Preparation of the Components of the Modified Method 5 (Method 0010) Sampling Train for Analysis by SW-846 Method 8270

Radian Corp., Research Triangle Park, NC

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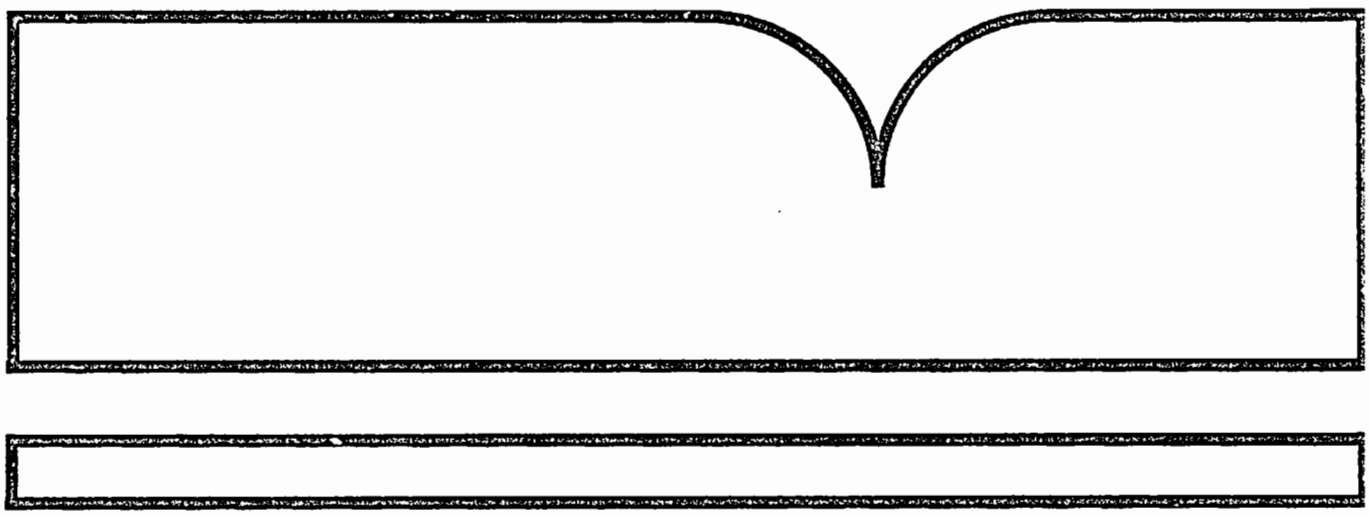

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16. ABSTRACT

To validate a source test method for EPA use, data on the method's accuracy and precision must be obtained at, at least, two different locations. While evaluating a new method for measuring source emissions of semivolatile halogenated compounds, data at one source were significantly different from previous laboratory and field measurements. Recoveries at this source, a chemical manufacturing facility with substantial moisture in the exhaust stream, were unacceptably low, ranging from 4 to 63 percent. Because these results were at variance with previous results, the sampling and analysis procedures were evaluated in detail. The quality control samples isolated the problem to the analysis procedures associated with transfer and extraction of the XAD-2 adsorbent, which was wet when it returned from the field test at this site. Sample preparation procedures had generally followed those specified by the Semi-Volatile Organic Sampling Train method (Semi-VOST; SW-846 Method 0010), but additional procedures, not specifically prohibited by the standard method, were utilized to extract the wet XAD-2 from the sample train before extraction and analysis. These techniques changed the nature of the resulting extract and suppressed recovery of the target compounds. A new protocol has been developed to address sample handling for XAD-2 under such conditions.

