DYNAMIC EXTRACTION: A NEW TECHNIQUE FOR MEASURING METALLIC EXTRACTABLES FROM CHEMICAL HANDLING SYSTEM COMPONENTS

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ABSTRACT

The extraction of inorganic contamination from fluid handling components degrades the quality of high purity semiconductor process chemicals. This paper presents a novel method, dynamic extraction, which measures the rate at which inorganic contaminants are extracted from components as a function of time. Dynamic extraction 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.

Dynamic extraction was used to measure metal ion extraction from pumps, piping and filters used in chemical handling systems. The extraction rate calculated for filters was compared to that predicted by theory. Comparison of the extracted metals and impurities in the piping polymer resins identified the source of the extractable contamination. Information concerning the amount and source of contamination added to process chemicals can be used to make informed decisions about selection and precleaning of components for chemical handling systems.

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, these chemicals must be manufactured cleanly and kept clean until they reach the wafer surface. The cleaning equipment and chemical delivery systems which 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 2001, based on the Semiconductor Industry Association roadmap [1]. Considerable improvements are required.

Table I: Projected semiconductor process 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 ≥ 0.20 μm	< 100	< 30	< 5	< 2	< 0.4
Total metals, ppb	< 150	< 50	< 10	< 5	< 1

To meet the chemical purity requirement, care must be employed in selection of components for process tools and chemical delivery systems. Only components with little or no metallic extractables should come into contact with chemicals. This paper describes dynamic extraction, a new method for measuring the rate of metal ion extraction from fluid handling components. From this extraction rate, the contribution of the component to the metallic contamination of the fluid in a chemical handling system can be calculated. Hence, components can be evaluated for their suitability for use in fluid handling systems. Dynamic extraction results can be used to predict when component cleanliness will need to be improved to meet future purity requirements.

SOURCES OF METALLIC CONTAMINATION IN COMPONENTS

Metallic contamination in components may be present in the component's raw material or may be picked up during manufacturing. Metal ions from these sources can leach into process chemicals. In addition, contamination can arise when a component fails and the chemical stream is exposed to a material which is not suitable for chemical contact. This paper addresses metal extraction from components in chemical delivery systems during normal operation.

Components which contact process chemicals are often manufactured from polymers such as perfluoroalkoxy (PFA), polyvinylidene fluoride (PVDF), polyethylene (PE), and polypropylene (PP). These polymers contain metallic contamination inherent in their raw materials, polymerization catalysts, and the resin manufacturing process. Information from component manufacturers on the metal ion content of the polymers can be useful in identifying the source of metallic contamination.

Components can also be contaminated during their manufacture. Tools used for molding, extrusion, or machining the component parts are often made of metal. Metal ions can easily be transferred to the components or small pieces of metal can become embedded in the component.

The contamination that arises from these sources is associated with different parts of the component. Contaminants which originated in the component raw material are distributed throughout the component in its bulk phase. Surface contamination is more likely to arise from a manufacturing tool or from the manufacturing and packaging environment.

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The use of the component dictates whether or not surface contamination is a concern. Chemical delivery systems are flushed with both water and chemical before they are commissioned. Consequently, the majority of surface contamination is removed from the system before it is used to deliver process chemicals. However, some components, such as filters and replacement parts, are installed in operating chemical delivery systems without precleaning. Surface contamination on these parts may degrade the quality of the chemicals and cause deleterious effects on the semiconductor manufacturing processes. Therefore, it may be advantageous to preclean components that are to be installed in an operating system. It is usually not efficient or necessary to preclean components to remove surface contamination in chemical delivery systems that will undergo a commissioning stage.

METHODS FOR MEASURING METALLIC EXTRACTABLES

Past Methods

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.

1. The components to be tested are rinsed in either DI water or the test chemical to remove surface contamination and contamination resulting from handling.
2. The concentrations of contaminants in the test chemical are measured.
3. The test components are immersed in the chemical for a predetermined period of time.
4. The components are removed from the chemical and the concentrations of the contaminants in the fluid are measured.
5. The amounts of contaminants extracted from the components are determined from the concentration differences.

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. Furthermore, the technique does not have enough resolution to detect very low levels of extraction because they are small relative to the background of sampling and analytical errors.

A second concern is that the parts are usually left stagnant in the chemical. This allows the contaminant concentration in the chemical near the surface of the test component to increase above the concentration in the bulk of the extraction solution. The decreased concentration gradient between the component and the extraction solution may result in an extraction rate which is 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.

