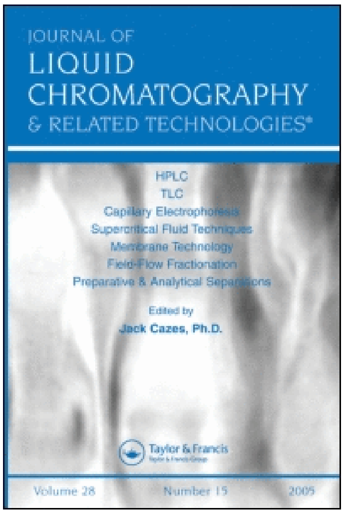

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# COMPARATIVE STUDY OF IONIC CONTAMINATION IN CLEANROOM WIPERS USING CAPILLARY ION ANALYSIS (CIA)

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## ABSTRACT

Several experimental approaches have been considered to address the problem of detecting and quantifying the ionic contamination in semiconductor cleanroom consumables such as wipers. A relatively new analytical technique called capillary ion analysis (CIA) appeared to us as an outstanding and convenient tool for the separation and quantification of both cationic and anionic species present in cleanroom wipers. Multiple wipers were used for extraction in high-purity deionized water to derive better sampling averages, as well as to enhance the levels of ions in solution. The resulting extract solution was preconcentrated by evaporation to further increase the signals from the released ionic species.

The instrumental capability was checked by estimating the limits of detection (LOD), as well as, limits of quantification (LOQ). For cations, LODs were as low as 0.05 µg/mL or 50 ppb; while for the anions, LODs were 0.1µg/mL or 100 ppb. A recovery study was conducted to determine the efficiency of the technique for ion removal from wipers. The study was also done to prove that for the detection of extremely low levels of ionic contamination, fluorinated plasticware is preferable over glassware to avoid risk of sodium contamination.

## INTRODUCTION

In the semiconductor and data storage industries, it is of utmost importance to control even the minute quantities of microcontaminants, such as particles and ions, in the manufacturing process. It is now well understood that a microelectronic device can fail not only because of the presence of “killer particles,” but also because of the ionic content in those particles. The ions can inadvertently dope the silicon wafer, interfere with the growing of the epitaxial layer, increase the rate of corrosion, and adversely affect the disk drive components and assemblies by creating read/write errors and disk failures. One critical source of ions is from consumables such as wipers used for controlling microcontamination in cleanrooms.

As wiping materials become cleaner, the ability to accurately measure the minute quantities of ionic content in the wipers is an increasing challenge. As the levels of ions in wipers are now well into the sub-ppm range, more sensitive and accurate measurement techniques are required to identify and quantify arrays of both cations and anions.

Capillary ion analysis (CIA), a technique derived from capillary electrophoretic (CE) methodology, currently has emerged as a powerful new analytical tool for the separation and quantification of both types of ions. The CIA instrumentation offers speed, automation, precision, high resolution, and the ability to quantitate extremely small sample volumes at ultra low concentrations. The technique is capable of delivering results equivalent to ion chromatography (IC), but with certain definite advantages such as faster analysis times. While the first separation of metal ions by capillary electrophoresis is 30 years old,[1] only recent advances in CE instrumentation have made it adaptable to both cation and anion analysis. The CIA technology itself has been addressed elsewhere[1-3] in detail in several previous publications.

The intent of this paper is not to discuss the technique itself, but to illustrate how the technology has been methodically applied in detecting and quantifying both cations and anions[4-6] that ordinarily could not be detected in clean room wipers by CIA. To improve the detectability of ions in the wiper samples, we found it necessary to increase the amount of material for individual testing, as well as to employ a more rigorous method for extracting the entire ionic content into solution. We presoaked the sample materials in high-purity deionized water at elevated temperatures for a period of time and followed this with evaporation/preconcentration of the resulting extract solution.

We evaluated and compared ions in five different wipers. They represent several manufacturers of wipers primarily used in critical environments. All the selected wipers were made from knitted, continuous-filament polyester material with hot-cut or border-sealed edges.

## EXPERIMENTAL

### Equipment and Materials

The study was conducted using a capillary ion analyzer that was equipped with a UV detector and power supplies of different polarities. The particular instrument, Model Quanta 4000E, was procured from Waters Corporation, Milford, MA. Polyimide-coated fused silica capillaries having 75 µm inside diameters and 60 cm in length, also purchased from Waters, were used as separation columns.

