

Measurement of Inorganic Contaminant Extraction from Fluid Handling Components by Dynamic Extraction

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ABSTRACT

This paper addresses extraction of inorganic contamination from fluid handling components into semiconductor process chemicals. It presents a novel method, dynamic extraction, which measures the rate at which inorganic contaminants are extracted from components as a function of time. The method overcomes many of the shortcomings of conventional techniques. It allows prediction of the amount of contamination added to chemical in a process tool with time. Examples of its use to measure extraction from all-Teflon 0.05 μm microporous membrane filters in 49% HF are included. Extraction from five different types of filters was measured. Each filter was tested for two to eight weeks with multiple samples taken during the course of the extraction for metal analysis. Filters of the same type had similar extraction rates and similar contaminant "fingerprints." There were large differences between filter types. Use of an inappropriate o-ring on a filter cartridge was identified. The decrease in the rate of extraction from the filters was similar to theoretical predictions.

INTRODUCTION

The decreasing feature size and increasing complexity of semiconductor devices make them increasingly sensitive to contamination. Inorganic species including aluminum, calcium, iron and sodium can greatly reduce yield and diminish device reliability. Many cleaning steps are presently required to remove contamination during device manufacturing. The cleaning processes often employ aggressive liquid chemicals including concentrated acids, bases and oxidizers. The chemicals used in cleaning must have very low contamination levels when they contact the wafer. Therefore, they must be manufactured cleanly and kept clean until they reach the wafer surface. The cleaning equipment and chemical delivery systems that handle the chemicals contain many fluid handling components such as tanks, valves, pumps, pressure regulators, filters, filter housings, fittings, tubing and piping. All of these can potentially add contamination to the chemical and subsequently to the wafer.

Because device sensitivity is increasing with time, the purity of the cleaning chemicals must also increase with time. Table I shows FSI's projection of chemical purity requirements through the year 2000 which is based on the SIA roadmap [1]. Considerable improvements are required.

HISTORY OF INORGANIC EXTRACTABLES MEASUREMENT

Measurement of inorganic ion extraction into semiconductor process fluids from fluid handling components is not new. Numerous studies have been performed using a procedure similar to the following [2,3,4]. The first step is not always included.

- The components to be tested are rinsed in either DI water or the test chemical to remove surface contamination and contamination resulting from handling.
- The concentrations of contaminants in the test chemical are measured.
- The test components are immersed in the chemical for a given period of time.
- The components are removed from the chemical and the concentrations of the contaminants in the fluid are measured.
- The amounts of contaminants extracted from the components are determined by difference.

Several problems are associated with this approach. There is a fairly large potential for error due to handling during sample bottle preparation, sample collection and handling, and analysis. Since there is usually only one starting sample and one final sample, there is no way to distinguish between extracted contaminants and sample contamination. A second concern is that the parts are usually left stagnant in the chemical. This allows the chemical concentration near the surface of the test part to increase above the bulk contaminant concentration resulting in inhomogeneities in the solution concentration. The stagnant extraction technique may also result in decreased extraction from the component due to a decreased concentration gradient. Hence, the measured rate of extraction might be lower than that which occurs in flowing systems. In addition, this technique only allows measurement of the average rate of extraction over a fixed time period. It does not allow determination of the extraction rate changes with time.

DESCRIPTION OF DYNAMIC EXTRACTION

Measurement of component cleanliness by dynamic extraction overcomes these shortcomings. In dynamic extraction the component to be tested is placed in a clean test system and chemical is circulated through the component as it would be in a chemical handling tool such as a chemical delivery system or a wet bench. Contaminant concentrations are measured with time, thereby allowing determination of the extraction rate as a function of time.

The procedure consists of the following steps:

1. A test system is assembled using components which are thought to have no measurable contaminant extraction.
2. The cleanliness of the system is verified in the test chemical to ensure that extraction from the system does not interfere with component tests.
3. The test component is installed in the system.

4. The system is filled with high purity chemical with a retain sample taken for analysis.
5. Circulation of the chemical through the component is initiated and a sample is taken shortly after circulation is started.
6. Circulation is continued with samples taken for analysis at defined times.
7. The samples are analyzed for contaminant concentrations.
8. The mass extracted from the component as a function of time is determined by comparing the contaminant concentrations in each sample with the initial concentration.

In order to maximize the sensitivity of the test, the volume of chemical in the system is kept to a minimum. The initial chemical volume equals the system holdup volume plus enough chemical for sampling. The change in volume as samples are withdrawn is accounted for in subsequent data analysis.

This method allows determination of both surface contamination and extraction from the bulk material of the component. Surface contamination is assumed to be removed within the first few minutes of exposure to the chemical, while bulk material contamination requires months to be removed.

The metal extraction from the bulk material can be predicted from theory [5]. If it is assumed that the contaminants are evenly distributed throughout the bulk material, that the material is an infinite plane, that the main resistance to extraction is diffusion through the solid, and that extraction takes place from both sides, then the rate of extraction can be predicted using equation (1):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left[-D(2n+1)^2 \pi^2 t / 4l^2 \right] \quad (1)$$

where M_t = Cumulative mass extracted at time t

M_∞ = Total extractable mass

D = Diffusion coefficient of the contaminant in the bulk material

t = Time

l = Plane thickness

Equation (1) indicates that the fraction of the contaminant extracted from the bulk material (M_t / M_∞) is a function of the diffusion coefficient of the contaminant in the bulk material, the thickness of the material and time.