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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 spray processor. 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. A known volume of chemical is transferred to the system. A sample of this chemical is retained 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.
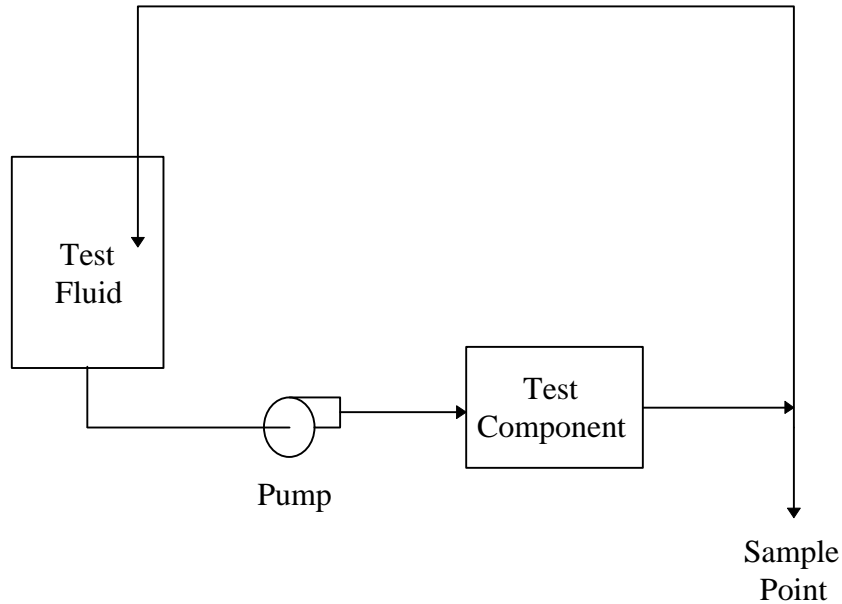
In order to maximize the sensitivity of the test, the volume of chemical in the system is kept to a minimum. The initial chemical volume equals the system holdup volume plus enough chemical for sampling. Subsequent data analysis corrects for the change in volume as samples are withdrawn.

The dynamic extraction method offers many advantages. Because of the small test chemical volume and use of multiple sample points, dynamic extraction is sensitive enough to detect very low levels of extractables. Dynamic extraction, unlike conventional extraction methods, can measure and predict the rate of change in the extraction rate. Furthermore, the test results can be used to construct a "fingerprint" of extracted metals for particular materials and components. These fingerprints can be used to identify the source of extraction problems of systems in the field. Finally, the extraction data can be used to predict a component's contribution to contamination in a process chemical stream.

EXPERIMENTAL METHODS

Several test systems were built to measure metal ion extraction from components. The systems were used to test filters, pumps, piping, and other components in several chemicals. All test systems were constructed of Teflon® polytetrafluoroethylene (PTFE) or perfluoroalkoxy (PFA)

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Figure 1: Test system schematic

components. The major components in the systems were a test fluid reservoir, a pump, and the component to be tested, as shown in the simplified schematic in Figure 1.

The test systems were cleaned by circulating either HF or HCl solution for 1-2 weeks. Following cleaning, the background metal ion concentration in the circulated chemical was measured to ensure there was minimal extraction without test components installed. Figure 2 presents the concentrations of selected elements measured in the filter test system background test. Curves are shown for 3 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 subsequently found to be extracted from test components, are commonly found in chemicals, or are known to cause considerable problems in semiconductor devices. The filled data points on the y-axis 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 measurable change in concentration during the course of the 350 hour test.

