CASE 5

Application of Dynamic Optimization in Ultra Trace Analysis

Abstract: Ultra trace analysis with physical and chemical methods is of considerable importance in various fields, including medicine, the food industry, and solid-state physics and electronics. For manufacturing electronic devices, ultrapure water has to be monitored for metallic contamination. Extreme demands exist related to the reliability and reproducibility of quantitative results at the lowest possible concentration level. With such data, interpretation of the linear response with the least variability and the highest sensitivity can be achieved. For proof, the lowest detectable concentration is calculated and a robust detection limit below 1 ppt has been confirmed for some elements.

1. Introduction

The analytical tool considered here is an inductively coupled plasma mass spectrometer (ICP-MS), used widely for the determination of metal impurities in aqueous solutions. The output signal of the measurement system responds to the concentration level of the metallic elements. For higher metal concentrations, the error portion of the signal can essentially be neglected, whereas for lower concentrations signal deviations become dominant. To avoid unwanted noise, ultrapure water sample preparation was carried out under flowbox conditions (class 10). The response (intensity/counts per time) is investigated for a variety of measurement conditions, equipment components, and sample preparation (10 control parameters and two noise parameters) as a function of the signal factor. Signal factor levels are ultrapure water solutions with calibrated metal concentrations from 2.5 to 100 ppt (= 10^{-9} g/L) and additional water samples for reference (blanks). This type of system, with its steadily increasing relative noise toward lower signal values, requires appropriate dynamic S/N ratio calculations. Analytical tools with more demanding requirements are used to elucidate process monitoring of metallic contaminations. Quantitative results must be reliable and reproducible from high metal concentrations to the lowest possible limit of detection (LOD). In the mass production of silicon wafers in semiconductor manufacturing, most metallic surface contaminations have to be below 1010 atoms/cm^2 to avoid malfunction of the final device, due to subsequent metal diffusion into the bulk.

In manufacturing, every process step is accompanied by or finishes with a water rinse. For this purpose, ultrapure water is prepared and used. Consequently, the final silicon wafer surface is only as clean (i.e., metal free) as the ultrapure water available. Therefore, water purity with respect to such common elements as Na, K, Cu, Fe, and others must be monitored routinely.

For stringent purity demands in semiconductor processing (metal concentration $<$2 to 10 ppt), easy methods (e.g., resistivity measurements) are not at all sufficient; the ion product of water at pH 7 corresponds to a salt concentration of less than 10 ppm. Instead, the Hewlett-Packard's ICP-MS 4500 analytical equipment is used, where the notation stands for the physical principle of an inductively coupled mass spectrometer.

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2. Equipment

The starting point for the raw material water is drinking quality. The following salt contents are presented with typical concentrations beyond 10 ppm:

Salts > 10 ppm: Na^+, K^+, Ca^{2+}, Mg^{2+}

Salts < 10 ppm: Fe^{2+}. Sr^{2+}, Mn^{2+}, NH_4^+

Salts < 0.1 ppm: As^{3+}, Al^{3+}, Ba^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Li^+, Rb^+

From this level any metal contamination has to be removed to ppt values for use in semiconductor cleaning. With numerous chemical and physical principles applied in multiple process steps (Figure 1), this can be achieved.

The ultrapure water output quality must be monitored (i.e., controlled routinely) to maintain the required low contamination level. For detection, liquid samples are fed into the ICP-MS 4500. Figure 2 shows the components of the inductively coupled plasma mass spectrometer. After ionization, the ions are focused and separated according to their charge/mass ratio, and the intensity is measured in counts per time.

Various equipment components can be tested combined with various measurement modes and methods of sample preparation. Altogether, 10 parameters have been defined, composed of