An example of the solution of equation (1) for a 0.5 cm thick plane is shown in Figure 1. Curves for several different diffusion coefficients ranging from 10^{-6} to 10^{-10} cm²/sec are shown. The curves in Figure 1 have a slope of 0.5 until most of the contaminant is extracted. A slope of 0.5 on a log-log scale as shown in Figure 1 indicates that during this time the mass extracted increases with the square root of time, as shown in equation (2):

$$M_t = k t^{0.5} \quad (2)$$

where k is a proportionality constant.

The rate at which mass is extracting at any given time (dM_t/dt) can be determined using the derivative of equation (2):

$$dM_t/dt = (k/2) t^{-0.5} \quad (3)$$

Equation (3) indicates that the rate of mass extraction decreases with $t^{-0.5}$.

Diffusion coefficients in solids are not well known and are difficult to measure. They range from $>10^{-7}$ cm²/sec for dilute concentrations of solvent in polymers to $<10^{-20}$ cm²/sec for solids in solids [6]. Hence, the curves shown in Figure 1 were prepared assuming relatively high diffusion coefficients. Actual extraction times are likely to be even longer than those shown.

The vertical lines shown in Figure 1 represent times equivalent to 2 weeks and 1 year of exposure to chemical. The percentages shown where the vertical lines intersect the extraction lines indicate the percentage of mass extracted. For example, only 12% of the contamination with a diffusion coefficient of 10^{-10} cm²/sec will be extracted after 1 year. Hence, if there is extraction from systems, it will continue for extended times.

EXPERIMENTAL

The dynamic extraction technique can be used to measure the extraction rate for many different components used in chemical handling systems. This paper describes its use for measuring extraction from filters in 49% HF. Examples of its use for measuring extraction from other components is described elsewhere [7].

A simplified schematic of the test system used to measure the rate of extraction from filters is shown in Figure 2. The major system components include a test fluid reservoir, a pump and a filter housing. All wetted parts in the system are Teflon[®] polytetrafluoroethylene (PTFE) or perfluoroalkoxy (PFA).

Prior to use, the system was cleaned by circulating 49% HF for 2 weeks. The background extraction rate from the system was then measured to ensure that there was minimal extraction from the system with no filter present. Figure 3 presents the concentrations of selected elements measured in the background test. Curves are shown for 5 individual

elements and for the total of 11 elements (aluminum, barium, calcium, chromium, copper, iron, magnesium, potassium, sodium, titanium and zinc). These 11 elements were chosen because they were either subsequently found to be extracted from test filters, commonly found in chemicals or known to cause considerable problems in semiconductor devices. The filled data points in the graph represent the contamination levels in the incoming chemical. The break in the x-axis represents a change from a linear scale to a logarithmic scale. There was no significant change in concentration during the course of the 350 hour test.

Five different types of filters were tested. All were 10" long all-Teflon cartridges with perfluoroelastomer o-rings.

The test procedure consisted of the following steps:

- The test filter was installed in the filter housing.
- The filter was wet by filling the filter housing with high purity isopropyl alcohol (IPA) using the pump.
- The IPA was allowed to remain in the housing for 5 minutes to ensure that the filter was totally wetted.
- The filter was flushed with high purity DI water at 3-5 gallons/minute for 10 minutes to remove the IPA from the system. The water was sent to drain.
- The bulk of the water was removed from the system.
- The reservoir was filled with Gigabit grade 49% HF from Ashland Chemical. This chemical contains < 1 ppb of most contaminants. Part of the chemical was retained for analysis.
- Circulation of the chemical through the test filter was initiated.
- Samples of the circulating chemical were taken for analysis. The samples were taken at intervals which were approximately evenly spaced on a logarithmic scale to maximize the accuracy of data analysis. The first sample was taken after 0.1 - 0.2 hours.
- The chemical was circulated for a minimum of two weeks, typically four to eight weeks.
- At the end of the test period, two samples were taken for analysis and the remaining chemical was removed from the system. Two samples were taken to allow duplicate analyses to be run to minimize error.
- The system was flushed with high purity DI water, drained and the test filter was removed.

Samples for chemical analyses were collected in PFA bottles which were precleaned to eliminate metallic extractables. Contaminants were measured using a combination of inductively coupled plasma-mass spectroscopy (ICP-MS) and graphite furnace atomic absorption (GFAA). Concentrations of 34 elements were determined using these methods. The detection limits of these combined techniques for the key elements are shown in Table II.

DATA ANALYSIS METHOD

An example of the data obtained from a filter with high extraction is shown in Figure 4. The data are presented in the same format as the background data. The figure indicates that there were significant increases in the concentrations of aluminum, magnesium, calcium and titanium. There was no significant increase in the concentration of copper. An example of a filter with minimal extraction is shown in Figure 5. There were no significant increases from this filter for any element.

