

# QUALIFICATION OF CHEMICAL DELIVERY SYSTEMS FOR ELEMENTAL EXTRACTION USING THE DYNAMIC EXTRACTION™ TECHNIQUE

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## ABSTRACT

A new method has been developed to measure the rate at which contaminants are extracted from chemical delivery systems. This method, called the Dynamic Extraction technique, is more sensitive, less costly to perform and faster than conventional techniques used to qualify chemical delivery systems. In addition, Dynamic Extraction measures contaminant extraction rate over time thereby allowing calculation of the mass of contaminants added to delivered chemical at any time.

Dynamic Extraction was used to measure extraction of elemental contaminants from six chemical delivery systems installed at Motorola MOS 13 in Austin, Texas. Each system was tested for extraction of 34 elements over a one week period. All of the systems were able to achieve the specification of < 1 ppb of total metals added within three days of initial contact with chemical. Data analysis showed that the systems would add < 0.1 ppb of total metals within 1 month. The systems typically met specification within one day.

## INTRODUCTION

Semiconductor microcircuit devices are extremely sensitive to metallic contamination, which can reduce device yield and performance. Process chemicals used in semiconductor manufacturing are a common source of metallic contamination. To minimize the defects caused by metal ions, many semiconductor manufacturers have strict limits on the metal ion content of liquid process chemicals. Motorola MOS 13 was designed to produce wafers with 0.5  $\mu\text{m}$  geometries at startup, with the geometries decreasing to 0.35  $\mu\text{m}$  by late 1996. These geometries require the use of very high purity chemicals. Incoming contaminant specifications for these chemicals ranged from < 1 part per billion (ppb) to < 10 ppb.

Chemical delivery systems are commonly used to provide chemicals to points of use (POUs) within a semiconductor fab from a central location. Newly installed delivery systems are qualified to demonstrate that they do not add significant metallic impurities to the chemical they transport. Standard qualification techniques are inadequate to verify the cleanliness of present day fabs. Therefore, a new method, the Dynamic Extraction technique, was developed to measure elemental extraction more quickly and reliably than standard qualification procedures. Dynamic Extraction also allows prediction of the amount of extracted metal ions that will be added to a chemical during system operation. It was used to verify the purity of 6 chemicals at Motorola MOS 13. The six chemicals were 49% hydrofluoric acid, 37% hydrochloric acid, 32% ammonium hydroxide, 30% hydrogen peroxide, 96% sulfuric acid and isopropyl alcohol.

## **STANDARD QUALIFICATION PROCEDURE**

In the standard qualification procedure, extraction of metallic impurities from chemical delivery systems is determined by taking simultaneous samples of the chemical entering the delivery system and at various locations throughout the system. The samples are analyzed for metallic impurity concentrations. The change in concentration between the various sample points is attributed to extraction from the delivery system.

The metal ion qualification procedure based on this method and used in the past at Motorola has been:

1. Fill the chemical delivery system with ultrapure water.
2. Check the system for proper operation and control.
3. Collect samples of incoming water, water exiting the chemical delivery module (CDM) and water at the POU for analytical testing to verify that the system does not add metallic contamination to water.
4. Drain the water from the system and purge with house nitrogen.
5. Fill the system with chemical and collect samples for analysis.
6. Verify through elemental analysis of samples that the system meets metal ion addition specifications in chemical.
7. If the system does not meet specification, flush the system with chemical and retest.

## **PROBLEMS ASSOCIATED WITH THE STANDARD PROCEDURE**

The standard qualification procedure often uses a single time interval to measure metal extraction. Relying on a single measurement has a high potential for error [1]. Contaminants introduced during **sample collection and preparation** are indistinguishable from extracted contaminants. Because the impurity levels in chemicals supplied by delivery systems are very low, small amounts of sample contamination can lead to large errors. Day to day variation in the **analytical tests** can also lead to incorrect determination of metal ion extraction. Use of data collected at a single time interval provides only a snapshot of system performance. It gives no indication of the rate of change in extraction with time. In addition, it is hard to predict the effect of changing parameters on system performance.