All other chemicals needed for the preparation of electrolytes, pH controls, and rinsing of capillaries were obtained from Waters. The sample bottles, Teflon PFA beakers, Eppendorf volumetric pipettes, clean room gloves, hot plates, and vacuum pumps were purchased locally from PCI Company, Fairfield, NJ. The membrane filtration apparatus and filters were obtained from Millipore Corporation, Bedford, MA. Ion standards, each 1,000 ppm solution, were obtained from High Purity Standards of Charleston, SC. A horizontal laminar flow Class 100 workstation and a source of very clean deionized water were used for all sample preparation.

### Experimental Overview

Separation of ionic species by CIA is based on differential migration under the combined effects of electrophoretic mobilities and electro-osmotic flows generated by the electric field across the capillary. Detection is based on indirect UV absorption. Anion-to-cation measurement modes were achieved simply by changing the polarity of the power supply so that capillary walls could attract positive ions instead of negative ions. Appropriate high-voltage power supplies and detection wavelengths of appropriate optical filters were used to switch from anion to cation runs. For the anions, we used negative 15 KV as the electrical power source and 254 nm as the detection wavelength. For cations, the corresponding numbers were positive 20 KV and 184 nm. We found it convenient to use separate capillaries for cations and anions.

The steps needed to accomplish ion analysis by CIA included preparation of proper electrolytic solutions, working standard solutions, and sample solutions of appropriate concentrations. The sample solutions prepared for the anion analysis were directly used for the cation analysis and vice versa. All experiments were run at a standard temperature of 25°C (+/-0.5°C).

After each CIA run, linear regression analysis was performed by plotting peak areas (y-axis) against corresponding ionic concentrations (x-axis) and determining the slopes by automatic data processing.

The quantification of the ionic concentrations in each wiper sample were determined by comparing the responses (peak areas) to the standard in the calibration curve and then compensating by the factor obtained by preconcentration.

## Experimental Procedure

The procedure consisted of preparing electrolytic solutions, working standards solutions, and sample wiper extract solutions; pre-concentrating the extract solutions; running samples in CIA; and quantifying ionic concentrations using computer software. Since several of these steps are part of instrumental routines, we will describe them only in summary and spend more time discussing important steps pertaining to actual ion analysis.

In CIA runs, vials containing various solutions are first placed in a sample carousel. The carousel contains 20 positions for the sample vials and four for the electrolyte solutions. The first four sample positions are used for vials with different concentrations of all the standard solutions, each diluted with deionized water. As an example, standard chloride solutions have concentrations of W, W/2, W/4, and W/8 respectively, where W is 2 ppm. The other positions are filled with vials containing deionized water and all samples to be determined, plus a vial containing system blank solution.

The loaded carousel is placed at the injection end of the capillary inside the CIA instrument. The analysis of anions in wipers included $Cl^-$, $SO_4^{-2}$, $NO_3^-$, $F^-$, and $PO_4^{-3}$ ions. The analysis of cations in wipers included $Na^+$, $K^+$, $Ca^{+2}$, $Mg^{+2}$, and $Li^+$. Ion standards included solutions of W (1 ppm), W/2, W/4, and W/8 of these ions.

The appropriate electrolyte solutions are placed in the locations specially designated in the carousel. The electrolytes along with buffers are used to facilitate the transportation of ions present in a sample solution across the capillary and the UV detector. The chemical composition of the electrolyte solutions is different for anions and cations. For example, the composition of the working electrolyte solution for the anions is as follows:

4.7mM Sodium Chromate;
4.0mM Waters OFM-OH;
0.1mM Ca Gluconate;
10.0mM CHES buffer solution, at pH = 9.1,

where OFM is the abbreviation for osmotic flow modifier. The chemical used for the OFM is tetradecyltrimethyl ammonium hydroxide. CHES is the abbreviation for 2-[-CycloHexylamino]-Ethane Sulfonic Acid.

The composition of the working electrolyte solution for the cation is as follows:

5.0mM Methylbenzyl Amine;
6.5mM Hydroxyisobutyric Acid;
2.0mM 18-Crown-6 ether, at pH = 4.5.