The amount of surface and bulk extraction from a filter can be determined by assuming that the difference between the incoming concentration and the concentration after 0.1 - 0.2 hours is due to surface extraction and that subsequent concentration increases are a result of extraction from the bulk material. Note that the surface contamination determined using this assumption only includes that contamination which is soluble in chemical and not soluble in either the IPA or water used in the filter wetting steps.

The mass extracted from the filter shown in Figure 4 calculated using this assumption is shown in Figure 6. The figure includes least squares best fits for each data set. The fits have slopes ranging from 0.38 to 0.8 which are close to the slope of 0.5 predicted by theory. The deviations from theory are possibly due to the geometry of the filter (the equation was solved for an infinite plane of uniform thickness) and non-uniform distribution of the contaminant in the bulk material.

The extraction rate as a function of time can be determined from the filter extraction data shown in Figure 6 by taking the derivative of the curve fit with time. For example the fit of the total metals extraction curve is:

$$M_t = 18.0 t^{0.739} \quad (4)$$

where the units for M_t are micrograms and for t are hours.

The derivative of this equation with respect to time is:

$$dM_t/dt = 13.3 t^{-0.261} \quad (5)$$

where the extraction rate (dM_t/dt) is in micrograms/hour.

This equation can be used to predict how much contamination would be added to a system using this filter. For example, if this filter were to be used in a chemical delivery system delivering 8.3 liters/hour (200 liters/day), the amount of contamination added (C_A) would be equation (5) divided by 8.3 liters/hour:

$$C_A = 1.60 t^{-0.261} \quad (6)$$

where the units of C_A are micrograms/liter or ppb and the units for t are hours.

Hence, after 1 hour this filter would add 1.6 ppb of contamination to the chemical. After one day it would add 0.70 ppb, after 10 days it would add 0.38 ppb and after 100 days it would add 0.21 ppb.

During the course of this study there were several occasions when samples were inadvertently contaminated. One example of obvious sample contamination is shown in Figure 7. In this example, the background calcium concentration was 0.2 ppb. The sample taken after 0.1 hours indicated a concentration of 2.1 ppb. Subsequent analyses indicated concentrations ranging from 0.1 to 0.3 ppb. Since the chemical in the system is not changed during this test, the only way for the concentration of an element to increase then decrease is for the element to be first extracted then re-absorbed. Since this is unlikely, the 2.1 ppb measurement is probably erroneous. Hence, in this method the data point at 0.1 hours was discarded and the remaining data show that the component is not adding contamination. If the old method of testing were performed, the data analysis would indicate that the chemical was being contaminated by calcium from the component.

FILTER COMPARISON

Three type A filters were tested. The total mass extracted from these filters is shown in Figure 8. The first two filters tested (Filters A1 and A2) had similar high extraction amounts. The data shown in Figure 4 were obtained from filter A2. When these data were presented to the filter manufacturer, they modified their manufacturing process to reduce the extractables and produced filter B1. The changes made reduced the extractables considerably. Total mass extracted after 1000 hours was reduced by a factor of more than 50.

Filter C1 had a very high level of barium extraction (approximately 80% of the total mass extracted), as shown in Figure 9. Figure 9 also shows the measured extraction from the filter without including barium. Previous studies have indicated that certain types of perfluoroelastomers contain high levels of barium [8]. Therefore, an identical filter (Filter D1) was tested with a different type of perfluoroelastomer o-ring. There was no measurable barium extracted from the filter with this o-ring. Therefore, it was concluded that the barium extracted from the first filter was from the o-ring. The total mass extracted from filter D1 after 1000 hours was less than 1/25 that of the mass extracted from filter C1.

Filter D1 had lower extractables than filter C1 excluding barium extraction. Since the filters were identical except for the o-ring similar performance was expected. The difference between the two filters may be due to variation between filters or to extraction of elements other than barium from the o-ring on filter C1.

Filter E1 had very low metallic extractables as shown in Figure 10. Total extractables were approximately 10 μg which is near the detection limit of this method. The flat slope

of the correlation shown in Figure 10 is also an indication of little or no extraction from the filter.

Table III presents an overall comparison of the mass extracted from the filters. The table includes measurements of the amount of surface contamination, the mass extracted during the first 2 weeks in chemical and the combination of the two. The surface contamination was fairly similar for the filters, ranging from $< 10 \mu\text{g}$ to $83 \mu\text{g}$. The mass extracted varied considerably, ranging from $< 10 \mu\text{g}$ to $1320 \mu\text{g}$. Filter types A and C had high extractables. Types B, D and E had low extractables.

Table IV compares the extraction rates from the filters tested as well as the concentration increase which would occur if the filters were installed in chemical delivery systems. The contamination increase was calculated assuming that 5 filters were installed in a system delivering 200 liters/day of chemical. Large differences between the filter types are evident. Filter types B, D and E all added fairly small amounts of contamination while filter types A and C added more contamination. Filter type A would be expected to add approximately 1 ppb to the chemical after 1 month while filter type E would only add 0.02 ppb after 1 day.

