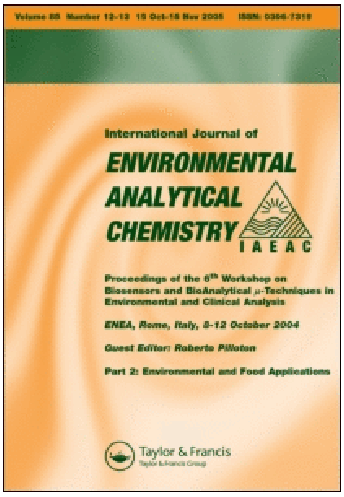

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Sample Composition Changes in Sampling and Analysis of Organic Compounds in Aerosols

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Effects of transportation and storage of air particulate filters on sample composition were investigated by GC and GC/MS analysis of 42-Hi-Vol filter samples taken in a large metropolitan city. One-half of the filters were transported and stored using paper envelopes while the others were individually wrapped in aluminum foil before transportation. One half of each filter received was extracted and analyzed immediately while the other half was stored in a refrigerator for later analysis. Significant losses of organic material from stored filters was observed for filters stored in paper envelopes and filters sealed in aluminum foil, although losses were less for filters wrapped in metal foil. There is some indication that metal foil may protect filters from external contamination after sampling.

KEY WORDS: Air particulates, sample storage, trace organics.

INTRODUCTION

Although the technique of sampling airborne particulate matter (aerosols) on a glass fiber filter paper using a Hi-Vol apparatus has been an established method for more than a decade, some of the analytical aspects of this technique have yet to be studied.[1] One important question concerns changes in sample composition of both inorganic and organic compounds with time as filtered particulate matter is allowed to remain on the filter paper prior to analysis. This is particularly important for analysis of organic compounds adsorbed onto the particulate matter, since many of these compounds are reactive and have appreciable vapour pressures at ambient temperature.

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This study involves 42 Hi-Vol filter samples taken in a large metropolitan city area on a 24 hour regular sampling period with a standard Hi-Vol apparatus. It was undertaken to examine the effects of transporting and storage of airborne particulate filter samples on the organic material originally present. The effects of storing unextracted filters under refrigeration for various time-periods were examined, in addition to effects of transporting and storing filters in foil-wrapped packets versus ordinary paper envelopes. The analytical data was obtained using a rapid method previously described for the extraction, concentration and analysis by gas chromatography and gas chromatography/mass spectrometry of such samples.[2]

EXPERIMENTAL

A. Sample collection, shipment and storage

Side-by-side Hi-Vol samplers were located on the roof of a building in a large downtown metropolitan area. Particulate matter was collected during 24 hour periods on 8 × 10 inch glass-fiber filters. Typical sample volumes ranged from 2000 to 3000 m^3 air per 24 hour period. No weekend samples were collected.

On each sampling day, two simultaneous samples were taken. Both filters were folded, particulate side facing inwards, and divided into halves.. Care was taken to handle filters only on the edges. The two halves of one filter were wrapped in aluminum metal foil and placed in a paper envelope for shipping while the halves from the other filter were separated by a piece of paper and placed in a second envelope for shipping with no additional protection. Both envelopes were received at the University of Waterloo within 1–3 days of sampling. Sampling and shipment of filters was performed by Ontario Ministry of the Environment personnel under the direction of Dr. A. Foldes.

Upon receipt of samples, one foil-wrapped filter-half (designated F1) and non-foil-wrapped filter-half (designated R1) were extracted immediately. The other halves of the foil-wrapped samples (designated F2) and non-foil-wrapped (designated R2) were stored in a refrigerator at 0 to 5°C for later extraction. A schematic diagram of the analysis scheme is given in Figure 1.