The method also utilizes a receiving carousel having six sample positions. In hydrostatic mode, four of the positions correspond to the specific electrolyte solutions similar to those used in the injection end. The fifth position is reserved for holding a bottle of deionized water. The water bottle serves as a waste reservoir for purging the capillary alternately after each sample injection. The sixth position is not used in the hydrostatic mode.

Capillaries are prewashed with 0.1M HCl for 10 minutes before running cations, and with 0.1M KOH before anion runs. After prewashings, the capillaries are rinsed with deionized water for 2 minutes and then equilibrated with the respective electrolyte solutions for 10 minutes.

### Preparation of Sample and System Blank Solutions by Preconcentration

The procedure for the extraction of ions from the wipers involves placing several preweighed (total weight 50–70 g) wipers in a PFA beaker containing 750 mL of hot deionized water (-70°C) for a period of 15 minutes, while prodding and stirring periodically using a Teflon rod. At the end of the soak period, the residual water in the wipers is mostly squeezed out by pressing against the flat bottom part of a precleaned plastic bottle. The extracted solution is recaptured in another PFA beaker. The squeezed wipers are taken out of the beaker and discarded. The total extract solution is then concentrated to a volume of less than 50 mL through evaporation, and the weight of the extract solution is determined. The weights of the dry wipers and the final extract solution are used in the final calculation.

The idea of preconcentration is to enhance the detection of all the ionic species, which were otherwise very low for accurate detection by CIA in the hydrostatic mode. In all extractions, a parallel preconcentration process is run by evaporating 750 mL of deionized water only (no wipers) to a final volume of less than 50 mL using the same PFA beaker. This water is used as a system blank solution and run, along with the respective wiper extraction solution, in CIA. The data are used for the background correction. The preconcentrated sample solution is injected hydrostatically into the capillary. The volume of the injected solution in the capillary is in the range of 10 nL (nanoliters). Anions and cations from the same extract solution are run separately by using an appropriate high-voltage power supply and appropriate dedicated capillaries. The electropherogram showing the array of ions is recorded in each case and analyzed separately using the computer software.

## RESULTS AND DISCUSSION

Since the idea of quantifying ions in cleanroom wipers by CIA was rather novel, we had to verify the reproducibility and overall effectiveness of the procedure by developing and understanding of:

1. The limits of detection (LOD) and limits of quantification (LOQ)
2. The extent of preconcentration of the sample solution to enhance detectability by at least an order of magnitude.
3. The ionic contribution from the sample preparation equipment (system blank).
4. The efficiency of the extraction process by recovery study.

A discussion of the above items follows.

### Determining Limits of Detection (LOD) and Limits of Quantitation (LOQ)

Detection limits of both cations and anions are obtained by running several ppm and sub-ppm range standards of the respective ions and performing the calibrations for each ion. Over time, we compared all the individual calibrations, their respective slopes, and the y-intercepts statistically to determine the detection limits using CIA in the hydrostatic mode. Typically, for cations, LODs are as low as 0.05 µg/mL or 50 ppb; and for the anions, LODs are 0.1 µg/mL or 100 ppb. Although the procedure firmly establishes the detection limits, we found it more accurate to calibrate the instrument using respective standard solutions prior to each sample run.

### Determining Extent of Preconcentration of the Sample Solution to Enhance Detectability by an Order of Magnitude

Wipers made from natural fibers (e.g., cotton or cellulose-based) and from various composite materials are usually high in ionic content. The procedure for the extraction of ions from these wipers requires only 15 minutes soaking in deionized water at 70°C, followed by injection of extracted solution in CIA using hydrostatic mode. However, for high-end clean room wipers (in particular those made from knitted, continuous-filament polyester materials), the ionic residues are very low, usually in the sub-ppm range. CIA technique is not able to detect or accurately determine such a low level of ionic contaminants. We found it necessary to improve the detectability by extracting multiple wipers and then pre-concentrating the extracted solution by evaporation prior to the injection.

Our method of preconcentration provides an improvement factor of close to 20 in detectability, thereby significantly enhancing the ability to quantify even trace amounts of ions present in very clean clean-room wipers. The electropherograms of anions from wiper samples both with and without preconcentration (Figure 1A) and again for cations both with and without preconcentration (Figure 1B) clearly depict the importance of preconcentration in detecting very low levels of ions by CIA.