The data obtained for these filters can also be used to calculate the time required for the extraction from a component to drop below a desired addition. Table V presents the calculated time for the contamination added by the filters to drop below 1, 0.1 and 0.01 ppb. Filter A has a very long clean up time with more than a year required before the filter will add < 0.1 ppb. Filter E cleans up very quickly, adding < 0.01 ppb within 2 days.

Table VI presents the composition of the mass extracted from the filters. The composition of both the surface contaminants and the mass extracted from the bulk is shown. The quantity and composition of the surface contamination was variable between filter type and for filters of the same type. It was mainly environmental or human contamination (aluminum, calcium, magnesium, potassium, sodium) or contamination from cartridge assembly equipment (iron). The notable exception was barium from filter type C. The variability may have been due to differences in handling or to differences in the IPA wetting/water flushing procedure.

The composition of the mass extracted from the bulk material in cartridges of the same type was consistent. The material extracted from filters A1 and A2 had very similar compositions. The mass extracted from filters C1 and D1 (the same type of filter with different o-rings) were similar when the barium extraction was not included. Hence, it appears that different filter types may have different elemental "fingerprints."

CONCLUSIONS

The data presented in this paper show that measurement of metallic extractables by dynamic extraction has clear advantages over conventional methods. These advantages include increased accuracy and sensitivity due to easy identification of sample

contamination and use of curve fitting to reduce analytical variability. The method also allows prediction of component performance in a chemical handling system, including the time required for a component to achieve a specification for maximum contamination added.

When used to measure the performance of all-fluoropolymer filter cartridges, the method was able to discern large difference between filter types and to assist the manufacturers in improving their products. Inappropriate manufacturing procedures and use of an improper o-ring were identified. The manufacturers were able to identify these problems and reduce the extractables from their products significantly. It was estimated that the “dirty” filters tested would add approximately 1 ppb of contamination to chemical delivered by a chemical delivery system supplying 200 liters/day of chemical after a month of use. “Clean” filters would add < 0.01 ppb within 2 days.

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Table I: Projected Chemical Purity Needs

Year	1988	1992	1995	1998	2001
DRAM Size	4 Mb	16 Mb	64 Mb	256 Mb	1 Gb
Minimum linewidth, μm	1.0	0.5	0.35	0.25	0.18
Particle Concentration $\#/ml \geq 0.20 \mu\text{m}$	< 100	< 30	< 5	< 2	< 0.4
Total metallics, ppb	< 150	< 50	< 10	< 5	< 1

Table II: Analytical Detection Limits

Element	Detection Limit, ppb
Aluminum	0.03
Barium	0.01
Calcium	0.05
Chromium	0.02
Copper	0.01
Iron	0.50
Magnesium	0.05
Potassium	0.04
Sodium	0.30
Titanium	0.01
Zinc	0.03

Table III: Summary of Filter Extraction Data

Filter	Surface contamination, μg	Mass extracted in 2 weeks, μg	Total contamination added in 2 weeks, μg
A1	27	860	887
A2	<10	1320	1320-1330
B1	<10	32	32-42
C1	83	310	393
C1 (No barium)	36	87	123
D1	36	11	47
E1	17	<10	17-27

Table IV: Expected Filter Extraction and Contaminant Additions

Filter	Extraction rate, $\mu\text{g}/\text{day}$			Expected contamination, $\text{ppb}^{(1)}$		
	1 day	1 week	1 month	1 day	1 week	1 month
A1	94	53	43	2.4	1.3	0.86
A2	140	83	57	3.5	2.1	1.4
B1	3.5	0.72	0.22	0.09	0.02	0.01
C1	42	14	6.0	1.1	0.35	0.15
C1 (no barium)	9.7	5.3	3.4	0.24	0.13	0.08
D1	1.2	0.70	0.46	0.03	0.02	0.01
E1	0.74	0.13	0.04	0.02	<0.01	<0.01

(1). Assumes 5 filters are installed in a system which is delivering 200 liters/day.

Table V: Expected Filter Cleanup Times

Filter	Time for contamination to drop below		
	1 ppb	0.1 ppb	0.01 ppb
A1	18 days	> 1 year	-
A2	120 days	> 1 year	-
B1	1.2 hours	< 1 day	15 days
C1	1.1 days	61 days	> 1 year
C1 (no barium)	< 1 hour	17 days	> 1 year
D1	< 1 hour	< 1 day	49 days
E1	< 1 hour	< 1 day	2 days

Table VI: Filter Elemental “Fingerprints”

Filter	Main Surface Contamination Elements (%)	Main Elements Extracted (%)
A1	Calcium (51) Aluminum (19) Magnesium (13)	Aluminum (63) Magnesium (16) Titanium (11)
A2	Aluminum (32) Calcium (27) Magnesium (16)	Aluminum (60) Magnesium (16) Titanium (10)
B1	Magnesium (57) Iron (29)	Titanium (39) Iron (27)
C1	Barium (55) Potassium (12) Iron (10)	Barium (79) Iron (10)
C1 (no barium)	Potassium (25) Iron (21) Magnesium (19)	Iron (37) Aluminum (15) Magnesium (15)
D1	Iron (48) Aluminum (17) Magnesium (10)	Iron (28) Calcium (18) Aluminum (14)
E1	Magnesium (40) Iron (22) Aluminum (14)	Calcium (42) Aluminum (21)