Qualification by the standard method is further complicated by other factors. A significant source of error is related to the **system holdup volume** and the **variability of the metal ion concentrations in the incoming chemical**. Samples taken from the CDM or POU may have been in the system for several days, and may have come from a different lot of chemical than the incoming chemical. Since the quality of the chemical varies from drum to drum, comparing concentrations of the incoming chemical to samples taken simultaneously at different locations can be misleading.

A model of a chemical delivery system was used to understand the effect of holdup volume and variation in incoming metal ion concentration [1]. The following assumption were made:

- A delivery system can be represented as a well mixed system with fresh chemical added as chemical is used. The system can be modeled as a continuously stirred tank reactor.
- The system holdup volume is equivalent to one day of chemical usage.
- The incoming chemical and the chemical initially in the system have equivalent impurity concentrations of 20 ppb.
- The incoming chemical impurity level changes from 20 ppb to 4 ppb after 4 days and returns to 20 ppb after an additional 4 days.
- There is no extraction of impurities from the system.

The incoming metal ion concentration of the model is shown in the top graph of Figure 1. The calculated concentrations in the model system are shown in the middle graph. The metal ion concentration within the system remains steady at 20 ppb until day 4. As the 4 ppb chemical enters the system and is mixed with the 20 ppb chemical, the metal concentration gradually decreases toward the 4 ppb level. After four days the system concentration is approaching the 4 ppb feed concentration. When the incoming concentration returns to 20 ppb on day 8, the mixing process is repeated in reverse.

The apparent change in metal ion concentration is shown in the bottom graph. A decrease in the incoming metal ion concentration causes an apparent concentration increase in the system. Conversely, a rise in incoming metal concentration causes an apparent decrease. Note that **these effects are seen in the absence of any metal ion extraction**. Data

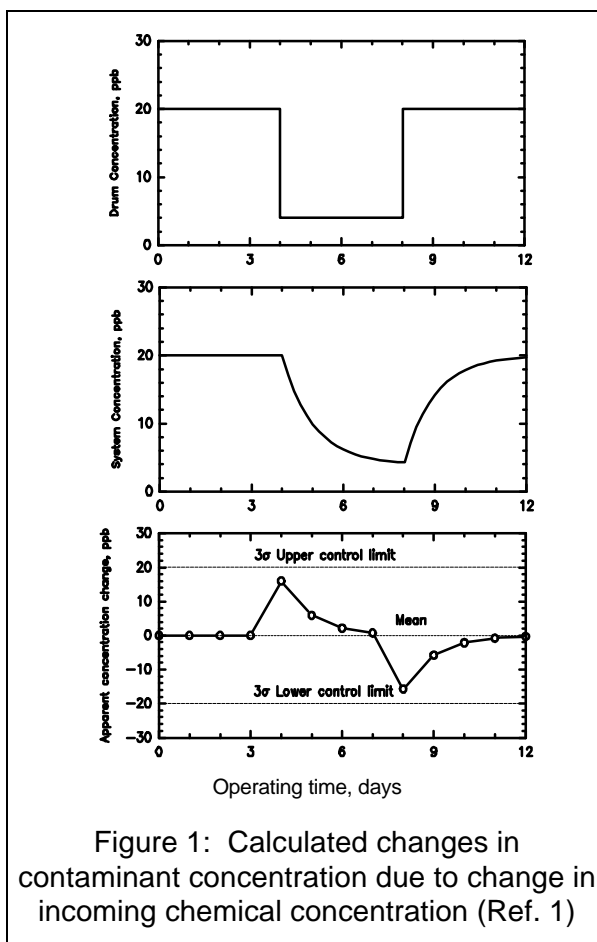


Figure 1: Calculated changes in contaminant concentration due to change in incoming chemical concentration (Ref. 1)

from 13 systems delivering chemicals at Motorola MOS 11 over a 28 week period corroborate this model.

In summary, the standard qualification method has large potential for error associated with sample handling, analytical methods and incoming chemical variation. Also, because this method gives only a snapshot of metal ion extraction, it provides no indication of the rate of change of metal ion extraction.