Both sets of electropherograms reveal that without the preconcentration, the CIA technique in hydrostatic mode is capable of detecting only a fraction of total ionic content. The level of detection and the number of ionic peaks are enhanced substantially after preconcentration.

### Determining Ionic Contribution from Sample Preparation Equipment

This determination is achieved by comparing extracts of deionized water boiled in a glass beaker with extracts of deionized water boiled in a Teflon PFA beaker. Both beakers are filled with 750 mL of deionized water and placed on a hot plate, where the volume in each is reduced close to 30 mL. Both cations and anions are examined. In cationic runs, appreciable response is observed from the sample solution prepared in the glass beaker, and the response peak is identified as sodium ion by the comparison with the peaks from the standard solutions. We believe this is due to slow leaching of the sodium silicate component of the glass material during the hot extraction process. No such peak is observed from the sample prepared in the PFA beaker. The result is very convincing and leads us to use PFA beakers for all sample preparations, especially when boiling is involved, to avoid cross contamination from glassware.

### Determining the Efficiency of the Extraction Process by Recovery Study

In order to develop confidence with the overall technique, we tested the effectiveness of the extraction and preconcentration processes by intentionally contaminating the wipers with known amounts of chloride and sodium ions. We then performed the recovery test by extracting those ions and determining the individual ion concentrations in the extracted solution using CIA.

First, sorption capacity of the test wipers is determined to establish the half saturation point. A 5.0 μg/mL chloride solution is prepared using pure NaCl salt. An aliquot of 6.0 mL (determined from half sorption) is added to each of the 10 wipers, resulting in the total addition of 60 mL solution, or 300 μg Cl-. For sodium, the equivalent addition results in a total of 194.5 μg for the 10

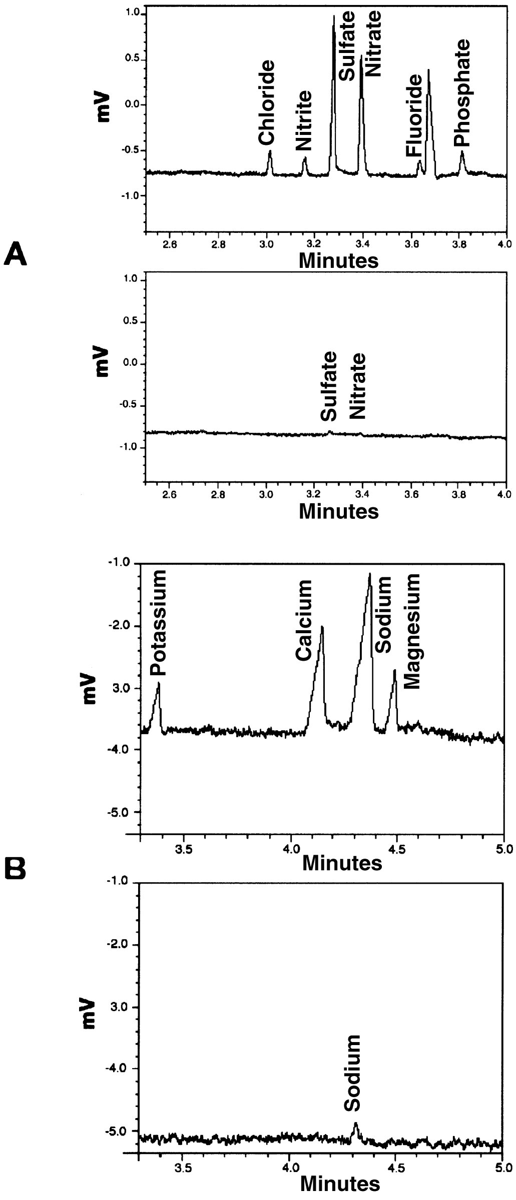

**Figure 1**. A: Anion Electropherograms, Top: sample solution after preconcentration, Bottom: normal sample solution; B: Cation Electropherograms, Top: sample solution after preconcentration, Bottom: normal sample solution.

wipers. The wipers are allowed to dry in a Class 100 workstation. The total weight of the wipers is recorded after drying as 60.81 g.