B. Extraction of air particulate samples

Air particulate filters were cut into approximately 1 cm^2 pieces, placed into a glass fritted extraction thimble, and extracted overnight (*ca* 16 hours) with 200 ml methanol by soxhlet extraction apparatus. All glassware was cleaned prior to use by 2% aqueous solution of Alcanox detergent in an ultrasonic bath, rinsed with water, deionized water, methanol, and dried in an oven at 120°C for one hour. Methanol used for extraction and cleaning was Distilled on Glass grade (Burdick and Jackson, Inc., Muskegon, MI.). Extracted samples were reduced to one milliliter final volume in a volumetric flask with a rotary evaporation apparatus under aspirator vacuum. All samples were centrifuged for five minutes at 3000 rpm to remove an inorganic precipitate which formed during the condensation stage. A detailed description of the extraction procedures has been given by Karasek.[1]

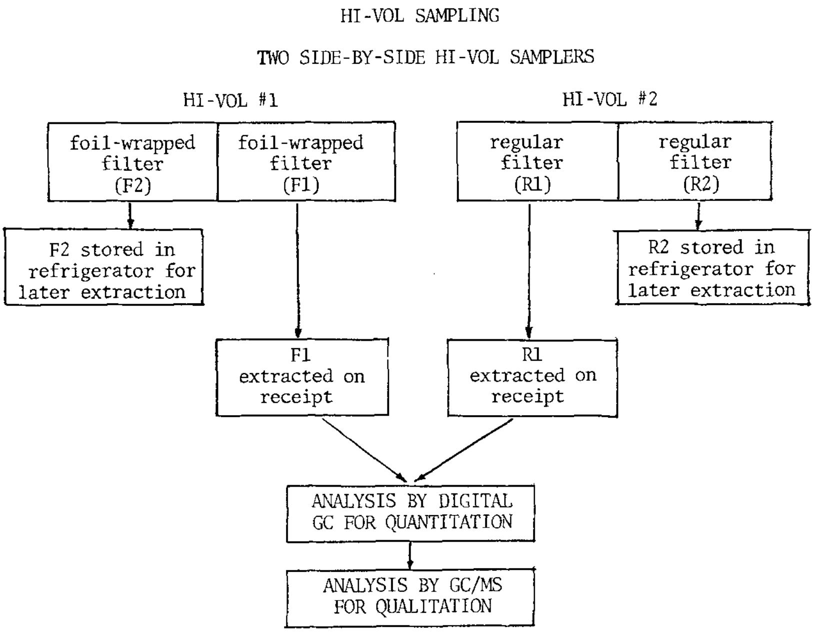

FIGURE 1 Schematic of Hi-Vol filters analysis procedure.

C. Analysis of samples by GC, GC/MS

Concentrated extracts were analyzed by gas chromatography (GC) using a Hewlett-Packard 5830A GC equipped with flame ionization detectors and a 6′ or 10′ × 2 mm id. glass column packed with Aue Packing.[3] Chromatographic conditions were; initial temperature, 80°C;

program rate, 4°/min; final temperature, 250° held for 20 minutes; injector, 250°; flame ionization detectors, 300°C; chart speed, 0.5 cm/min; slope sensitivity, 0.1 mv/min; attenuation, 32 or 64; He carrier flow rate, 30 to 32 ml/min; area reject, 1000. All injections were made using Hamilton 701N (10 μl) syringes. Injection volumes were measured by drawing the entire sample into the syringe barrel, measuring the volume, injecting, then measuring the volume of sample left in the syringe. A hydrocarbon standard was run each day for calculation of Kovats retention indices.

Identifications of compounds were made using a Hewlett-Packard 5992 GC/MS/Calculator system equipped with X–Y plotter and floppy disk. Chromatographic conditions described earlier were employed, with the exception that an initial temperature of 90°C was used. Mass spectra were scanned continuously from 500 to 40 amu at a rate of 330 amu per second. Mass scans taken at the top of eluting GC peaks were stored on the disk memory along with a scan taken at the lowest valley between each peak for use in a later background subtraction step to provide corrected mass spectra. The mass spectrometer was tuned each day using the manufacturer-supplied program AUTOTUNE.

D. Computer analysis of data

Computer-generated plots were obtained by calcomp plotter using computer programs previously described.[4] All programs were written in the FORTRAN IV language to run on the University of Waterloo IBM 360/75 computer with the WATFIV compiler.

E. Reproducibility of data

As a check on reproducibility of total peak areas, replicate GC injections were made for 23 of the concentrated extracts. Variation in total peak areas between replicate samples ranged between 0.2% to 31%, and averaged less than 12%. Nine of the replicates were within 5%. No bias favouring regular or foil-protected samples was detected as observed variations appeared to be random. Data are comparable to those of a previous study in which areas of a hydrocarbon standard for replicate runs made over a period of several months were within 10%.[4]

RESULTS AND DISCUSSION

Results of the chromatographic analyses show that losses of organic material from glass fiber filters stored at reduced temperatures occurs for both foil-protected filters and filters stored in paper envelopes. However, losses were greater for filters not protected by foil. There is also some indication that foil pouches may better protect filter samples from external contamination during transportation after sampling.