Figure 1: Theoretical extraction from a planar sheet with uniform initial contaminant concentration and constant surface contamination

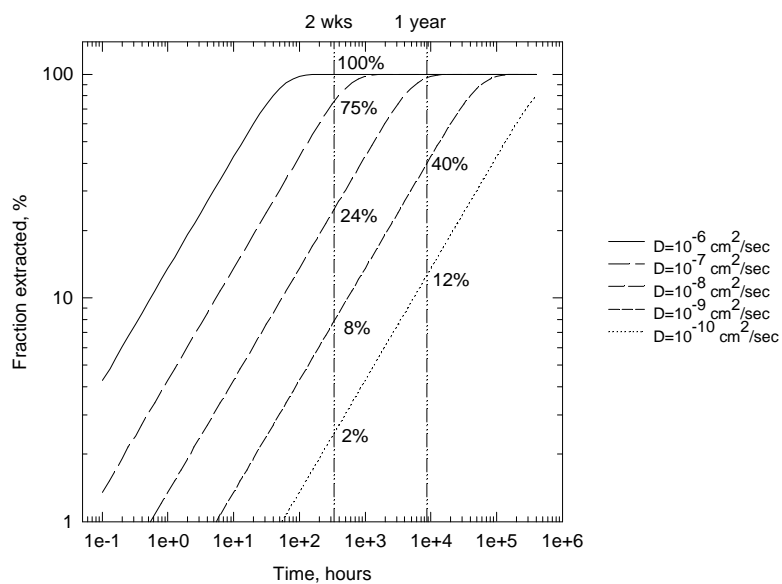


Figure 2: Simplified test system schematic