The test procedure for most test components, performed after verification of system cleanliness, consisted of the following steps:
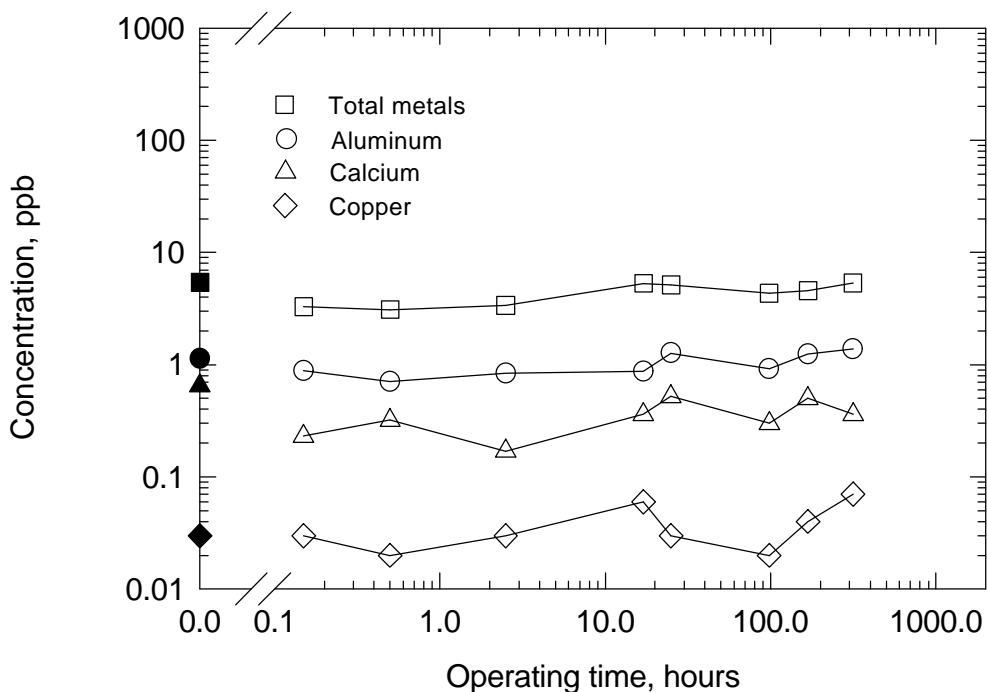
1. The test component was installed in the system.
2. The system was filled with high purity DI water and flushed for 24 hours.
3. The water was drained from the system.
4. The system was filled with DI water and drained 2 additional times.
5. A known volume of chemical was transferred to the fluid reservoir. A sample was reserved for analysis.

6. Circulation of the chemical through the test component was started.
7. Samples of the chemical were periodically removed. Sampling times were recorded.
8. At the end of the test period the system was flushed with water and the component was removed.

This procedure was adapted to simulate use conditions for each component type. Filters were wet with IPA and rinsed with DI water before testing. Test filters were enclosed in a filter housing. Because in the field filters are not flushed before use, steps 2-4 were omitted. Extractable contamination from pumps was measured while the pumps were operating. Thus, a system pump was not required in this case.

Samples for chemical analyses were collected in PFA or HDPE 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.

Figure 2: Test system background

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THEORETICAL EXTRACTION RATE

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

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

where M_t = 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 3. Curves for several different diffusion coefficients ranging from 10^{-6} to 10^{-10} cm^2/sec are shown. The curves in Figure 3 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 3 indicates that during this time the mass extracted increases with the square root of time, as shown in equation (2):

$$M_t = k\, t^{0.5} \tag{2}$$

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):