The extraction process is then conducted on these wipers for 15 minutes using 750 mL deionized water at 70°C, followed by preconcentration by evaporation, as described earlier. The final volume was adjusted close to 20 mL. Theoretically, this solution should contain slightly higher than 300/20 μg/mL or 15 ppm of chloride ions and 194.5/20 μg/mL or 9.73 ppm of sodium ions. Any additional amounts should be proportional to the actual chloride and sodium ions inherently present in the wipers as contaminants.

The final theoretical values for chloride (15.44 μg/mL) and for sodium (10.21 μg/mL) are obtained by adding the ion values inherent to the wipers ($Cl_-$ = 0.44 ppm and $Na^+$ = 0.48 ppm).

The above solution is run in CIA to determine the actual $Cl^-$ and $Na^+$ ions recovered by the extraction process. From the peak area in the anion electropherogram (see Figure 2A), the concentration of $Cl^-$ is calculated to be 14.84 ppm. The result suggests 98% recovery in the case of $Cl^-$. From the peak area in the cation electropherogram (see Figure 2B), the concentration of sodium is calculated to be 8.35 ppm, which means 82% recovery in the case of $Na^+$. The electropherograms under both figures represent respective ions with another batch of "wipers only, no spiking" conditions.

Considering the extent of precision needed to perform this particular microanalysis technique, the recovery results are very convincing and provide us with great confidence in methods of extraction and subsequent accurate quantification of ions.

## Determining Ion Contents in Cleanroom Wipers

Based on the methodologies and experimental observations on LODs, the preconcentration of solutions, and the recovery study, we learned that the CIA technique indeed can be used with a high degree of reliability for accurate determination of ionic content of cleanroom wipers.

Examples of typical electropherograms for both anions and cations as seen in a cleanroom wiper analysis are shown in Figures 3A and 3B (standards and a sample wiper). The electropherograms of all the individual wipers are not shown here, but basically they have similar formats varying only in peak heights and areas.

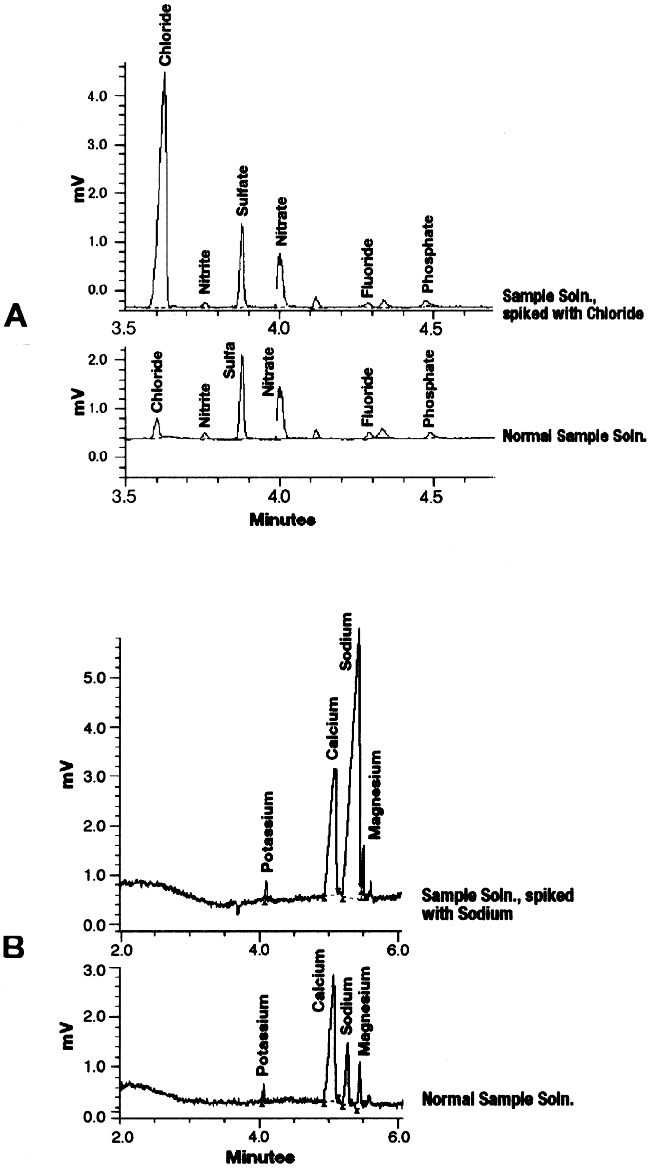

**Figure 2**. A: Anion Electropherograms, Top: solution spiked with chloride, Bottom: normal sample solution; B: Cation Electropherograms, Top: solution spiked with sodium, Bottom: normal sample solution.