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PREPARATION OF THE COMPONENTS OF THE MODIFIED METHOD 5 (METHOD 0010) SAMPLING TRAIN FOR ANALYSIS BY SW-846 METHOD 8270

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ABSTRACT

In a field evaluation study for semivolatile halogenated organic compounds listed in Title III of the Clean Air Act Amendments of 1990, dynamic spiking experiments using a liquid solution were performed in the field. Two of four quadruple sampling trains were spiked for eight sampling runs. Method 0010 train components were prepared and analyzed in three parts: filter/front half rinse, XAD-2® resin, and condensate/condensate rinse. In sixteen spiked trains, spiked analytes were detected with reasonable recoveries (>50%) in only four runs. In general, surrogate compounds spiked during preparation of the samples showed low recoveries from XAD-2®, and recoveries of spiked analytes which were observed ranged from 4 to 63 percent. Because these results were at variance with results obtained for analytes spiked in laboratory studies and a previous field study, the sample preparation process was investigated in detail. Sample preparation procedures had followed Method 0010, but use of some procedures which were not specifically prohibited by Method 0010 had depressed compound recoveries. Laboratory studies were performed to evaluate the effects of various sample preparation parameters on compound recoveries. To ensure that the sample preparation procedures for Method 0010 train components were clear and unambiguous, a new protocol to address preparation of Method 0010 train components for Method 8270 analysis was written. The new protocol has been used in a subsequent field study with excellent results.

INTRODUCTION

In order to evaluate the performance of SW-846 Method 0010 for sampling and Method 8270 for the analysis of semivolatile halogenated organic compounds listed in Title III of the Clean Air Act Amendments of 1990, a field study was performed using dynamic spiking techniques to establish the precision and bias of the overall methodology. Using the guidelines of EPA Method 301 (Protocol for the Field Validation of Emission Concentrations from Stationary Sources) for statistical design of the field testing experiments, quadruple Method 0010 sampling trains with four collocated probes were used. Dynamic spiking equipment and procedures had been developed and evaluated to allow dynamic spiking of a methylene chloride solution of the compounds of interest for the duration of each Method 0010 sampling run.

According to the guidelines of Method 301, two trains were spiked and two trains were unspiked.

EXPERIMENTAL

The field evaluation study was conducted at a chemical manufacturing facility where waste chemicals were incinerated in a coal-fired boiler. A "biosludge" consisting of 10 percent organic matter and 90 percent water was fed continually to the incinerator. A site presurvey, when preliminary samples were taken, showed that none of the proposed analytes was present in the background emissions from the boiler, and that the emissions were wet (approximately 10 percent moisture). Method 0010 sampling trains were recovered in the field, and components were shipped to the laboratory for preparation and analysis. Extracts (three per sampling train) were generated from methylene chloride extractions of the following train components:

- Filter/front half rinse;
- XAD-2® sampling module; and
- Condensate/condensate rinse.

The final extract volume for these sampling train components was 5 mL, rather than the 1 mL final volume specified by Method 8270.

Results for the GC/MS analysis are summarized in Table I. To perform a thorough statistical analysis according to Method 301 procedures, results from six paired spiked runs are required. Eight sampling runs using quadruple trains had been performed in the field; acceptable results were obtained for only four runs (1,2,3,6). For those four runs, most compounds results appear generally comparable to laboratory and field results obtained previously (Table II). However, results from other sampling runs showed very low recoveries for the surrogate compounds and many of the spiked compounds were not detected.

PLACE TABLE I HERE

PLACE TABLE II HERE

RESULTS AND DISCUSSION

Careful examination of the data for all of the sampling runs showed that, in general:

Table I

Summary of Results for All Eight Runs and All Sampling Trains, Using Surrogate-Corrected Data

	Train A Spiked			Train B Spiked			Train C Unspiked			Train D Unspiked		
Run	X	C	F	X	C	F	X	C	F	X	C	F
1	y	y	y	y	y	y	y	y	y	y	y	y
2	y	y	y	y	y	y	y	y	y	n	y	y
3	y	y	y	y	y	y	y	y	y	y	y	y
4	n	y	n	n	y	n	y	y	n	y	y	y
5	Z	y	y	Z	y	n	y	y	y	y	y	y
6	y	y	n	y	n	n	Z	y	y	Z	y	y
7	n	n	n	y	y	y	Z	y	Z	y	y	Z
8	n	y	Z	y	y	y	Z	y	y	y	y	Z

Note: Recoveries for C and D Trains refer to recoveries of surrogate compounds and isotopically-labeled analogs.