## **DYNAMIC EXTRACTION PROCEDURE**

A qualification procedure using the Dynamic Extraction technique was developed for use at Motorola MOS 13. It is based on a technique developed to determine the cleanliness of components used in semiconductor chemical handling equipment [2,3]. This procedure was used instead of the standard qualification procedures on 6 chemical delivery systems. The Dynamic Extraction procedure consists of the following steps:

1. The newly installed chemical delivery system is flushed with ultrapure water. The system is checked for leaks and smooth operation.
2. The system is flushed with dilute hydrogen peroxide until the start of the Dynamic Extraction test.
3. The system is filled with clean chemical. A sample is retained for analysis.
4. The chemical is circulated through the system.
5. A set of chemical samples is collected within 30 minutes. Samples include the incoming chemical, chemical exiting the CDM and chemical at the POU.
6. Additional samples are collected at predetermined intervals.
7. Samples are analyzed for metal ion concentration.
8. Surface contamination and bulk extraction rate with time are calculated.

The amount of surface contamination in the system can be determined by assuming that the metal ion content of the first set of samples relative to the incoming chemical consists solely of contaminants rinsed from the surfaces of the delivery system components. Subsequent increases in metal ion concentration are attributed to extraction from the bulk material of the system. Note that surface contamination as measured in this procedure includes only contaminants not soluble in water or dilute hydrogen peroxide.

## **THEORETICAL EXTRACTION RATE**

Metal extraction from a bulk material is described by diffusion theory [4]. The fraction of the contaminant extracted from the bulk material is a function of the diffusion coefficient of the contaminant in the bulk material, the thickness of the material and time. A detailed description of the theoretical extraction equation is presented elsewhere [3].

When graphed on a log-log scale, the extracted fraction of the contaminant mass increases with a constant slope of 0.5 until most of the contaminant is extracted, if the contaminants are evenly distributed throughout the bulk material and if extraction takes place from both sides of an infinite

plane. Different slopes occur with different geometries or nonuniform contaminant distribution. Equation (1) shows the relationship of total mass extracted as a function of time during this period.

$$M = kt^m \quad (1)$$

where  $M$  = Total mass extracted at time  $t$   
 $t$  = Time  
 $m$  = slope  
 $k$  = a proportionality constant

The rate at which mass is extracted at any given time ( $dM/dt$ ) can be determined using the derivative of equation (1):

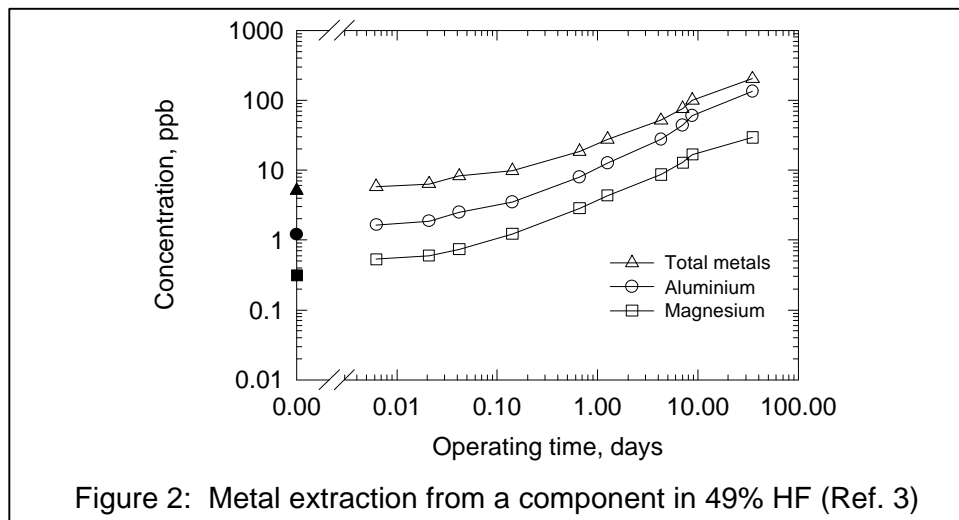
$$dM/dt = mk t^{m-1} \quad (2)$$

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 [5]. The magnitude of these diffusion coefficients implies that extractable contaminants, when present, will be extracted throughout the life of the component, although the rate will decrease with time [4].