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

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

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Figure 3: Theoretical extraction from a planar sheet with uniform initial contaminant concentration and constant surface contamination
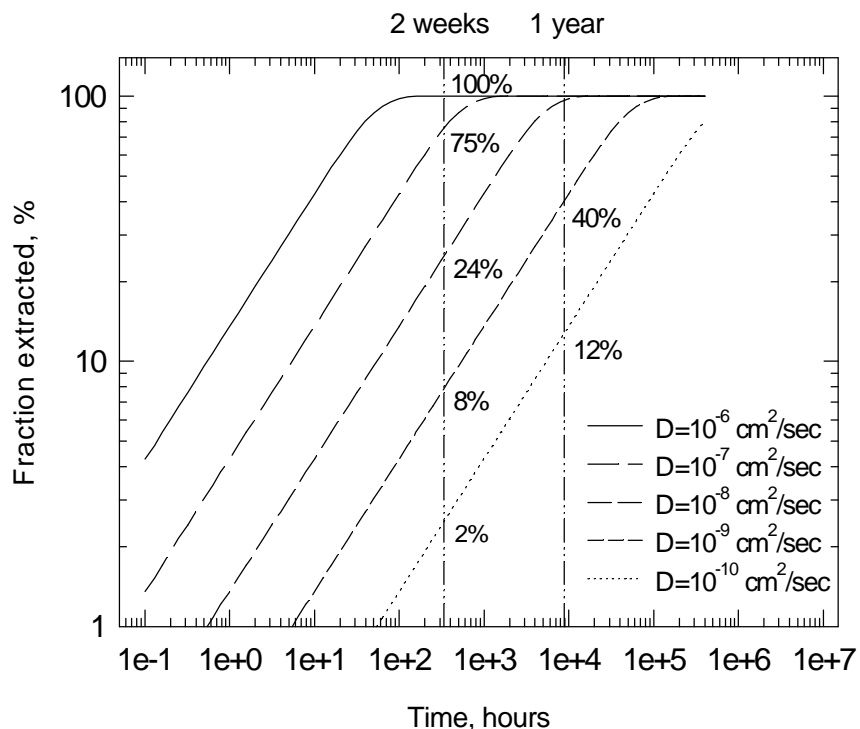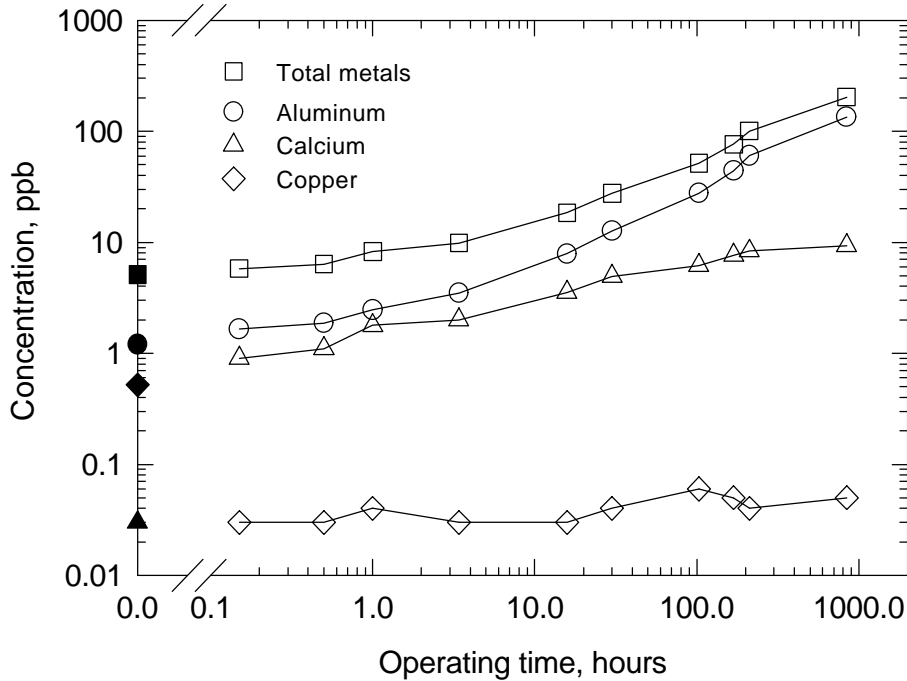

The vertical lines shown in Figure 3 represent 2 weeks and 1 year of exposure to chemical. The percentages shown where the vertical lines intersect the extraction lines indicate the percentage of mass extracted. For example, only 12% of the contamination with a diffusion coefficient of 10^{-10} cm^2/sec will be extracted after 1 year. Diffusion coefficients in solids are not well known and are difficult to measure. They range from $>10^{-7}$ for dilute concentrations of solvent in polymers to $<10^{-20}$ for solids in solids [6]. Hence, if there is extraction from a component, it will probably occur throughout the life of the component, although the extraction rate will decrease with time.

DATA ANALYSIS METHOD

An example of the data obtained from a filter, Filter A, 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 and calcium. Other metals not shown in Figure 4 with detectable extraction from Filter A were magnesium and titanium. There was no significant increase in the concentration of copper. The results of dynamic extraction from Filter B, an example of a filter with minimal extraction, are shown in Figure 5. There were no significant increases from this filter for any element.

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Figure 4: Example of extraction from Filter A, a highly contaminated filter