X = XAD-2® module.
C = Condensate fraction.
F = Filter fraction.
Z = Partial success; some but not all analytes detected.
y = All analytes detected.
n = No analytes detected.

Table II

Comparison of Percent Recoveries of Semivolatile Halogenated Organic Target Compounds in Laboratory and Field Studies (Uncorrected for Surrogate Recoveries)

Compound	Mean Results		
	Laboratory[1]	Field 1[2]	Field 2[3]
Bis(chloromethyl)ether	18.3	0.0	0.0
Epichlorohydrin	75.2	6.0	13.4
cis-1,3-Dichloropropene	21.9	49.1	50.3
trans-1,3-Dichloropropene	20.4	52.0	79.8
1,1,2-Trichloroethane	53.1	56.4	60.3
1,2-Dibromoethane	66.3	58.9	62.5
Tetrachloroethene	49.7	53.2	49.4
Chlorobenzene	76.0	62.3	65.1
Bromoform	99.3	59.8	69.3
1,1,2,2-Tetrachloroethane	81.1	64.0	73.9
Dichloroethyl ether	75.8	60.9	77.0
1,4-Dichlorobenzene	68.2	56.2	73.5
Benzyl chloride	78.7	67.4	73.9
Hexachloroethane	85.4	74.0	70.9
1,2-Dibromo-3-chloropropane	66.2	44.8	73.8
1,2,4-Trichlorobenzene	58.2	59.5	76.1
Hexachlorobutadiene	58.3	65.4	77.1
Benzotrichloride	67.0	60.1	72.4
2-Chloroacetophenone	79.7	56.0	79.5
Hexachlorocyclopentadiene	513.0	42.3	59.6
2,4,6-Trichlorophenol	45.6	49.8	75.4
2,4,5-Trichlorophenol	52.7	62.7	76.6
Hexachlorobenzene	32.9	44.6	56.5
Pentachlorophenol	8.9	42.4	60.3
Pentachloronitrobenzene	38.2	43.4	58.5
Chlorobenzilate	43.6	40.7	61.8
3,3'-Dichlorobenzidine	86.4	4.4	0.6

[1]Mean of 16 replicates.
[2]Mean of 12 replicates.
[3]Mean of 4 replicates.

- Recoveries of the surrogate compounds spiked in the laboratory were low for the XAD-2®, where most of the organic compounds were expected to be retained;

- Isotopically-labeled compounds spiked in the laboratory to track recovery were frequently not observed at all; and

- The majority of the analytes spiked in the field were not observed. Recoveries for field-spiked analytes that were observed ranged from 4 percent to 63 percent.

Since the surrogate compounds and isotopically-labeled compounds are spiked in the laboratory after return of the sampling train components, problems were obviously encountered in the laboratory preparation rather than in the field spiking.

The critical parameter is recovery of spiked compounds from XAD-2®. Recovery results for these field samples were sufficiently at variance with previous recovery results from a laboratory study[1] and a field study[2] that an explanation for the low recoveries was pursued. Quality Control results from Method Blanks were examined. Method Blanks consist of sampling train media (filters, water, solvents, XAD-2®) that are spiked with surrogate compounds in the laboratory, extracted, and analyzed. Recoveries from Method Blanks were acceptable to high, indicating that general laboratory sample preparation and analysis procedures were done properly.

Method Spike recovery data were also examined. Method Spikes consist of train components spiked with analytes and surrogate compounds in the laboratory. The Method Spikes are extracted and analyzed with the field samples. The results obtained for the XAD-2® Method Spikes are typical (Table III): acceptable to high recoveries indicated that surrogate and sample spiking, preparation, and analysis procedures were in control.

