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## DERTERMINATION OF PERFLUORINATED COMPOUNDS (PFCs) IN MAIN CHROME MIST SUPPRESSANTS IN CHINESE MARKET

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### Introduction

Using fluorocarbon surfactants as chrome mist suppressant (CMS) is an essential practice in electroplating industry, especially for hard chrome plating. In China, metal industry has more than 15,000 enterprises, with the annual production value of about 200 billion RMB. The consumption of Cr(VI) mist suppressant in China is about 30 tons.<sup>1</sup> There are lots of CMS products in Chinese market. Available information reveals that the most commonly used are based on perfluorooctane sulfonate acid and its salts (PFOS, C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>-), such as FC-80 (C<sub>8</sub>F<sub>17</sub>O<sub>3</sub>SK, CAS No: 2795-39-3) and FC-248 (C<sub>16</sub>H<sub>20</sub>F<sub>17</sub>O<sub>3</sub>NS, CAS No: 56773-42-3). Besides, there's a China-specific mist suppressant, 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFAES, CAS No: 73606-19-6) with the trade name of F-53B.<sup>1,2</sup> In addition, some non-PFOS CMS products have been imported in recent years, which actually are still based on fluorinated chemicals.

Perfluorinated compounds (PFCs) in the CMS added into the plating bath will finally enter into the environment with the discharge of wastewater, which will cause significant risk to the environment and human health. For the purpose of exposure assessment, it's essential to know the exact contents of PFCs in various CMS products in the market. However, very few data about this topic are available now. In most cases, such information can be found in neither the label nor the product sheet. Also the producers or vendors are not willing to provide such information. It's also very important to know whether various CMS products contain PFOS, which should no longer be used due to the Stockholm Convention.

The present study presents a preliminary survey on the PFCs concentration in various CMS products collected from Chinese market. The results are expected to provide useful data for the related risk assessment caused by PFCs used in chrome plating industry.

### Materials and methods

#### Chemicals and materials

6:2 Cl-PFAES (F-53B) was obtained from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, with a purity of >98%. Standard solutions of PFCs (including PFOS, PFHpS, PFHxS, PFBS, 6:2 FTS) were purchased from Wellington Laboratories Inc. (ON, Canada). Other materials include: methanol (HPLC grade, Fischer), acetonitrile (HPLC grade, Fischer), NaH<sub>2</sub>PO<sub>4</sub> (HPLC grade, Fluka), Pure water (generated by Milli-Q system, Millipore); 100 mL volumetric flask, sample bottles (PP, 1.5 mL, J&J Industries), adjustable micro-pipette (20-200  $\mu$ L, 200-100  $\mu$ L, Eppendorf), syringe (1 mL, Shanghai Zhiyu Medical Instrument Co., Ltd.), thimble filter (Nylon, 0.22  $\mu$ m  $\times$  13 mm, Shanghai Anpel Scientific Instrument Co., Ltd.), Oasis HLB SPE cartridge (200mg/6mL Waters).

#### Samples of CMS products

Totally 28 CMS products in Chinese market were collected via the following approaches: (1) purchased from the vendors, whose contact information were collected from the world's largest online business-to-business trading platform for small businesses [www.alibaba.com](http://www.alibaba.com); (2) obtained from the producers with the help of China Association of Fluorine and Silicone Industry (CAFSI); (3) provided by chrome plating companies as the end users.

#### Sample preparation

For liquid sample, take the required volume of liquid sample into the flask, dilute using the mixture of methanol and pure water (1:1, V/V), remove potential solid particulates from the solution using the thimble filter before injection. For solid sample, Take the required weight of solid sample into the flask, dissolve in pure water, remove potential solid particulates from the solution using the thimble filter before injection. When necessary, small amount of methanol or acetonitrile was used to enhance the solubility.