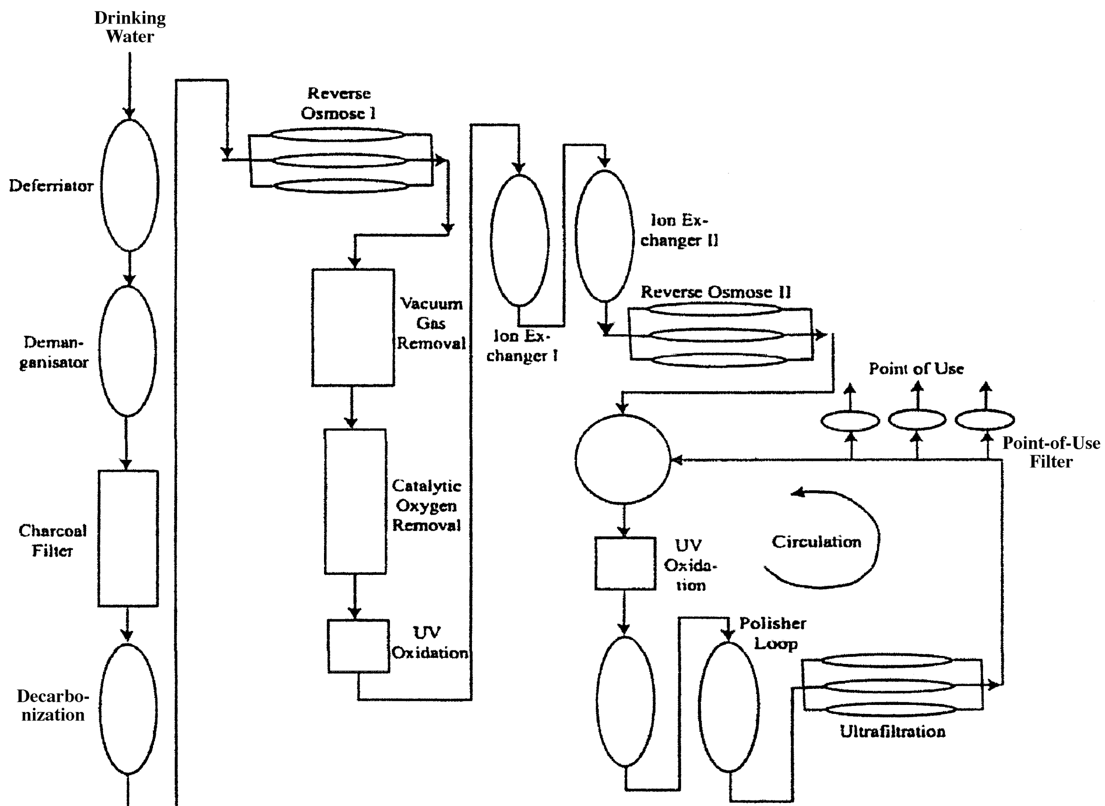

Figure 1
Ultrapure water supply system

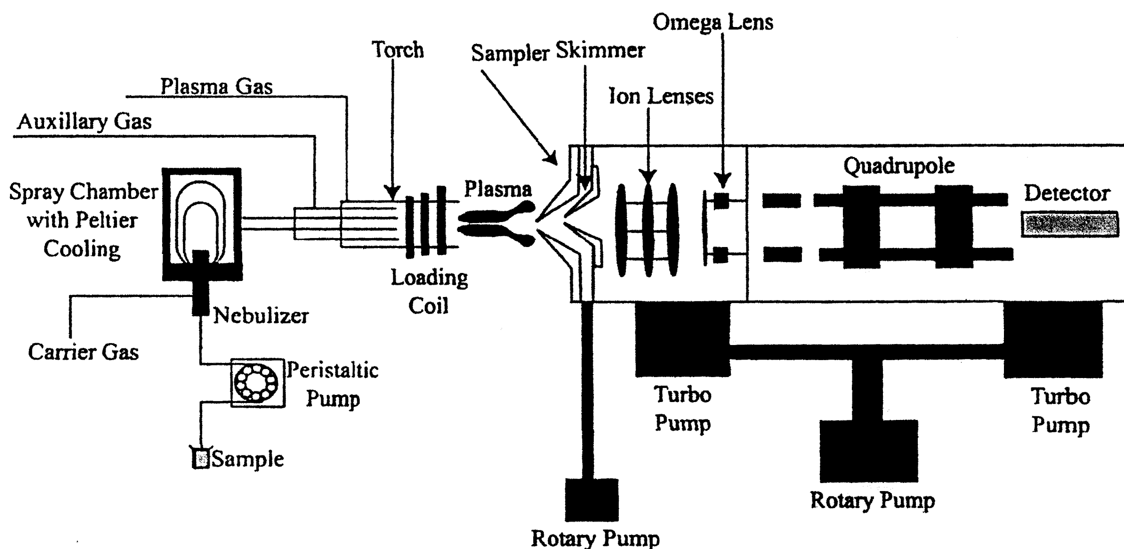

Figure 2
ICP-MS 4500 schematic

exchangeable hardware, measurement points and time, cleaning procedures, and sample handling.