PLACE TABLE 3 HERE

From an examination of the Quality Control samples, we concluded that a systematic error in sample spiking, sample preparation, or analytical procedures did not appear to be the cause of the low recoveries: Method Blanks and Method Spikes were prepared and analyzed with the field samples, using the same spiking solutions and the same procedures. The original extracts, which had been archived after mass spectral analysis, were next examined visually to determine if the appearance of these extracts was qualitatively or quantitatively different from the appearance of the Quality Control samples. Several key differences were observed:

Table III

Spiked Compounds and Surrogates Recovered from Dry Method 0010 XAD-2® Traps

Compound	Theoretical Amount	% Recovery			
Surrogate	(μg)	MS-A	MS-B	MS-C	MS-D
2-Fluorophenol	991	107	99	108	102
Phenol-d_5	1010	112	106	113	108
Nitrobenzene-d_5	509	112	95	104	98
2-Fluorobiphenyl	490	119	115	122	111
2,4,6-Tribromophenol	997	67	74	73	66
Terphenyl-d_{14}	501	135	112	115	108
Epichlorohydrin-d_5	250	99	68	76	71
Chlorobenzene-d_5	350	94	91	106	93
1,1,2,2-Tetrachlorotthane-d_2	254	114	93	99	91
Bis(chloroethyl)ether-d_8	333	104	91	95	87
Benzyl chloride-d_7	244	103	122	130	117
2,4,5-Trichlorophenol-d_2	129	ND	ND	106	ND
Targets	(μg)	% Recovery			
Epichlorohydrin	199	991	68	72	74
cis-1,3-Dichloropropene	159	87	67	71	76
trans-1,3-Dichloropropene	34	365	77	80	86
1,1,2-Trichloroethane	195	98	77	84	86
1,2-Dibromoethane	196	95	84	94	95
Tetrachloroethene	195	86	82	92	92
Chlorobenzene	200	99	92	96	100
Bromoform	202	101	104	120	127
1,1,2,2-Tetrachloroethane	200	101	84	91	92
Bis(chloromethyl)ether	252	80	70	72	74
1,4-Dichlorobenzene	226	96	119	125	131
Benzyl chloride	202	102	95	105	104
Hexachloroethane	185	107	103	112	114
1,2-Dibromo-3-chloropropane	272	103	109	118	121
1,2,4-Trichlorobenzene	198	104	120	132	135
Hexachlorobutadiene	200	107	126	139	148
Benzotrichloride	199	106	126	141	142
2-Chloroacetophenone	229	112	108	116	120
Hexachlorocyclopentadiene	204	135	133	133	133
2,4,6-Trichlorophenol	237	109	121	129	129
2,4,5-Trichlorophenol	194	101	127	130	139
Hexachlorobenzene	222	102	110	124	121
Pentachlorophenol	202	83	100	87	54
Pentachloronitrobenzene	216	101	106	113	114
Chlorobenzilate	200	116	110	123	130
3,3'-Dichlorobenzidine	190	142	140	171	158

- Method Blanks and Method Spikes were light yellow in color and had the appearance of several mL of clear organic solvent. The color of field sample extracts ranged from clear to nearly brown.

- Some of the field extracts were clearly completely aqueous, with only small pools of organic liquid floating on top;

- Two phases were clearly visible in some of the field extracts; and

- Many of the field samples were not methylene chloride extracts, since only a slight odor of methylene chloride was detected when vials were opened.

Laboratory sample preparation procedures and observations were carefully reviewed with laboratory staff. The observation was reported that many of the field samples required far longer (3-4 hours) than the usual amount of time (20-30 minutes) to achieve concentration to 5 mL using Kuderna-Danish concentration procedures.

The obvious difference between the Quality Control samples and the field samples was that the laboratory-generated sampling train media were dry, while the field XAD-2® samples were wet because of the moisture content of the source. Dry XAD-2® can simply be poured from the sampling module to the Soxhlet extraction apparatus. Wet XAD-2® does not pour: the wet resin sticks to the glass walls of the sampling module and is not readily moved from the sampling module with methylene chloride rinses. Typical procedures used for the removal of wet XAD-2® from the sampling module include repeated rinses with methylene chloride, which frequently leaves significant amounts of the wet XAD-2® in the sampling module, or tapping the sampling module against the laboratory bench top, which often results in breakage of the sampling module. Laboratory staff had tapped the XAD-2® from the modules to remove as much as possible, rinsed the walls of the module with methylene chloride to remove as much of the remaining wet XAD-2® as possible, and performed a final rinse of the sampling module with methanol to remove all of the remaining XAD-2®. If a sufficiently large amount of methanol is present when sample concentration is performed, methylene chloride will be driven off rather than methanol, and the final extract will consist of a methanol solution with significant losses of surrogate compounds and analytes.