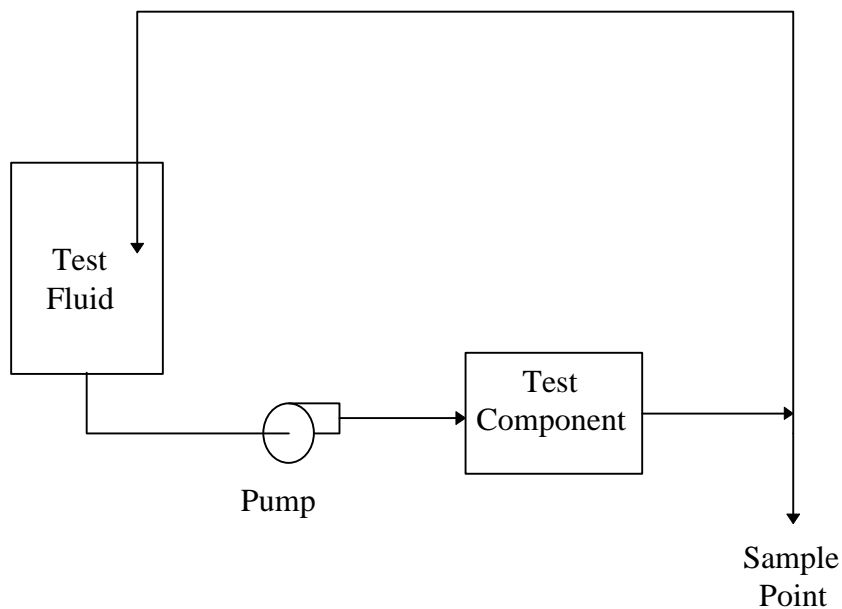


Figure 3: Test system background

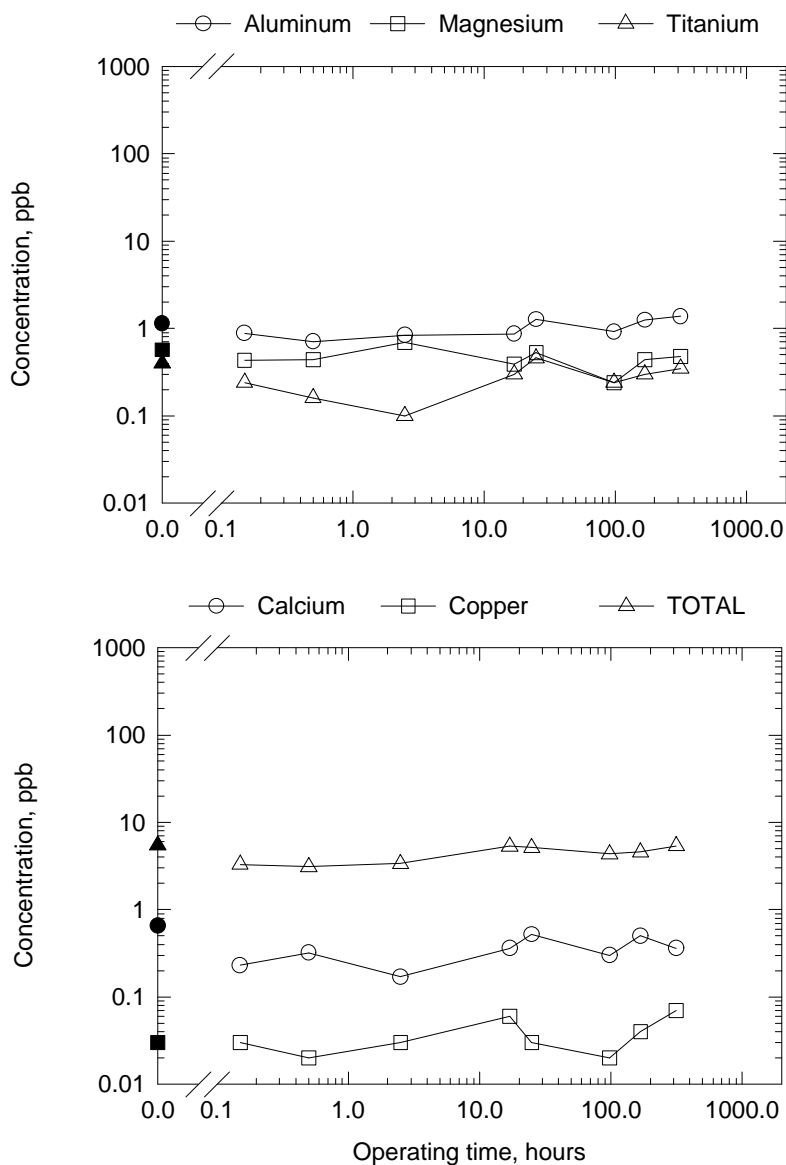


Figure 4: Example of extraction from a highly contaminated filter

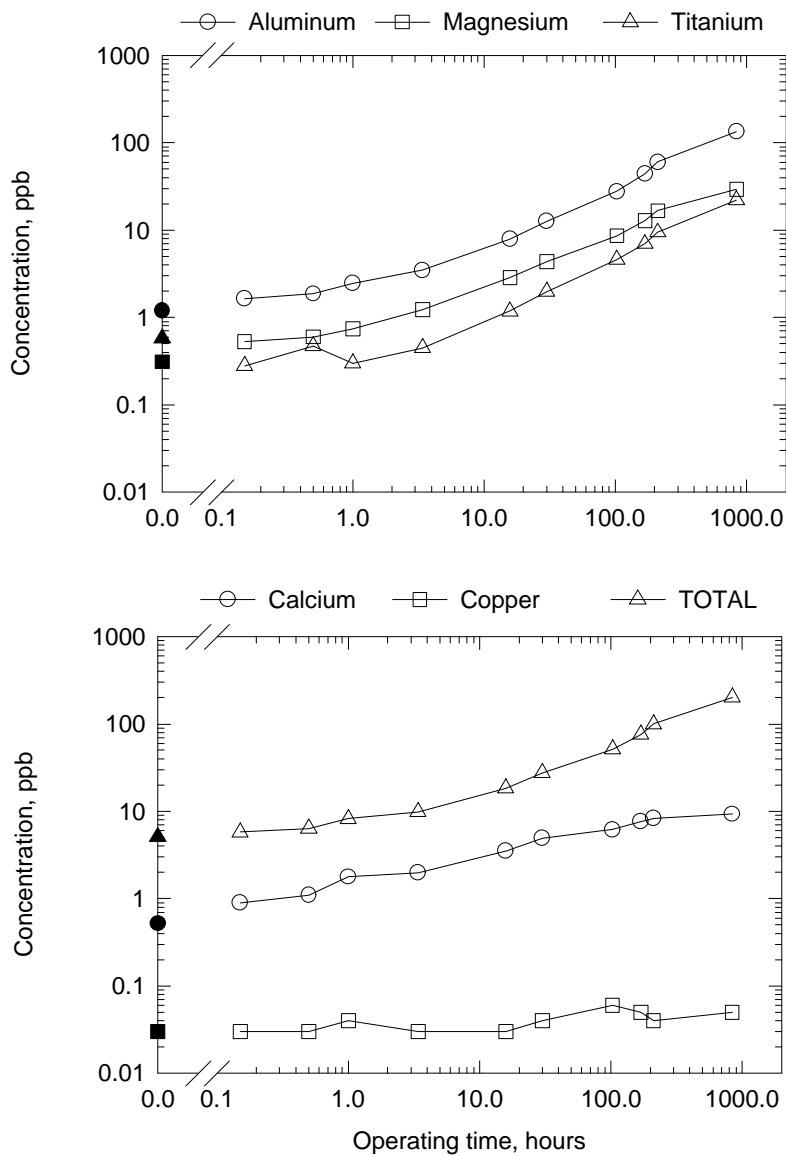