3. Concept of Experiments

Mass production of semiconductor wafers requires a constant low-level ultrapure water supply. In principle, it is sufficient to prove the maintenance of a contamination level below an upper limit for the elements monitored. In common analytical practice, the measured sample is compared with a blank (sample without intentional content of elements to be detected). The information on the count rate of the blank alone does not allow one to calculate the lowest possible detection limit. Therefore, sample series with a calibrated content of elements are prepared and measured. Thus, a concentration range is covered and deviation of the signal output becomes visible. For physical reasons, the system is expected to behave linearly (plasma equilibrium), which means that the count rate (output) is proportional to the concentration of the elements. In designed experiments with 10 parameters, dynamic optimization enables one to reduce variation at the highest equipment sensitivity with the goal of achieving the lowest possible limit of detection. The corresponding SN figure can be calculated according to the zero-point-proportional characteristic. However, this is valid only for a few elements that occur rarely in nature and usually not in contact with water (e.g., Li, Cs, Co, Pb). Of more interest are widespread elements such as salts (e.g., Na, K, Al, Fe). Here the relative detection error (noise) increases toward lower concentrations, and at a certain point the limit of detection is reached when the output signal of the element detected becomes too low and disappears in the system noise. Original count rates are plotted for two elements in Figure 3.

For this reason, appropriate SN figures with the smallest error have to be calculated. In most cases the dynamic SN ratio for a linear function (no origin) is used.

4. Experimental Design

Equipment parameters (hardware), measurement parameters (count sampling), and preparation steps total 10 parameters on two levels:

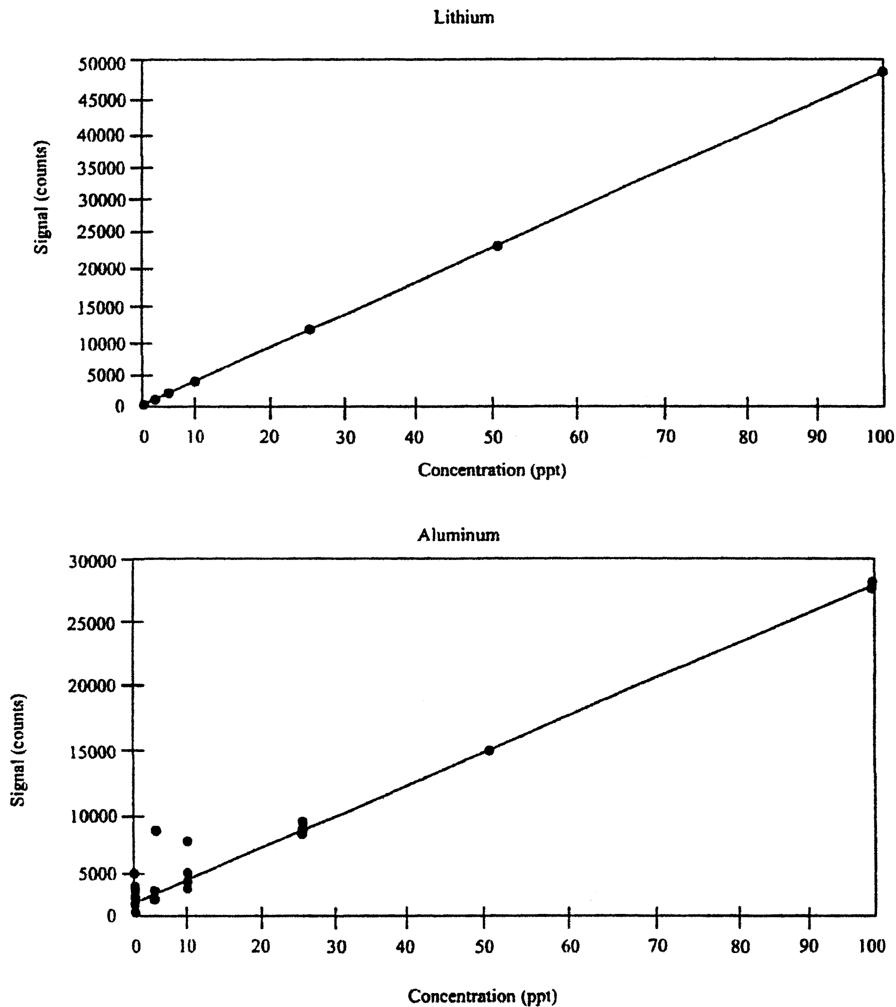

Figure 3
Element-specific count-rate deviations

A: component 1 (interface cone)

B: component 2 (plasma torch)

C: component 3 (spray chamber)

D: component 4 (nebulizer)

E: cleaning time

F: stabilization time

G: measurement points (sampling q/m)

H: integration time

I: spectrum scan

K: probe cleaning

L: error

The L_{12} layout has enough space for the parameters and additional error calculations. The calibration series are prepared with concentrations of (ppt).