The rinses used in the field recovery of Method 0010 train components consist of 50:50 methylene chloride: methanol, which form a homogeneous solution. The methanol can be separated from the methylene chloride only if sufficient water is added to create two distinct phases. However, 100 mL of methylene chloride can hold up to 15 mL of water without separating into two distinct phases. According to the method, sample extracts are dried by filtering through a bed of dry sodium sulfate. If sufficient water is present, the sodium sulfate will cake and will not dry the extract efficiently. Thus, after drying, if the sodium sulfate cakes, an extract may consist of methylene chloride, water, and methanol, all in one phase. If a solution of this composition is concentrated, methylene chloride will be lost before the water and methanol are lost, resulting not only in a

water/methanol solution if sufficient quantities of water and methanol are present in the original extract but also in lost of target compounds due to higher concentration temperatures. However, if sufficient water (50-100 mL) to effect separation of phases is added prior to extraction, the methanol will be driven into the aqueous phase and excellent recoveries of spiked surrogate compounds and analytes can be obtained.

Laboratory experiments were conducted to reproduce the conditions under which the field samples had been extracted. Replicate samples of dry XAD-2® were spiked with surrogate compounds and analytes to provide a baseline for recovery. Excellent recoveries and good reproducibility were obtained. Next, wet XAD-2® was prepared and spiked with surrogate compounds and analytes. The 40 g quantity of XAD-2® which is contained in the sampling module of the Method 0010 train retains approximately 50 mL of water when water is poured through the resin bed. This 50 mL of retained water does not produce a distinct water layer when the spiked wet XAD-2® is extracted and analyzed. When the extracts from the wet XAD-2® were concentrated and analyzed, recoveries were slightly lower than the recoveries obtained with dry XAD-2® and reproducibility was slightly poorer, but both recovery and reproducibility were acceptable. The wet XAD-2® was prepared and spiked in the Soxhlet extractor, so no transfer of wet XAD-2® was required. Wet XAD-2® alone does not depress recoveries significantly.

The major problem appeared to occur in the transfer of the wet XAD-2®. A procedure was therefore developed to transfer the wet XAD-2® without the use of methanol. The apparatus shown in Figure 1 is used to transfer the XAD-2® if the resin is too wet to pour. The glass wool is removed from the end of the sampling module and placed in the Soxhlet extractor to ensure extraction. A small piece of pre-cleaned glass wool is placed in the arm of the Soxhlet extractor to ensure that no XAD-2® enters the side-arm. The XAD-2® sampling module is inverted (glass frit up) over the Soxhlet extractor, approximately 5-10 mL of methylene chloride is added above the glass frit, and air pressure created by squeezing the rubber bulb shown in Figure 1 is used to gently but firmly push the methylene chloride through the frit, forcing the XAD-2® out of the sampling module. This process is repeated 3 to 5 times, and a Teflon® wash bottle containing methylene chloride is used to rinse the walls of the sampling module to transfer XAD-2® which adheres to the walls of the sampling module. After 3-5 methylene chloride rinses, no more than a monolayer of XAD-2® usually remains in the sampling module. This XAD-2® transfer procedure has been used successfully to transfer XAD-2® from sampling modules used in sampling a source with 55 percent moisture: excellent recoveries of both surrogate compounds and spiked analytes were obtained. In addition, this procedure is far more efficient than the procedure of tapping the resin out of the sampling module: three transfers using the rubber bulb can be performed in one or two minutes.