Table I is a list of the samples received, giving for the stored filter-halves the length of time from sampling to extraction. The first halves of the filters were extracted within four days of sampling for most of the filters. Storage times for the second halves of the filters ranged from two weeks to a year. A total of 82 filter-halves were received for analysis, of which 42 were shipped in foil pouches. Comparisons between samples were made on the basis of total chromatographic areas.

Figure 2 illustrates the type of data generated. It is a comparison of four chromatograms produced by the program GCPLOT. All four samples are extractions of filter-halves from two glass-fiber filters which were sampled on the same day using two side-by-side Hi-Vol samplers. Filters 11R1 and 11F1 were extracted immediately upon receipt of the samples while 11R2 and 11F2 were extracted after storage for 45 days (see Table II) in a refrigerator. The foil-protected sample 11F1 contains fewer peaks and at lower concentrations than the corresponding non-protected sample 11R1, although the pattern and relative concentrations of components are similar. All samples in Figure 2 were normalized to area counts per cubic meter of air sampled before plotting.

Figure 3 is a plot of log total area counts from GC-FID versus sample number which shows that the foil-protected filters (F1) generally were found to contain lesser total amounts of detected organics than their corresponding non-protected (R1) filters, although this observation did not hold for all samples.

Figure 2 also shows that losses during storage occurred for both the regular and foil-protected filters. In particular, many of the early-eluting components are absent or at greatly reduced concentrations. Some components were detected at significantly higher levels in the stored filters than in the early-extracted filter-halves. It is not known whether this phenomenon can be attributed to external contamination or internal sample changes. However, this does serve to emphasize the complexity of changes which may occur in stored samples. Many of the stored samples exhibited a loss in total organics extracted as compared to the corresponding filter-half which was extracted immediately. This is shown by Figures 4 and 5 which are log area count versus sample number plots of the first (early) versus second (later) extractions of the regular (Figure 4) and foil-protected (Figure 5) filters. Percent losses based on areas are listed for each sample in Table I. There seems to be no correlation between amount of loss and storage time.

Table II summarizes the data presented in Figures 3–5 by comparing

TABLE I

Storage times and percent losses of organic compounds for aerosol samples

Sample Number	Sampling Date (YY/MM/DD)	Sampling Volume (M^3)		Storage Time days	% Loss after Storage	
		Regular	Foil		Regular	Foil
01	780614	2348	2448	379	35	0
02	780615	2375	2626	378	19	7
03	780616	2318	2388	378	—	91
04	780620	1929	2373	374	51	88
05	780626	2360	2508	57	42	0
06	780627	2358	2411	63	42	70
07	780628	2345	2426	63	38	21
08	780629	2406	2457	190	0	0
09	780705	2163	2451	184	18	16
10	780706	—	2496	183	—	16
11	780707	2739	2435	45	56	37
12	780711	2658	2524	42	19	0
13	780712	2745	2560	42	0	—
14	780713	2517	2240	154	27	54
15	780714	792	709	31	65	71
16	780718	2595	2503	29	68	15
17	780719	2549	2467	27	50	48
18	780720	2569	2472	23	0	—
19	780721	2562	2457	23	14	24
20	780725	2793	2308	142	62	48
21	780726	2737	2263	16	—	4

†Loss in terms of percent of total chromatographic area.