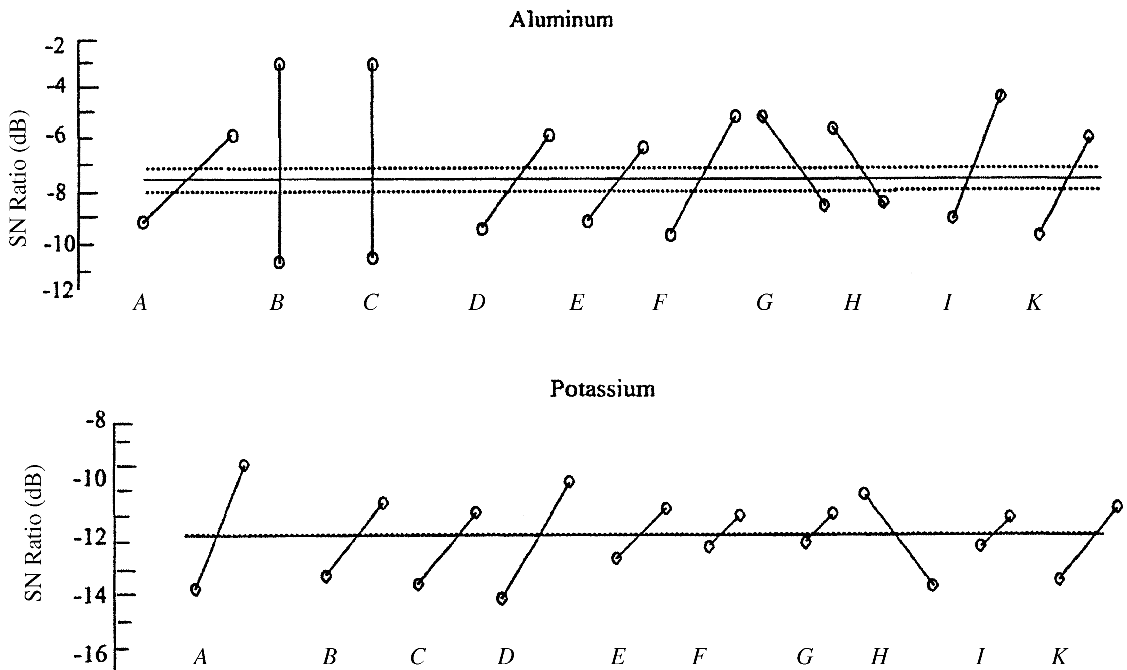

Figure 4
Results for aluminum and potassium

2.5 5 10 25 50 100 blank 1 blank 2

for two noise conditions (four combinations): long-term stability and dilution steps. In total, 12 experimental configurations (L_{12}) are carried out for eight samples with four replications (two noise factors) and one repetition; in each case 21 elements (under cold plasma conditions) are characterized, resulting in 16,128 calculations.

5. Data Analysis and Interpretation

System function is of type I: $Y = \beta M$ (M = signal factor, concentration of elements; β = slope) or of type II: $Y = \beta M + t$ (t = offset, sources of noise). The preparation conditions (long term/dilution) proved to be very stable and the SN calculations were performed for all noise conditions with the appropriate function. Surprisingly, the parameter effects for all elements were identical for the sensitivity of the count rate (slope); effects on the slope deviation were element-specific. Results are presented for selected elements, classified for environmental occurrence: for example, Al and K compared with Li and Co (Figures 4 and 5).

SN Linear Function

In a coarse estimation, hardware parameters *A* to *D* (i.e., equipment components) have a greater influence than parameters *E* to *K*, which define measurement mode and preparation techniques. In addition, parameter settings for *E* to *K* have to be at the “low” level, which means short and quick measurements. For example, extended integration time does not improve the SN ratio of the output signal, because with increasing time and repeated cleaning procedures, the probability for contamination through the environment increases as well.