PLACE FIG. 1 HERE

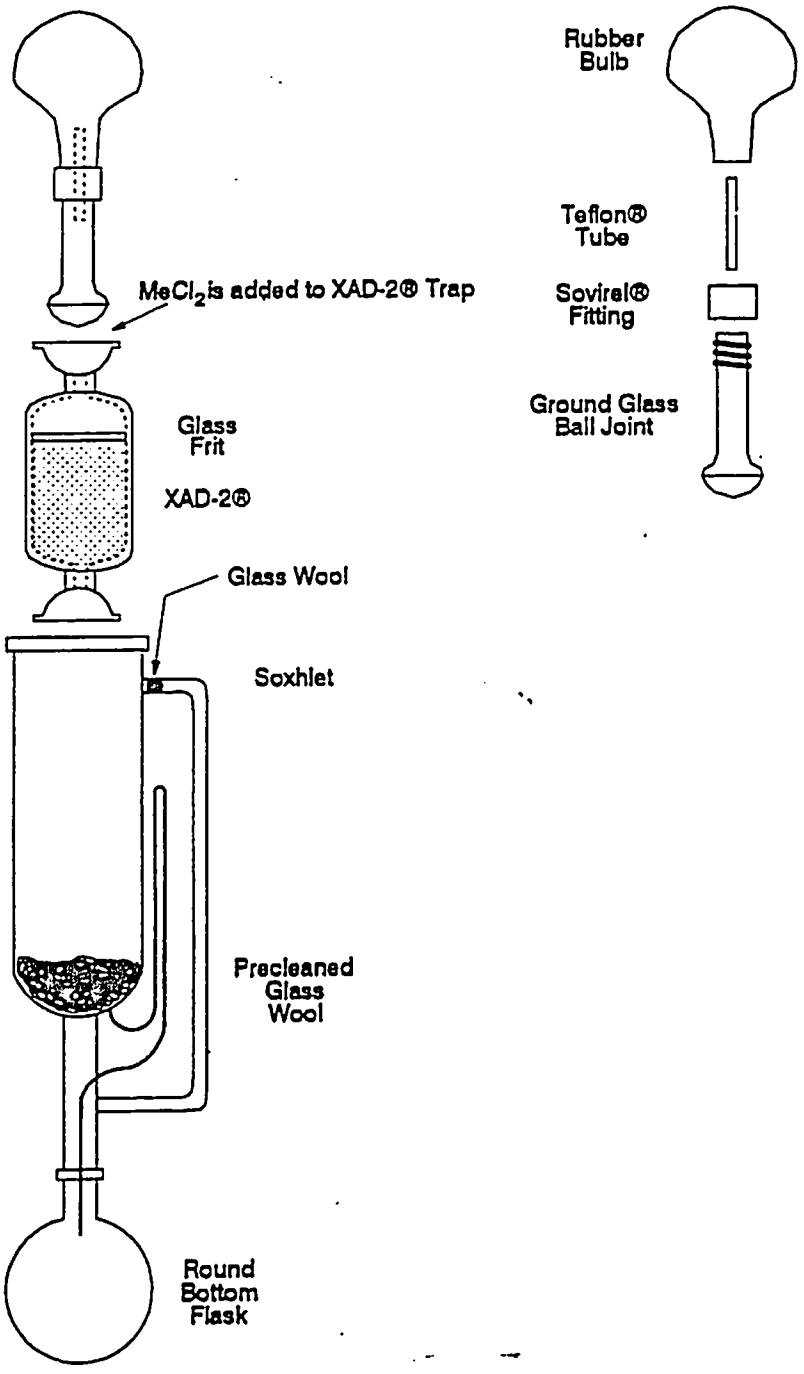

Figure 1. Transfer of Wet XAD-2®

The investigation with subsequent laboratory study illustrates the value of sufficient Quality Control data in determining the cause of a problem with data quality. A new procedure for the preparation of Method 0010 train components for analysis by SW-846 Method 8270 has been written. A flowchart for the overall method is shown in Figure 2. In this procedure, the use of methanol in the laboratory is directly and specifically prohibited to ensure that the final extracts consist of methylene chloride, not a mixture of methylene chloride and methanol. Also, addition of sufficient water to ensure that two distinct phases are produced when both water and methanol are components of the solution (for example, in the sampling train rinses of the front half and the condensate) is a required part of the procedure. This procedure is being subjected to EPA review.