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 for filters determined using this assumption only includes that contamination which is soluble in chemical and not soluble in either the IPA or water used in wetting the filter.
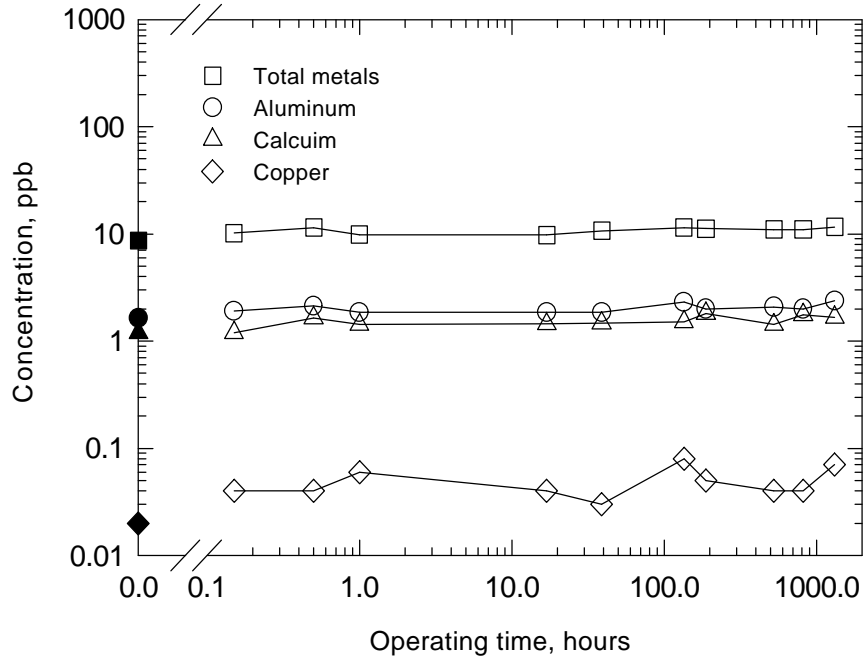
This assumption was used to analyze the data from Filters A and B. The mass extracted from Filter A and the least squares best fits for each data set are shown in Figure 6. The fits for all filters had slopes ranging from 0.38 to 0.8 which are close to the slope of 0.5 predicted by theory. The deviations from theory are possibly due to the geometry of the filter (the equation was solved for an infinite plane of uniform thickness) and nonuniform 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 respect to time. For example the fit of the total metals extraction curve is:

$$M_t = 18.0 \, t^{0.739} \tag{4}$$

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

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Figure 5: Example of extraction from Filter B, a clean filter

Figure 6: Calculated mass extraction from Filter A, a highly contaminated filter

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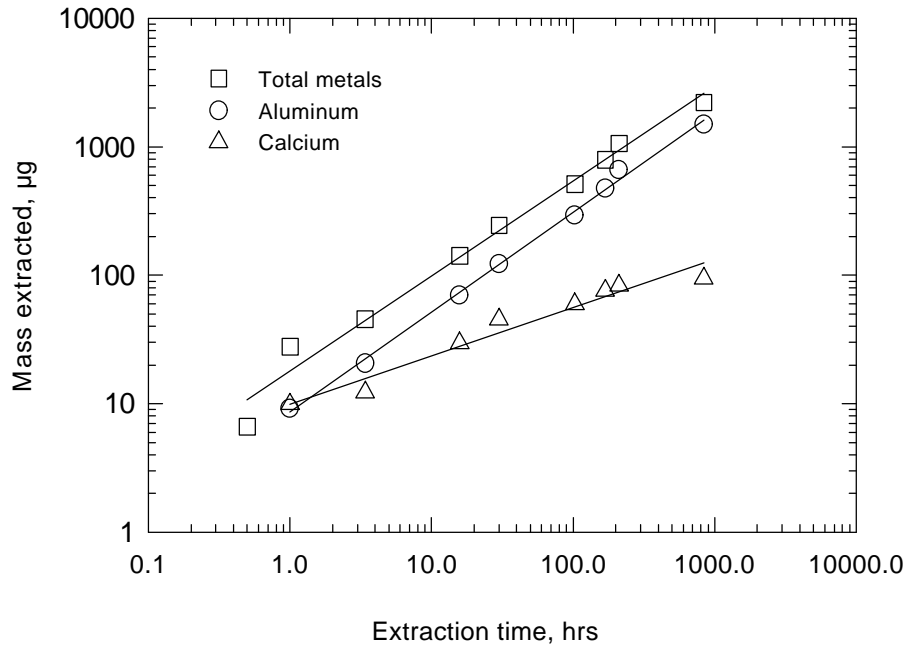
The derivative of this equation with respect to time is:

$$d\,M_t/dt = 13.3\,t^{-0.261} \tag{5}$$

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

Extraction rates, shown in Table II, were calculated using this equation.