## DATA ANALYSIS

Data collected in a previous study will be used to demonstrate the data analysis method [3]. Figure 2 shows the concentrations with time of aluminum, magnesium and total metals extracted from a component into 49% HF. The initial metal concentrations are shown as filled circles on the y-axis.

As explained above, this method assumes that surface contamination is removed in the first few minutes of chemical exposure. Hence, the masses of contaminants on the surface and in the



incoming chemical are subtracted from the mass in later samples to give the extracted mass. The graph of the total extracted mass as a function of time is shown in Figure 3. A curve fit of the data was used to determine the relationship between time and mass extracted:

$$M = 188 t^{0.739} \quad (4)$$

where  $M$  is the total mass in  $\mu\text{g}$  extracted at time  $t$ , and  $t$  is in days.

The derivative of equation (4), which describes the extraction rate ( $dM/dt$ ) in  $\mu\text{g}/\text{day}$ , is shown in equation (5).

$$dM/dt = 139 t^{-0.261} \quad (5)$$

The extraction rate can be used to predict the amount of contamination that will be added to chemicals handled by a delivery system. The extraction rate in equation (5) is divided by the volume of chemical handled daily. Assuming that the flow rate of the delivery system is 200 liters/day, the contamination added,  $C$ , is

$$C = 0.70 t^{-0.261} \quad (6)$$

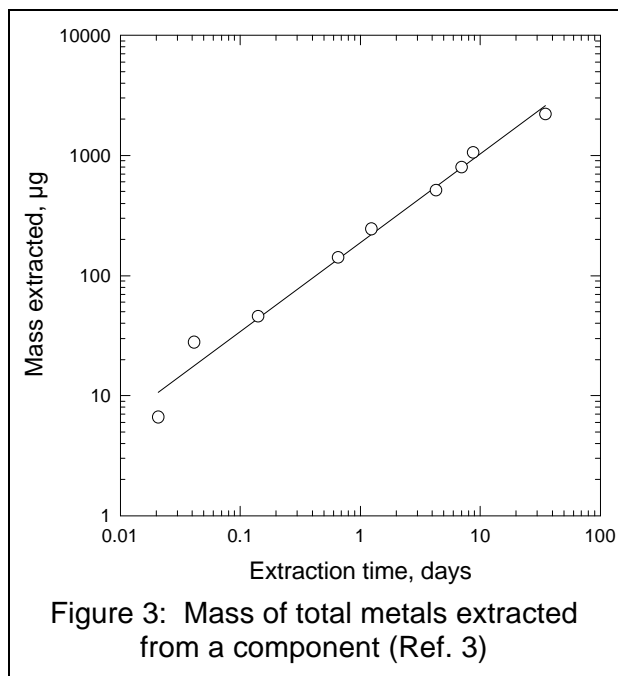
where  $C$  is in ppb and  $t$  is in days.

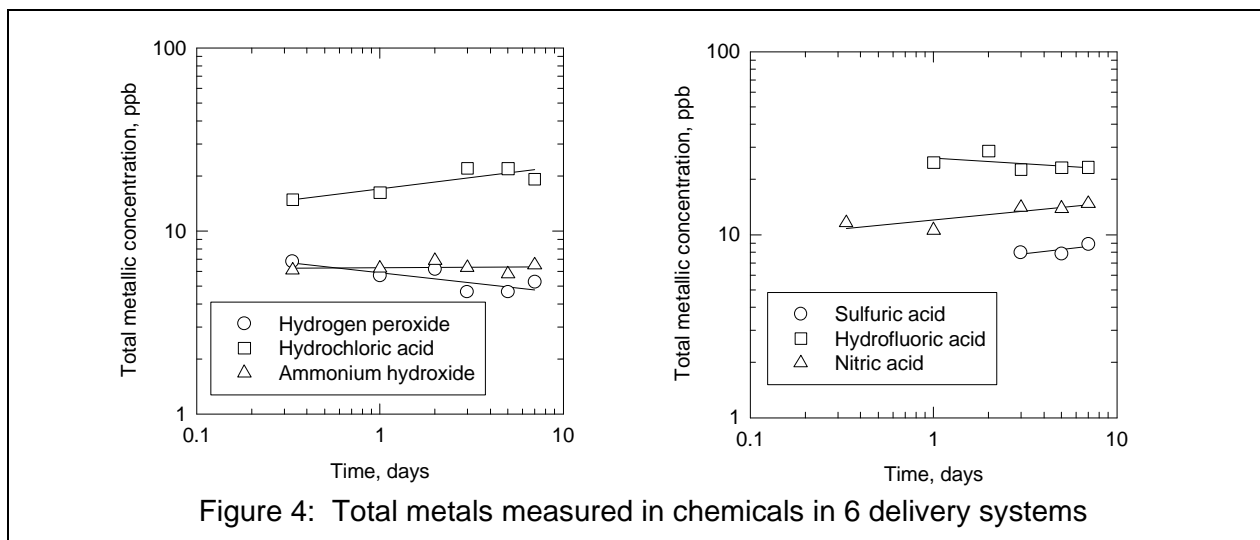
For certification of chemical delivery systems, it is essential to know when a system meets the specification for metal ion addition. This information can be determined from equation (6). At MOS 13, the specification was  $<1$  ppb total metals added. Equation 6 indicates that the amount of metal added by this component dropped below 1 ppb after 0.25 days (6 hours) of chemical contact.