PLACE FIG. 2 HERE

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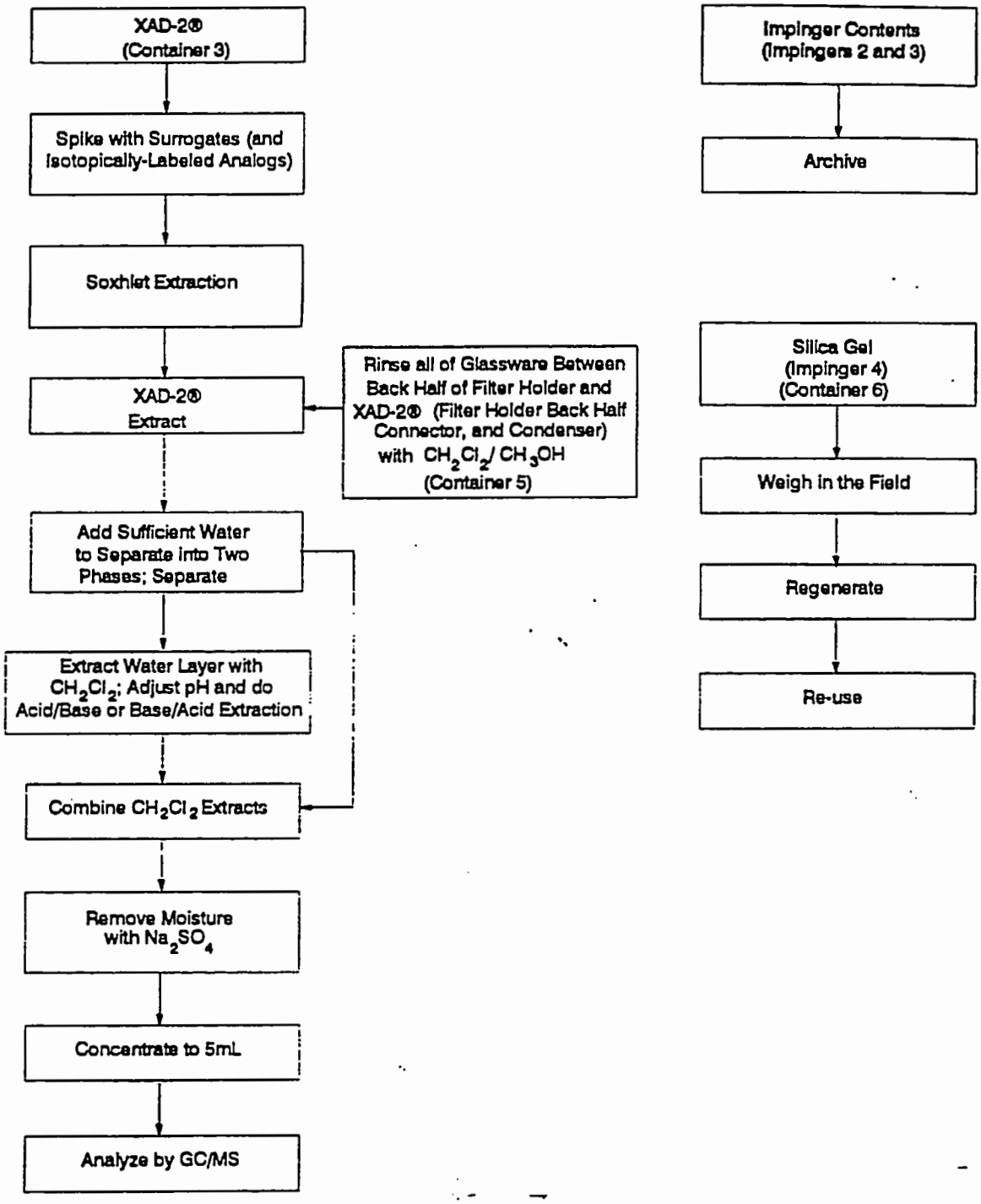