Figure 5: Example of extraction from a clean filter

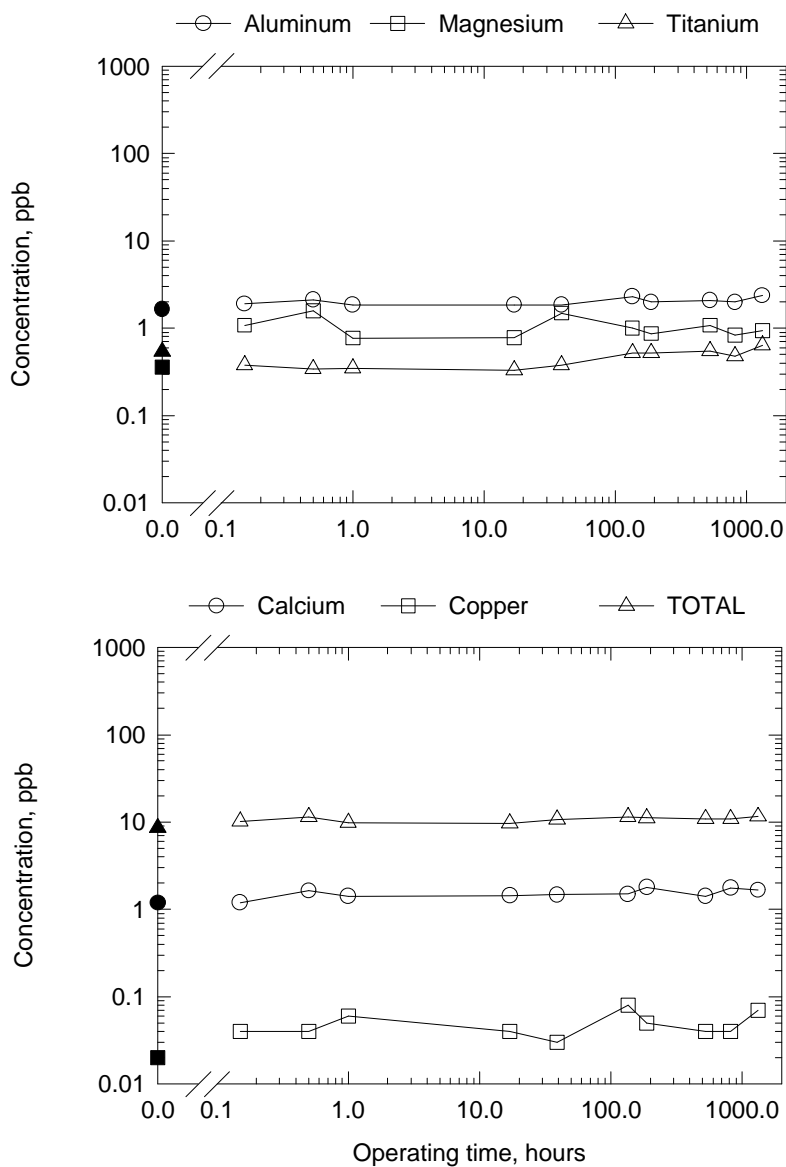


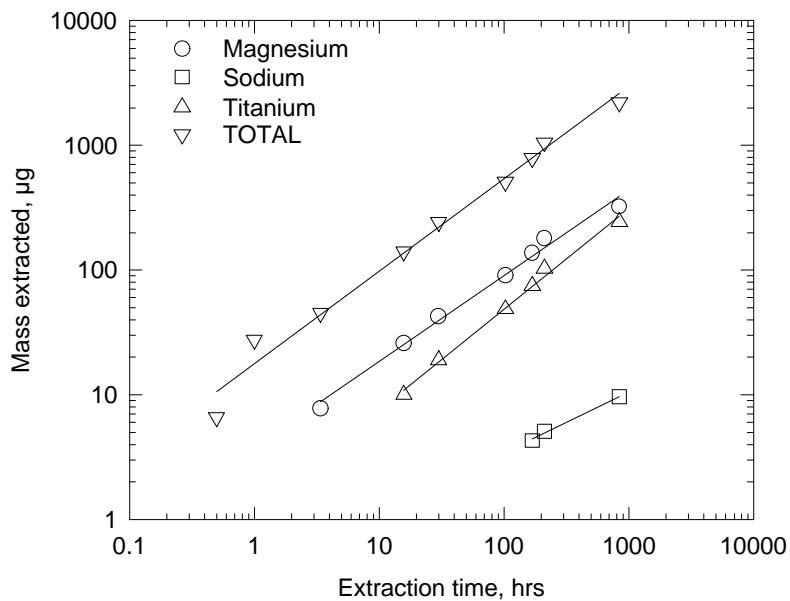
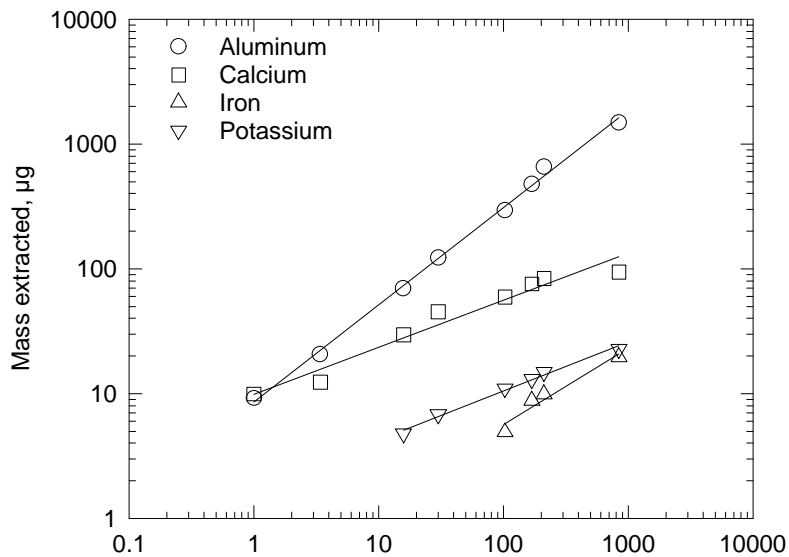
Figure 6: Calculated mass extraction from a highly contaminated filter