## RESULTS

Total metals concentrations in the six systems tested by the Dynamic Extraction technique are shown in Figure 4. Each system was tested for extraction of 34 elements using a combination of inductively coupled plasma - mass spectroscopy (ICP-MS) and graphite furnace atomic absorption (GFAA). In determining the total concentration, the concentrations of undetectable elements were assumed to be at their detection limits. The system cleanup times calculated from these data are shown in Table I.

The detection of high levels of calcium was unexpected because calcium has not been identified as a common contaminant in the components of delivery systems. This concern prompted a closer look at the results of the chemical analyses.





The concentrations of calcium, potassium and zinc measured in ammonium hydroxide during the first 7 day of operation are listed in Table II. There was a discontinuity in the levels of all three metals between days 2 and 3. A similar discontinuity was found in the calcium concentration in all six chemicals when the raw data were reexamined (Table III). The discontinuity was the result of differences in the procedures and equipment used to perform the analyses.

Table I: Cleanup times for all six chemical delivery systems

Chemical	Time to < 1 ppb added, days	Time to < 0.1 ppb added, days	Main elements extracted
29% Ammonium hydroxide	< 1	<1	Calcium
37% Hydrochloric acid	18	240	Calcium, Iron
49% Hydrofluoric acid	< 1	< 1	Calcium
30% Hydrogen peroxide	< 1	< 1	Calcium
70% Nitric acid	2	30	Calcium
96% Sulfuric acid	2	16	Iron

Table II: Metal ion concentration over a 7 day period showing analysis lab variability

Time, days	Calcium, ppb	Potassium, ppb	Zinc, ppb
0.3	<0.6	<0.6	1.41
1	<0.6	<0.6	1.43
2	<0.6	<0.6	1.43
3	2.2	0.29	0.73
5	1.9	0.41	0.71
7	1.7	0.48	0.88

Table III: The daily concentrations of calcium in 6 chemicals as evidence of variability in chemical analyses (Numbers in parentheses indicate the number of samples analyzed.)

Date	NH <sub>4</sub> OH	HCl	HF	H <sub>2</sub> O <sub>2</sub>	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
7/18	<0.6 (2)		<0.6 (2)	<0.6 (2)		
7/19	<0.6	<0.6 (2)	<0.6	<0.6	<0.6 (2)	
7/20	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6 (2)
7/21	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
7/22	2.2		1.3	1.1		
7/23		4.3			3.8	
7/24	1.9		1.4	1.1		0.92
7/25		5.3			3.9	
7/26	1.7			1.2		0.92
7/27		3.3	1.7		3.9	
7/28						0.84

The concentrations of metals in semiconductor process chemicals is very low, frequently at or near the detection limits of the assay. For this reason small variability in the chemical analyses can lead to misinterpretation of the data. It is possible to avoid the problem encountered here by submitting all samples for analysis at the same time.