Figure 2. Sample Preparation Scheme for Method 0010 Train Components

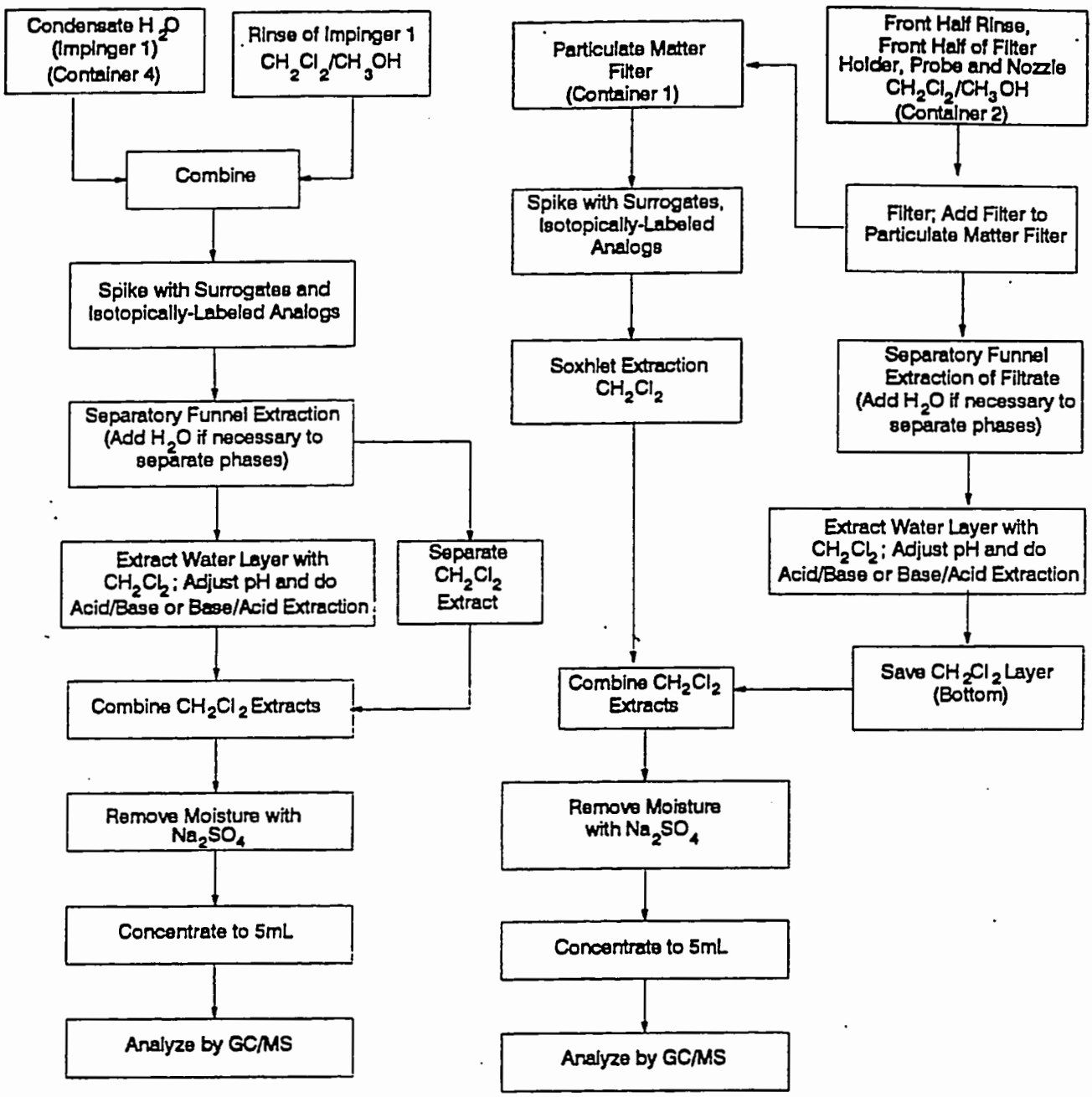

Figure 2. (Continued)

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