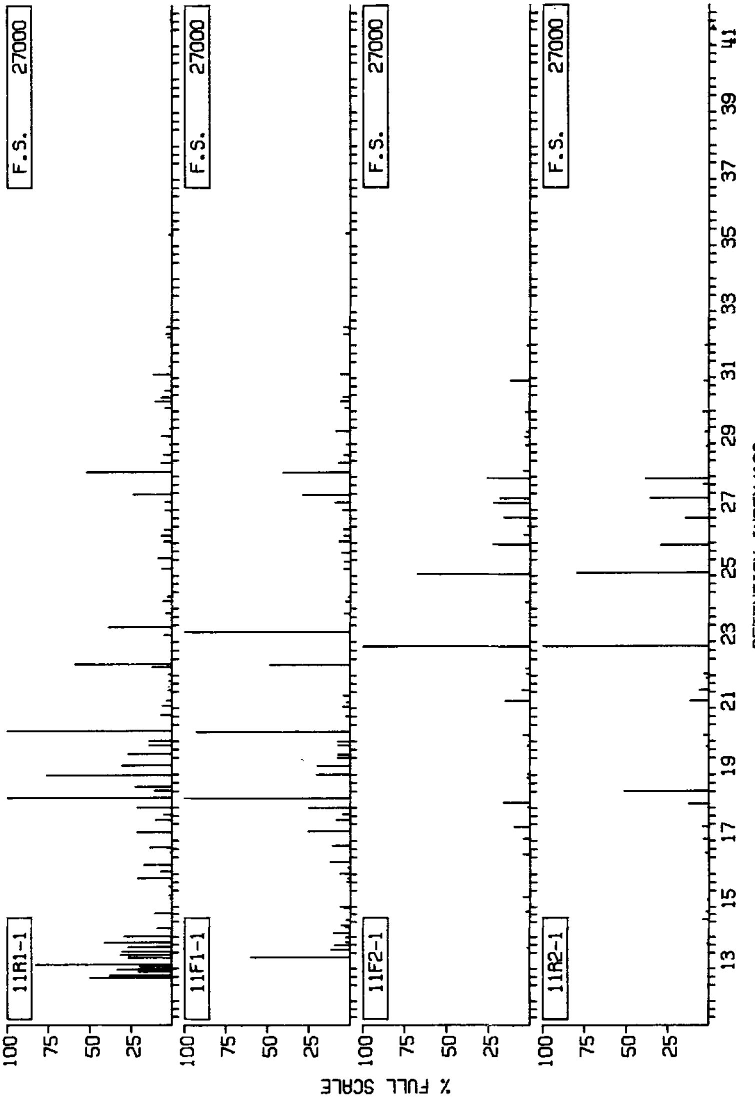

FIGURE 2 GCPLOT comparison of four chromatograms.

average total chromatographic areas per cubic meter of air sampled for regular and foil-protected filters. Filters stored in paper envelopes lost an average of 40 percent of chromatographic area compared to corresponding filter-halves extracted upon receipt of the samples, while filters shipped and stored in foil pouches lost an average of 22 percent. Comparison between regular and foil-protected filters sampled on the same day shows that although the regular filters have an average of 18 percent greater GC peak area before storage, the foil-protected filters have 6% greater average area after storage. Therefore, while significant losses still occur from filters stored in foil pouches, these results suggest that losses occur at a slower rate than for filters stored in paper envelopes.

TABLE II

Average total areas for regular and foil samples

	Extracted early	Extracted after storage
Shipped in paper envelopes	167118	100504
Shipped in foil pouches	136937	106440

Results of GC/MS analysis on several of the samples showed the major components to be methyl esters, phthalates and various saturated and unsaturated hydrocarbons. No polynuclear aromatic hydrocarbons were detected, with the exception of fluoranthene at very low levels. The composition of all samples analyzed was similar. Detailed comparison of components is difficult to perform due to complexity of the samples. Results of GC/MS work are presently under study to determine in detail whether major losses are specific to particular compounds or compound classes, and will be presented at a later date. Preliminary results, however, do not suggest that particular compound classes are lost at significantly greater rates than others during storage while unextracted on the filter paper.

For several of the samples, one major peak was observed in the regular but not foil-protected filters. Figure 6 shows the GCPLOT comparison of 08R1, 08R2, 08F1 and 08F2. The changes in retention indices observable between the 8R1, 8F1 and 8R2, 8F2 GC runs corresponds to a GC column change between these sets of analyses. The major peak near the retention index value 1900 was identified by GC/MS as a diethyl phthalate. Since this peak was observed in several regular but not corresponding foil-protected filters, it appears to be a contaminant introduced after sampling