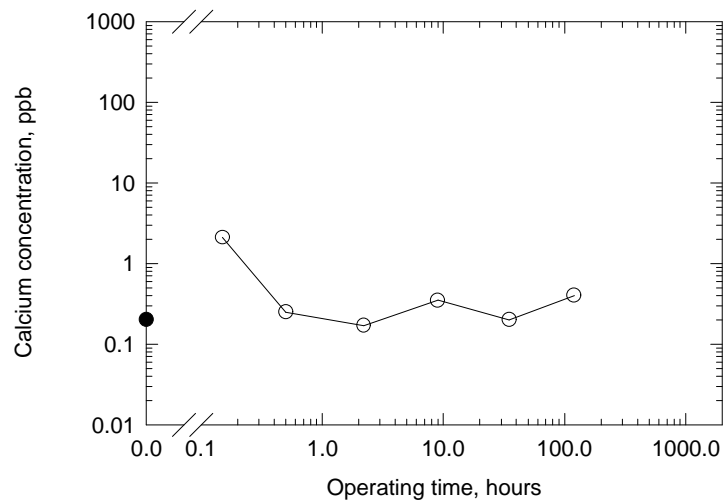
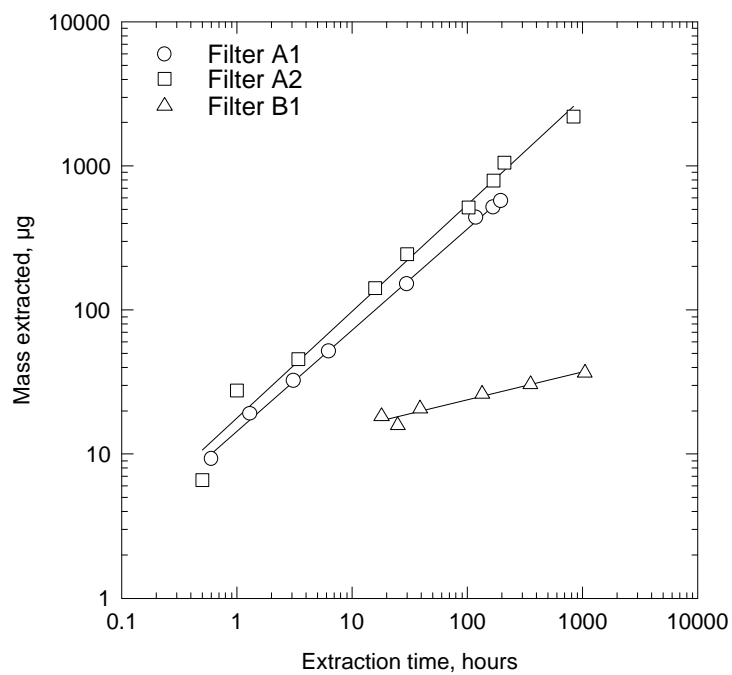
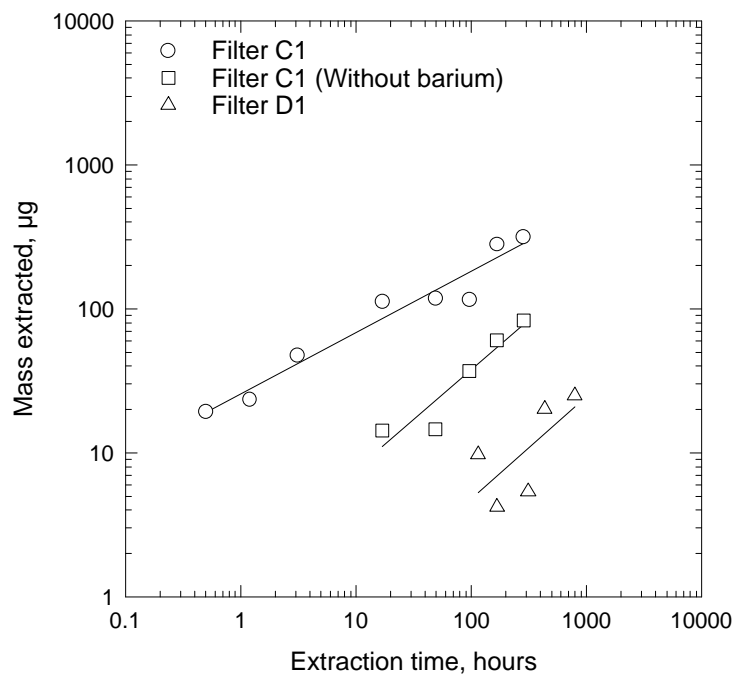
Figure 7: Example of sampling/analytical procedure variability**Figure 8: Total mass extracted from type A and B filters**

Figure 9: Total mass extracted from type C and D filters**Figure 10: Total mass extracted from filter E1**