Table II: Calculated component extraction rates

Component	Extraction rate, µg/day		
	1 day	1 week	1 month
Filter A	94	53	43
Filter B	0.74	0.13	0.04
Pump A	51	18	8.4
Pump B	102	35	16
Pump C	130	63	37
Piping A	60	22	10.5
Piping B	1540	1400	1300

Equation (5) can be used to predict how much contamination would be added to a system by a component. For example, if Filter A were 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:

$$C_A = 1.60\,t^{-0.261} \tag{6}$$

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

The amount of contaminants added to a chemical stream by Filters A and B and the filter cleanup times are shown in Table III. The times required for the filters and other components to meet several different specifications for metal ion contamination are included.

This interpretation of the data gives good indication of the suitability of components for use in chemical handling systems. However, the predicted cleanup times should be considered an approximation of the time required for a component to reach system specifications.

Table III: Expected contaminant additions and cleanup times
(based on 5 filters, 1 pump or 350 ft of piping per system)

Component	Expected contamination, ppb			Time for contamination to drop below		
	1 day	1 week	1 month	1 ppb	0.1 ppb	0.01 ppb
Filter A	2.4	1.3	0.9	18 days	> 1 year	>> 1 year
Filter B	0.019	0.003	0.001	< 1 hour	< 1 day	2 days
Pump A	0.26	0.092	0.042	2 hours	6 days	1 year
Pump B	0.51	0.18	0.081	7 hours	19 days	> 1 year
Pump C	0.63	0.31	0.24	8 hours	170 days	>> 1 year
Piping A	1.47	0.56	0.26	50 hours	210 days	>> 1 year
Piping B	38	35	32	>>1 year	>>1 year	>> 1 year

RESULTS AND DISCUSSION

The components used in this study were tested under simulated use conditions. Because the expected use of the filters, pumps and piping varied, their test conditions were different. A direct comparison of different types of components is not valid. However, a comparison of components from different manufacturers can be used to demonstrate the wide variability in metal ion extraction and suitability of components for use in a chemical handling system.

The extraction rates for all components tested are listed in Table II. Surface contamination was not included in the table. The expected contamination and component cleanup times listed in Table III were calculated by the data analysis method used for filters.
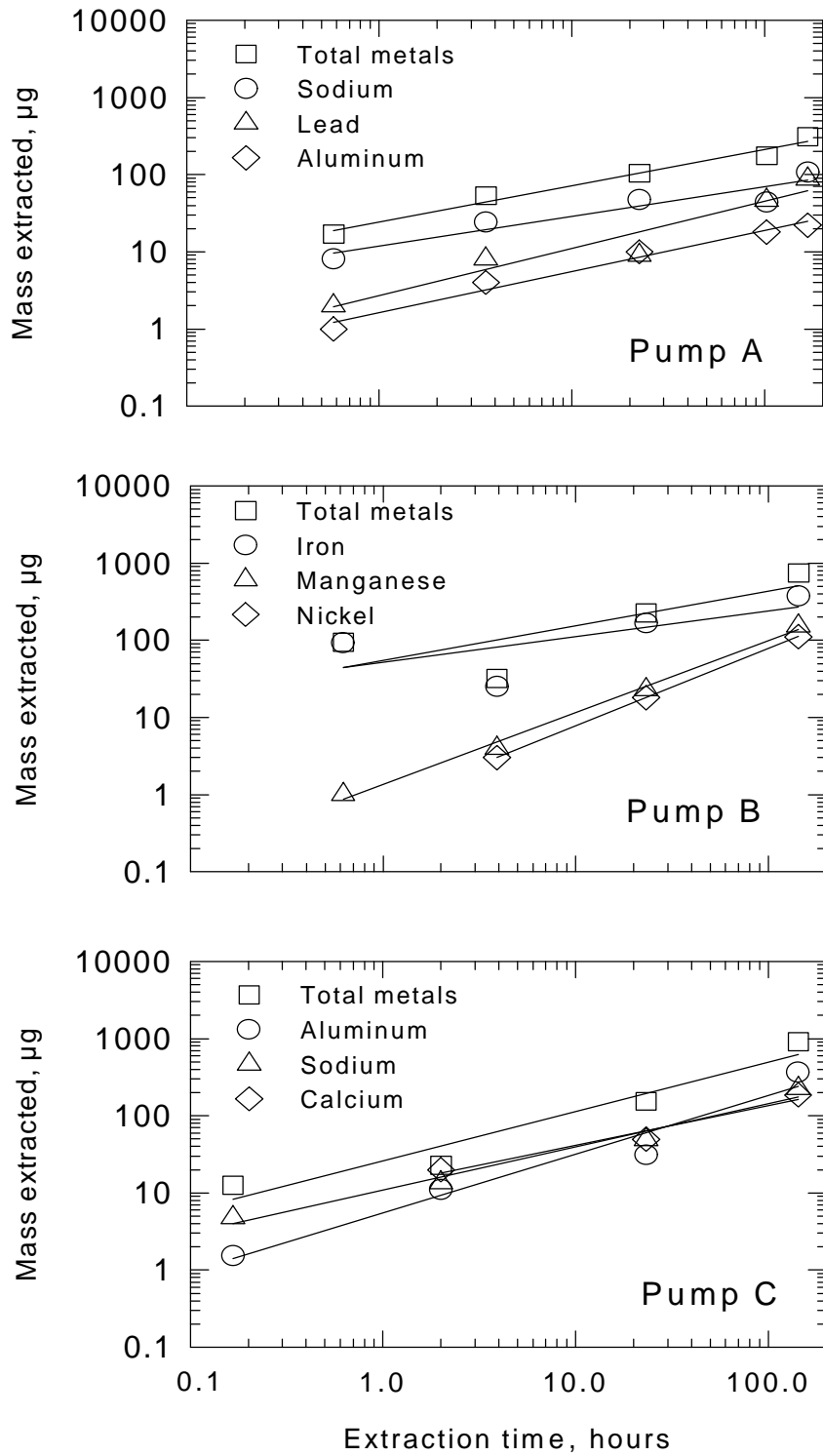
Filter comparison