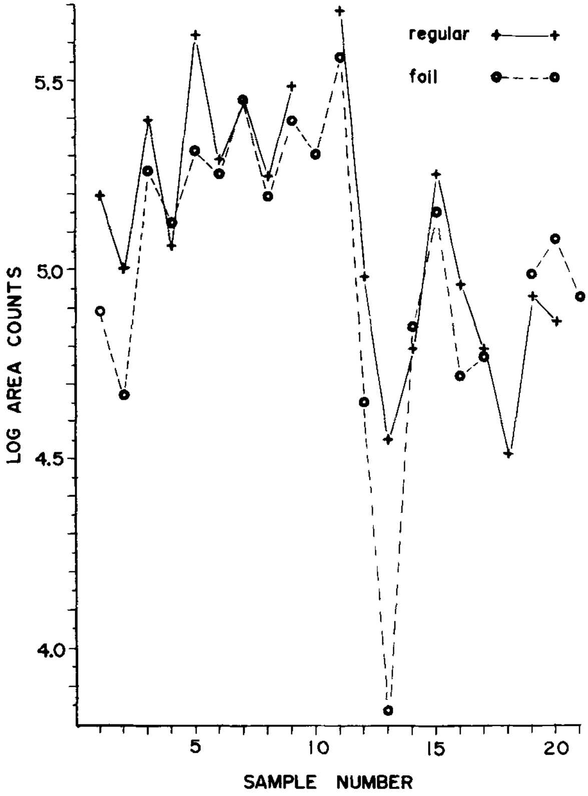

FIGURE 3 GC-FID Total response comparison between regular and foil filters extracted immediately.

and after the protective pouch had been placed around the protected filters. Therefore, some evidence exists that foil pouches may serve to better protect filters from external contamination.

Although significant losses and composition changes were observed throughout this study, no consistent pattern of sample loss or storage effects was established. Necessary assumptions were that side-by-side Hi-Vol samplers operating simultaneously gave samples of similar composition and that separate halves of the same filter initially were also very similar in composition.[5] Although some variations are expected, data do not suggest the presence of a bias in favour of a particular set of filters. Therefore, results presented here suggest that preserving sample integrity during storage of Hi-Vol filter samples is difficult at best. Foil packets may serve to better maintain sample composition, but another reason for their use would seem to be protection from external contamination.

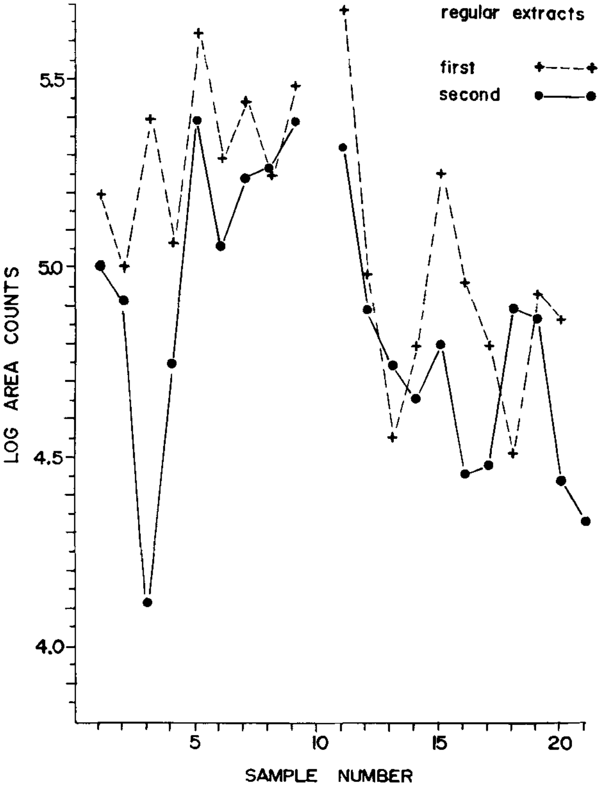

FIGURE 4 GC-FID Total response comparison of regular filters before and after storage.