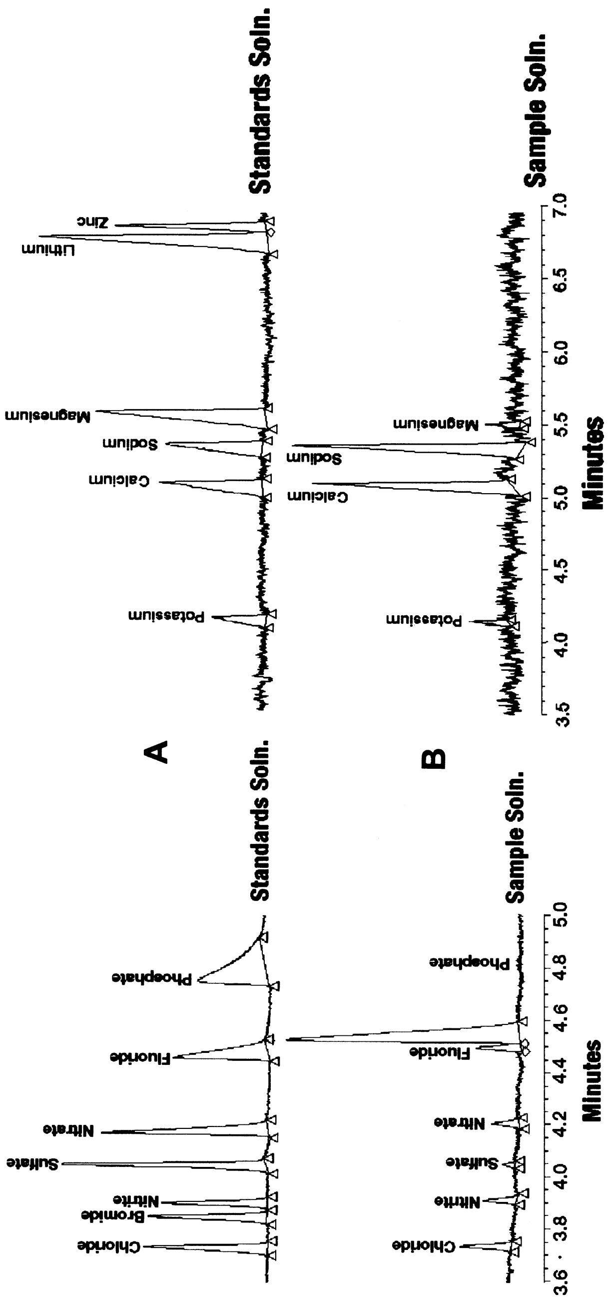

**Figure 3.** Typical electropherograms for standards and sample solutions.A: Anion Electropherograms, B: Cation Electropherograms.

### Examples of Calculation of Ionic Contents in Samples

From the resulting peak areas of individual ions in the standard solutions, a linear regression line was generated for each ionic species by plotting concentrations on the abscissa and corresponding areas on the ordinate.

Concentration of an ion in the unknown sample was obtained using individual peak area and the slope and intercept of the calibration curve. For example, if the linear plot of the standard solutions provides a slope with a value of 998 and intercept value of 85 and the $Cl^-$ (chloride ion) in the wiper sample shows a peak with an area of 492, then the concentration of chloride ions is:

$[Cl^-] = (492-85)/998 = 0.408$ ppm = 408 ppb.

The above number when multiplied by the extraction ratio, R, converts the concentration value to per gram of the wiping material, where,

$$R = \frac{\text{(Weight of final extract solution)}}{\text{(Total weight of wiper materials)}}$$

Typically R is between 0.5 to 1.