The data from Filters A and B were presented as an example of the data analysis method. The results show the large variability in metal ion extraction from comparable components when tested under the same conditions and in the same chemical. The times required for Filter A to reach specified contamination levels were more than 100 times those for Filter B. This variability demonstrates the need to test components for extractables.

Pump comparison

The most prominent extractables from three types of pumps, Pumps A, B, and C, are shown in Figure 7. All showed some level of extraction. Extraction from Pump A was approximately 1/10 that of Pumps B and C. The rate of extraction from Pump C decreased much more slowly than predicted by theory. The reason for this is not apparent.

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Figure 7: Extraction of metal ions from pumps

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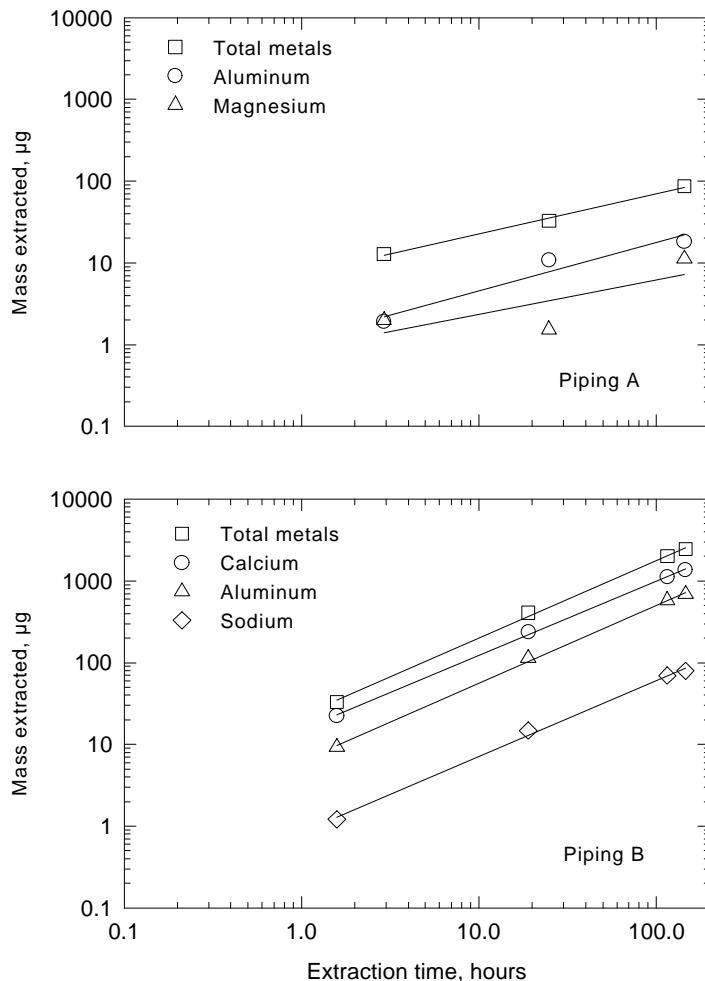
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The elemental "fingerprints" of the contamination extracted from the three pumps were different. Identification of the type of extractant can be useful in identifying its source. For example, initial tests of Pump A revealed high levels of extracted lead. By working together, FSI and the pump manufacturer were able to identify and eliminate the source of the lead contamination in the manufacturing process.