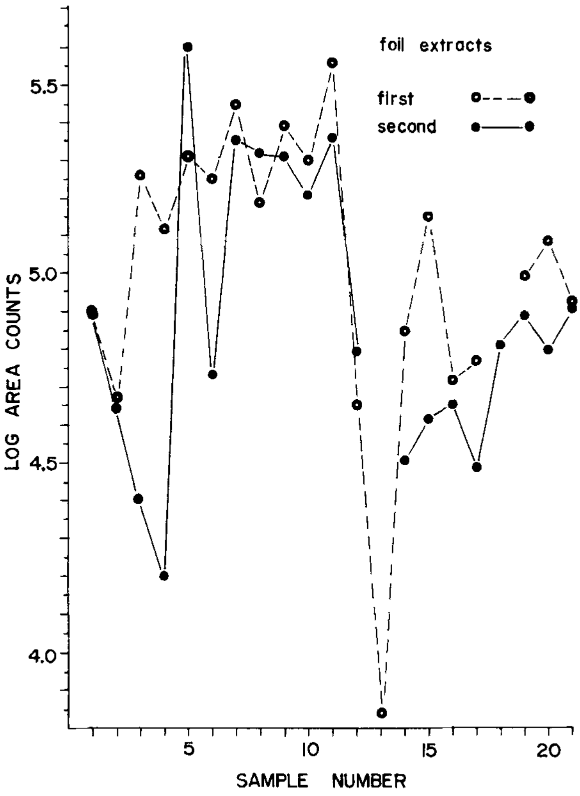

FIGURE 5 GC-FID Total response comparison of foil-protected filters before and after storage.

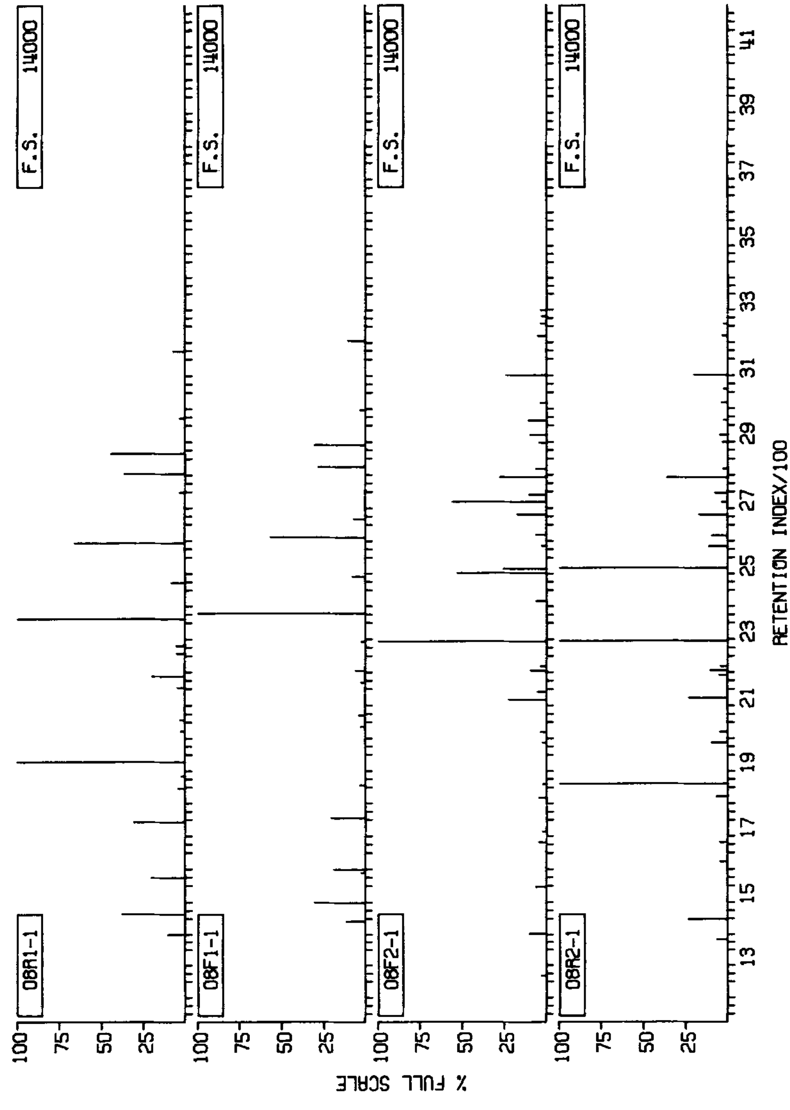

FIGURE 6 GCPLOT comparison of 08R1, 08R2, 08F1, 08F2 showing contaminent peak in regular filters.

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