The qualification of the chemical delivery systems usually depends on the change in metal ion concentrations rather than on the absolute concentrations. With the understanding that the abrupt rise in calcium concentrations was not due to extraction of calcium, the results of the tests were reevaluated. Calculations were repeated using the total concentrations of all elements except calcium. These results are presented in Figure 5, with revised system cleanup times listed in Table IV.

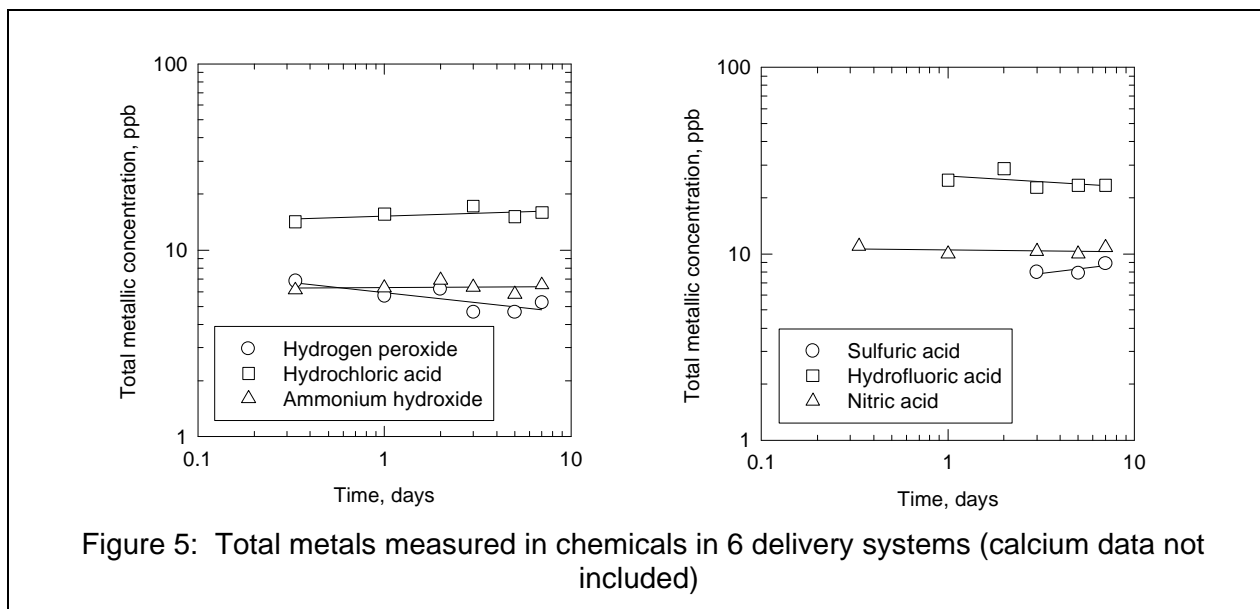


Figure 5: Total metals measured in chemicals in 6 delivery systems (calcium data not included)



Table IV shows that all of the chemical delivery systems were qualified within 3 days of chemical contact. Hence, all systems qualified before the test was completed. The time required for metals added to fall below 1 ppb was typically less than 1 day. All of the systems had less than 0.1 ppb measurable extraction within 1 month of startup.

Table IV: Delivery system cleanup times (without calcium)

Chemical	Time to < 1 ppb added, days	Time to < 0.1 ppb added, days	Main Elements Extracted
29% Ammonium hydroxide	< 1	<1	None
37% Hydrochloric acid	3	31	Iron
49% Hydrofluoric acid	< 1	< 1	None
30% Hydrogen peroxide	< 1	< 1	None
70% Nitric acid	< 1	< 1	None
96% Sulfuric acid	2	16	Iron

To confirm the absence of calcium extraction, a second Dynamic Extraction test was conducted for the hydrochloric acid, nitric acid and sulfuric acid systems. Samples were collected over a 2 to 5 day period. Data analysis showed no evidence of calcium extraction.

## CONCLUSION

The Dynamic Extraction method is a rapid and accurate method for qualifying chemical delivery systems. It was used at Motorola MOS 13 to demonstrate that total metal ion extraction from 6 chemical delivery systems was less than 1 ppb within 3 days of initial chemical contact. Total metal ion extraction was predicted to be less than 0.1 ppb within 1 month, and often within 1 day.

## REFERENCES

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