS: Preliminary Results



• Apply EPA Method 6800 to determine interconversions between Cr (VI) and Cr (III)

Answer: Both IC and SIDMS methods can effectively analyze for Cr(VI), but will have different detection limits. However, in our work with Applied Isotope Technology, isotopically spiking a filter at a time coincidental with sampling will provide data on the interconversion process during storage and extraction.

REFERENCES

1. Results presented at the 2016 EPA National Environmental Monitoring Conference, presented by Tamutsiwa Mutuvari
2. Rubenstein, M. Hexavalent chromium and total chromium removal from Polyvinylchloride (PVC) polymers. U.S. Patent 8,415,452, April 9, 2013
3. Determination of Trace Levels of Hexavalent Chromium on PVC Filter Media, Zhen Xu, Jianguo Li, Tamutsiwa M. Mutuvari, Kim Phuong Tran
4. https://www3.epa.gov/ttnamti1/files/ambient/airtox/hexchromsop.pdf(accessed 5/31/2017)
5. Evaluation of Chromium Stability on Filters, Tamutsiwa M. Mutuvari, Kim Phuong Tran, Zhen Xu, Jianguo Li, Jessica Orak, Eden Couch
6. Speciated Chromium kits available from Applied Isotope Technologies (www/sidms.com)

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