Assuming R = 0.5, $[Cl^-]$ in sample wiper = 0.408 x R = 0.204 ppm = 204 ppb.

The preceding calculation is applicable to all other anions detected in the wiper sample solution.

The calculation for cations in wipers by CIA is similar to that described for anions, except that the slope and intercept are determined by plotting the resulting peak areas of a particular cation such as sodium against standard sodium concentrations. The peak area of a particular cation obtained from the wiper sample solution is then utilized the same way as shown above to determine the concentration of that ion in ppm or sub-ppm.

Table 1 shows the values of anions from five wiper samples. Table 2 shows the values of cations from the same five wiper samples.

The current study reveals that in order to obtain an accurate picture of the soluble ionic contaminant in a cleanroom wiper, one must examine the full range of ions. The CIA method is capable of providing a broad picture of total ion content. From the above results it would be difficult to conclude which cleanroom wiper has overall lowest ionic contamination; however, a conclusion on contamination risk can be drawn through comparison of the individual ions.

**Table 1**

**Anions* (in ppb)**

| | **Chloride** | **Sulfate** | **Nitrate** | **Fluoride** | **Phosphate** |
|---|---|---|---|---|---|
| Wiper A | 267 | 363 | 134 | 13 | 49 |
| Wiper B | 255 | 153 | 55 | 5 | 31 |
| Wiper C | 204 | 127 | 50 | 23 | 11 |
| Wiper D | 524 | 107 | --- | 15 | 58 |
| Wiper E | 262 | 459 | 947 | --- | 77 |

---

*** The results are for the wipers from the same bag, and each number is an average of three experimental runs. The marker (---) means below detection limits.**

Based on this information, a user can decide which wiper would meet specific requirements. While concentrations of sodium and chloride ions in wipers are most closely scrutinized, other anions and cations can be extremely detrimental to the critical manufacturing process. The semiconductor industry, in general, prefers to use wipers with the least amount of overall ionic burden to avoid any contamination risk from the disposables.

## CONCLUSION

A new comprehensive test method for measuring ionic contaminants was used to compare samples of five different knitted polyester cleanroom wipers.

**Table 2**

**Cations* (in ppb)**

| | **Potassium** | **Calcium** | **Sodium** | **Magnesium** | **Lithium** |
|---|---|---|---|---|---|
| Wiper A | 132 | 844 | 394 | 72 | --- |
| Wiper B | 37 | 221 | 247 | 57 | --- |
| Wiper C | 63 | 231 | 270 | 7 | --- |
| Wiper D | 93 | 141 | 209 | --- | --- |
| Wiper E | 86 | 414 | 552 | 40 | --- |

---

*** The results are for the wipers from the same bag, and each number is an average of three experimental runs. The marker (---) means below detection limits.**

By examining the merits and drawbacks of CIA, we concluded that the method provides an excellent technique for the accurate measurement of both cations and anions and is very useful in routine determination of the true ionic burdens in cleanroom wipers. The procedure for sample preparation and subsequent data analysis is very time consuming and requires a good deal of precision and expertise. We made our sample preparation technique more robust to improve the level of detection by more than an order of magnitude and also to enhance run-to-run reproducibility. The study has been designed to accurately determine the ionic contamination risk imposed in the selection of cleanroom wipers.

## REFERENCES

1. S. Hjerten, "Free Zone Electrophoresis," Chromatogr. Review, **9**, 122 (1967).
2. P. Jandik, G. Bonn, **Capillary Electrophoresis of Small Molecules and Ions**, VCH Publishers, New York, 1993.
3. M. Chen, R.M. Cassidy, "Separation of Metal Ions by Capillary Electrophoresis," J. Chromatogr., **640**, 425 (1993).
4. P. Gupta, S. H. Tan, "Capillary Electrophoresis Analysis of Metal Ions in High Purity Water, Ultrapure Water, **11**, 54 (1994).
5. G. Bondoux, P. Jandik, W. R. Jones, "New Approach to the Analysis of Low Levels of Anions in Water," J. Chromatogr., **602**, 79 (1992).
6. P. E. Jackson, P. R. Haddad, "Optimization of Injection Technique in Capillary Ion Electrophoresis for the Determination of Trace Level Anions in Environmental Samples," J. Chromatogr., **640**, 481 (1993).

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