Piping comparison

Large differences in extractables were evident for the two types of piping tested, as shown in Figure 8. The cleanup times for Piping B were more than 1000 times those of Piping A. The difference reiterates the need for component testing. The high level of extractables from Piping B make it totally unacceptable for use in chemical delivery systems. Piping A also has high extractables, but can be used for delivering some chemicals because of the precleaning that occurs during system installation and qualification.

Figure 8: Extraction of metal ions from piping as a function of time

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Comparison of resin contaminants and metal extractables

Dynamic extraction can be used to identify sources of contamination. Extracted contaminants which are not found in the component resin are most probably acquired during its manufacture. The metallic extractables from two types of piping will be used as an illustration.

The extracted metals and the major metallic impurities in the piping resins are listed in Table IV. Information on metallic impurities in the resins was obtained from the resin manufacturers. Most of the metals extracted from Piping A were not present in the resin. The source of these metals was probably the manufacturing equipment. Magnesium appears in both the resin and the extracted metals. Magnesium may be more easily extracted than the other impurities in the polymer matrix or it may originate from a manufacturing tool. Because contaminants that originate in the manufacturing process are located near the surface of the component, they should leach out more quickly than contaminants located throughout the bulk of the component. A component precleaning step or longer system flush may eliminate or reduce the contaminant to acceptable levels.

Table IV: Metallic impurities in polymer resin and extracted from piping, listed in order of concentration

Component	Resin impurities (based on manufacturers' claims)	Measured extractables from the component
Piping A	Chlorine Magnesium Calcium	Aluminum Magnesium
Piping B	Calcium Titanium Aluminum Sodium	Calcium Aluminum Boron Sodium Magnesium

Most of the metallic impurities in the resin for Piping B were detected as extractables. This agreement indicates that the extractable calcium, aluminum, and sodium ions originated in the component resin. Since these contaminants are dispersed throughout the bulk phase of the component, the extraction will most likely continue for an extended time. Component precleaning or system flushing will not significantly reduce the extraction of these impurities.

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CONCLUSIONS

The levels of metal contamination in process chemicals need to decrease to meet future purity requirements. The systems used to deliver these chemicals must not add contaminants; hence, they must be assembled of high purity components. Highly accurate test methods are needed to verify component cleanliness. A new method to measure extraction of metals from components, dynamic extraction, overcomes many of the problems associated with traditional methods. Because dynamic extraction measures extraction with time, it can be used to determine extraction rates, to assess the impact of component contamination on process chemicals, and to predict the duration of metal extraction above specification. Analytical and sampling errors are minimized by using multiple samples. Comparison of individual metal contaminants in components' raw materials with those extracted helps identify the contamination source. The source and level of contamination and the expected use of the component determine if precleaning is beneficial.

REFERENCES

1. Semiconductor Industry Association, "The National Technology Roadmap for Semi-conductors," San Jose, CA, 1994.
2. Hedge R, V Anantharaman and J Zahka, "Measurement of Ionic Extractables from Millipore's All-Teflon Wafergard PF Filter Products," Microelectronics Application Note MA018, Millipore Corporation, Bedford, MA, January 13, 1992.
3. Hurd TQ, "A Comparison and Evaluation of 0.05 μm Chemical Filters," 11th Annual Microelectronics Symposium, Millipore Corporation, Bedford, MA, July 19, 1993.
4. Goodman JB and PM Van Sickle, "Extraction of Ionic Species from Perfluoroalkoxy (PFA) Polymeric Material," Proceedings of the 37th Annual Technical Meeting, Institute of Environmental Sciences, pp 551-556 (1991).
5. Crank J, The Mathematics of Diffusion, Oxford University Press, Bristol, England, 1975.
6. Cussler EL, Diffusion: Mass Transfer In Fluid Systems, Cambridge University Press, Cambridge, UK, 1984.
7. Grant DC, T Lemke, G Duepner, D Wilkes and N Powell, "Measurement of Inorganic Contaminant Extraction from Fluid Handling Components by Dynamic Extraction," Journal of Institute of Environmental Sciences, in preparation.

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