Cleanup of complicated sample: For some complicated sample, Oasis HLB SPE cartridge was used for cleanup purpose, in order to avoid or minimize the matrix interfere. The operational procedure is as following: Place the Oasis HLB cartridge on vacuum manifold, add to and draw through the cartridge 5 mL methanol for twice. Determine the dilution factor based on the results from LC-CDD measurement, load the sample (i.e. draw sample through the cartridge at the flow of 3-5 mL/min), hold the vacuum for 0.5 h to dry the cartridge, elute the cartridge twice using 8 mL methanol, dilute the collected eluent to 10 mL. Take 1 mL and remove potential solid particulates from the solution using the thimble filter before injection.

#### Instrument analysis

A two-step strategy was adopted for the determination: first to make a rough determination by LC-CDD method; then to make the quantitative analysis by LC-MS/MS method. Such a strategy can make sure the consistency of the testing with the existing standards, also to avoid the potential overload of LC-MS/MS with an estimated concentration from LC-CDD before the injection into the LC-MS/MS. National standard GBT24169-2009 has been adopted as reference,<sup>3</sup> while the target chemicals extended from PFOS to multiple PFCs (including PFOS, PFHpS, PFHxS, PFBS, 6:2 FTS, 6:2 Cl-PAES).

A Shimadzu high performance liquid chromatography system (LC-20A) equipped with a conductivity detector (CDD-6AVP) and an autosampler system (SIL-20A) was used for rough determination. A reversed phase column (TC-C18, 4.6 mm×250 mm×5 $\mu$ m, Agilent) was used, and the column temperature was set at 40°C. The mobile phase was the mixture of methanol and 0.02 mol/L NaH<sub>2</sub>PO<sub>4</sub> with the V/V ratio of 70:30 (for PFOS, PFOA) or 60:40 (for PFHxS, PFHxA, PFBS, and PFBA), and the flow rate was set at 1.0 mL/min.

An ultra-high performance liquid chromatography (UltiMate® 3000 UHPLC, Dionex) coupled to a mass spectrometer (API 3200, AB Sciences) equipped with an autosampler was employed for the quantitation of PFOS and related PFCs. Chromeleon 6.80 workstation and Analyst 1.5.1 software were used. A reversed phase column (ZORBAX Eclipse XDB-C18, 3.5  $\mu$ m×2.1 mm×150 mm, Agilent) was used, and the column temperature was set at 30°C. The mixture of 2 mmol/L NH<sub>4</sub>AC (A) and methanol (B) was used as the mobile phase, with the flow rate of 0.35 mL/min.

## Results and discussion

#### PFCs in solid samples of CMS product

The detected concentrations of PFCs in solid CMS product samples are shown in Table 1.

As shown in Table 1, the detected PFCs in solid CMS product samples are mainly PFOS and 6:2 Cl-PFAES (i.e. F-53B). If converted into the chemical purity, the range of PFOS in CMS-S-01 to CMS-S-08 is 70%~99%, while that of 6:2 Cl-PFAES in CMS-S-09 and CMS-S-10 is 55%~87%.

For the CMS-S-11 and CMS-S-12, the purities are much lower, with the range of 12%~13%. Such result suggests that the vendor has made the formulation with the PFOS purchased from original producers.

#### PFCs in liquid samples of CMS product

The detected concentrations of PFCs in liquid CMS product samples are shown in Table 2.

As shown in Table 2, the detected PFCs in liquid CMS product samples are mainly PFOS, 6:2 FTS, 6:2 Cl-PFAES (i.e. F-53B) and PFBS. Normally only one of the above three PFCs can be detected as the predominant component, however in CMS-L-07 all three have been detected. The vendor of this product is a local company, which seems to have adopted a complicated formulation.