SN Zero-Point Proportional

Compared to the previous situation, the stronger effects are now from the software parameters, *E* to *K*,

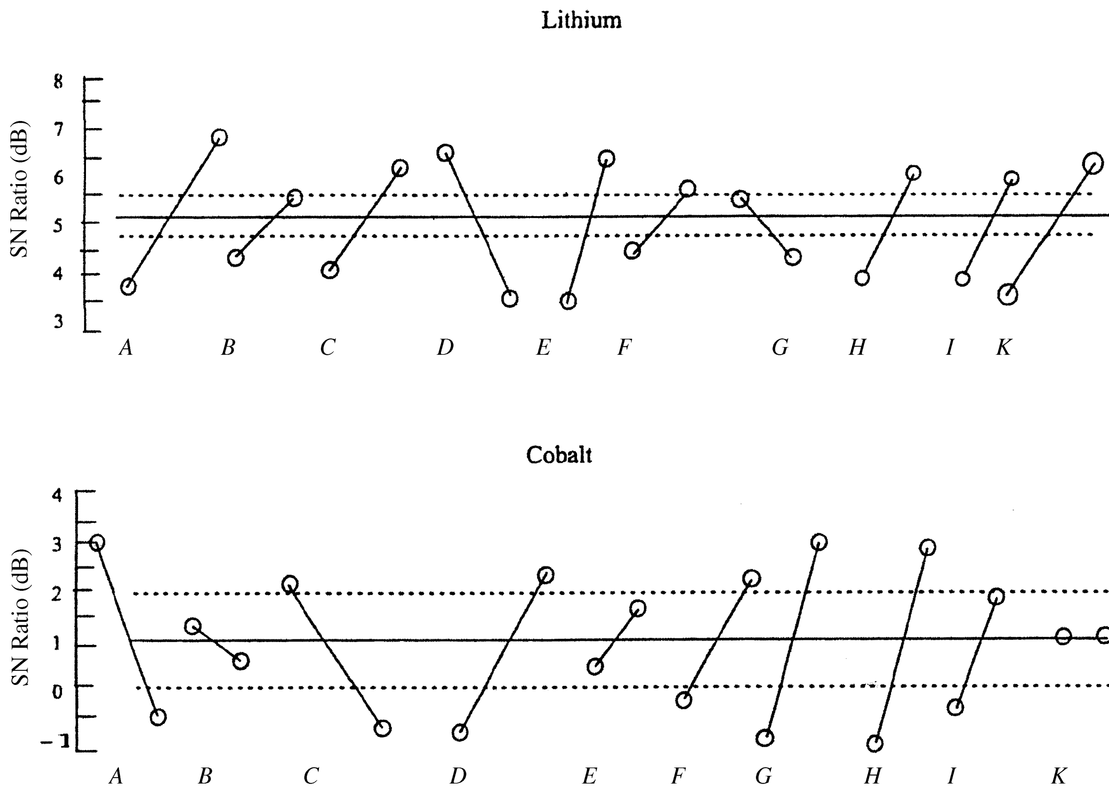

Figure 5
Results for lithium and cobalt

with a tendency toward increased integration time, higher measurement points, and enhanced cleaning procedures. Obviously, the risk of contamination from the environment is much less severe.

6. Prediction and Confirmation

Data analysis points out element-specific parameter settings due to individual occurrence in the environment and different ionization properties. If a specific element has to be detected at the lowest possible concentration, all parameters can be tuned element-specifically. More convenient is some type of average parameter setting that fits most important elements. Moreover, the interesting question is how low the detection limit appears for these parameter levels. Therefore, the real practical proof is reproducible detection at the lowest possible metal concentration predicted. For selected parameter settings, calculations are performed to predict the σ/β value of the linear function. This represents the tolerance (standard deviation) of element concentration; by convention three times this value is defined as the limit of detection. Results are presented in Table 1.

7. Conclusions

With appropriate tuned analytical equipment detection, limits below 1 ppt can be achieved for relevant metallic contaminations in ultrapure water:

Table 1
Predicted and confirmed detection limits (3σ) (ppt)

Element	Prediction	Confirmation	Element	Prediction	Confirmation
Ag	2	3	Li	0.6	1
Al	0.7	0.6	Mg	3	0.7
Ca	6	2	Mn	1.5	0.6
Co	2	0.6	Na	5	2
Cr	1	0.6	Ni	3	0.8
Cs	1	1	Pb	6	3
Cu	2	0.6	Rb	2	0.7
Fe	2	2	Sr	2	0.7
Ga	0.9	0.9	Ti	2	2
In	3	3	Zn	9	4
K	5	6			

0.1–0.2 ppt: Co

0.3–0.4 ppt: Al, Mg, Li, Cr, Mn, Rb, Sr, In, Cs

0.5–0.6 ppt: Fe, Ni, Ga, Ti, Pb

0.7–1.0 ppt: K, Zn, Ag, Cu, Na

Requirements in the semiconductor industry are thus fulfilled and can be guaranteed. Further improvements concern sampling techniques to benefit from this ultra-trace analytical capability. Future steps will lead toward new industrial cleaning procedures below the ppt level for the most important raw material: water.

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