The trade name of both CMS-L-02 and CMS-L-03 is “Fumetrol 21” produced by ATOTECH, which is claimed as “the first released low foaming, non-PFOS mist suppressant for the chrome plating market”.<sup>4</sup> According to its MSDS, the key ingredient is 1-2.5% of 6:2 FTS acid (CAS No.: 27619-97-2). According to the evaluation report from Danish Ministry of Environment, the effectiveness, the durability, and the price level of Fumetrol 21 were similar to that of PFOS. This non-PFOS alternative is an environmental improvement as it is less persistent, less bioaccumulative, and less toxic than PFOS. <sup>5</sup>

#### CMS products without detected PFCs

As shown in Table 2, no significant PFCs have been detected in two samples of CMS products, i.e. CMS-L-10 and CMS-L-13. Actually the trade name of CMS-L-10 is “MISTSHUT UP” produced by JCU Corporation, which is claimed as a “mist suppressor complying with the PFOS restrictions” to replace its old product “MISTSHUT CRL”.<sup>6</sup> Such statement can be supported by the determination results in this study. The trade name of CMS-L-13 is “WK-301” produced by Shenzhen Huakai Surface Finishing Technology Corporation. However, no detailed information about its key ingredient can be obtained from the producer.

#### Conclusion

A preliminary survey on the contents of PFCs in main chrome mist suppressants (CMS) products in Chinese market was conducted. The results clearly show that: (1) PFOS is still widely adopted in CMS products; (2) Besides PFOS, other PFCs have also been used currently, including 6:2 FTS, 6:2 Cl-PFAES (i.e. F-53B) and PFBS; (3) Imported products are mainly based on 6:2 FTS or other PFCs-free chemicals. The diversity in key ingredients highlights the necessity to improve the chemical transparency. For example, the information of key ingredient should be clearly indicated in the label or specification sheet of the CMS product.

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Table 1 Detected PFCs in solid CMS product samples (unit: mg/g)

Sample	PFBS	PFHxS	PFHpS	PFOS	6:2FTS	6:2 Cl-PFAES
CMS-S-01	ND	22.7	55.5	989	ND	ND
CMS-S-02	ND	17.3	32.7	737	ND	ND
CMS-S-03	ND	27.7	3.46	704	ND	ND
CMS-S-04	ND	ND	ND	905	ND	ND
CMS-S-05	ND	ND	ND	846	ND	ND
CMS-S-06	ND	ND	19	866	38.4	ND
CMS-S-07	ND	ND	4.53	872	41.9	ND
CMS-S-08	ND	ND	10.2	863	ND	ND
CMS-S-09	ND	ND	ND	ND	ND	545
CMS-S-10	ND	ND	6.74	ND	ND	874
CMS-S-11	ND	22.5	12.2	122	ND	ND
CMS-S-12	ND	47.5	14.4	132	ND	ND

ND = not detected

Table 2 Detected PFCs in liquid CMS product samples (unit: mg/L)

Sample	PFBS	PFHxS	PFHpS	PFOS	6:2FTS	6:2 Cl-PFAES
CMS-L-01	ND	ND	39.4	30000	ND	ND
CMS-L-02	ND	ND	ND	ND	16580	ND
CMS-L-03	ND	ND	ND	ND	17260	ND
CMS-L-04	2.85	ND	1.2	74.6	3.07	ND
CMS-L-05	ND	0.0456	ND	0.233	1.57	0.0842
CMS-L-06	ND	0.00546	0.0292	0.742	0.165	0.238
CMS-L-07	ND	ND	284	13520	3440	21400
CMS-L-08	ND	ND	609	45325	ND	ND
CMS-L-09	ND	ND	ND	11500	ND	ND
CMS-L-10	ND	ND	ND	ND	0.0097	ND
CMS-L-11	ND	ND	4.37	389	ND	ND
CMS-L-12	ND	ND	ND	11.4	ND	ND
CMS-L-13	ND	0.000459	0.000233	0.00404	0.0000423	0.0000733
CMS-L-14	54	ND	ND	ND	ND	ND
CMS-L-15	ND	0.374	0.211	2.08	ND	ND
CMS-L-16	ND	ND	ND	748	ND	ND

ND = not detected