Big Problems with Small Ions

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Introduction

Cleanroom personnel are well aware that they must be vigilant against small items that can ruin manufacturing processes – entities like particles, fibers, bacteria, and viruses. But, even smaller contaminants – ions – can wreak havoc in electronic products made in highly efficient cleanrooms. The bad news is that ions in these microelectronic environments can ruin products worth hundreds of thousands of dollars. There's no real good news, except that the problem is confined to the electronics industry. Healthcare companies that manufacture products such as pharmaceuticals, biologics, and biomedical devices get a free pass on the ion problem. Ion levels normally found in cleanrooms in these industries are rarely a problem since ions don't compromise the end product in any material way.

How Small Is Small?

So, what exactly is the problem for the electronics industry? To get a better understanding, let's compare various contaminants by size. Particles can range from hundreds of micrometers (μm) down to fractions of a micrometer. Remember, 1 micrometer = 0.00004 inches. The eye can typically resolve items as small as 50 μm (i.e., 0.002 inches). By comparison, the E. coli bacterium is about 2 μm in size, while the infective Ebola virus can be as small as 1 μm. The ions that cause electronic problems can be as small as 0.0001 μm (sodium ion) in size – approximately one thousandth the size of the smallest detectable particles and totally invisible to the naked eye or even to the best scanning electron microscope.

Mobile Ion Contaminants

The very small size of these ions permits them to enter the electronic transistor devices and compromise device performance. The "nano" size of these contaminants also permits them to migrate through the device (usually a transistor) in a Murphy's Law type of behavior to find the area where they can cause the most damage. Since they can move so easily, they are called "mobile ion" contaminants. To compound the problem (no pun intended), the positively charged ions (cations) are accompanied by negatively charged ions (anions) to ensure that electrical neutrality is maintained; thus, doubling the danger.

To illustrate: imagine that a single sodium ion accompanied by a single chloride ion finds its way onto and into a semiconductor device. The sodium ion can penetrate the transistor gate (the portion of the transistor that controls the flow of electricity through the device – hence the name "gate"), and while that's happening, the chloride ion can nestle down onto the electrical wiring that connects the various layers in the device and cause corrosion. Double danger.

Enter the Periodic Table

These are just two of the problems that ions can cause with transistor devices. There are many others. Consequently, microelectronics manufacturers are diligent about specifying extremely low levels of ions in the chemicals and consumables that they use in their processes. Typically, they worry about the presence of ions of the alkali metals (sodium and potassium), the alkaline earth metals (calcium and magnesium), and the transition metals (copper, nickel, zinc, and iron) to name just a few examples. All of these metallic ions are positively charged (i.e., they are all cations). As noted, positively charged ions must be accompanied by an equivalent number of negatively charged ions – anions – to provide electrical neutrality. Typical anions that provide this balancing of charge are chloride, nitrate, and sulfate ions, all of which are also of concern to the microelectronics manufacturers. It is not uncommon for manufacturers to specify ion levels in the low ppb range for the chemicals and consumables that they purchase.

How Low Can You Go?

The challenge for suppliers to the microelectronic industries is that they must ensure that their raw materials and internal processes can produce end products with ion levels at the absolute minimum. To accomplish that, suppliers must monitor both their raw materials and their end products for ion levels on an ongoing basis. If there is a requirement that the end product can contain no more than 10 ppb of sodium ion, that means that detection capability of 10 nanograms of sodium ions in 1 gram of product is needed. Expressed another way, that is equivalent to about 1 ounce of sodium ions in 3000 tons of product! Fortunately, two types of instrumentation – ion chromatography and inductively coupled plasma mass spectrometry - are available that are capable of ion measurements down to the low parts per billion (ppb) range or even below.

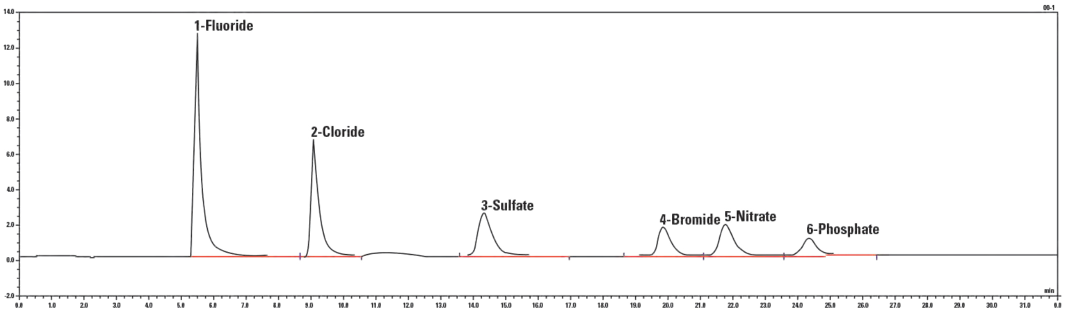
Ion Chromatography

Ion chromatography (IC) is simple in concept. A liquid sample containing the ions of interest is injected onto a column containing an adsorbent material. The ions in the sample have different levels of affinity for the adsorbent material – that is, they bond more or less strongly to the adsorbent material. As the ions move down the column, they separate into bands – sodium ions in one band, calcium ions in another band, etc. When these various bands exit the column, they are detected by a sensor that indicates how much of each ion is present in the sample. Thus, the method provides qualitative and quantitative information as to the ion profile in the sample. Furthermore, both anions and cations can be detected in the sample by using different types of columns. The cations best determined by IC are the alkali metals and the alkaline earth metals, as well as ammonium ion. For the cations, the order of appearance is lithium, sodium, ammonium, potassium, magnesium, and calcium – six cations identified and quantitated in one scan. For the anions, the order of appearance is fluoride, chloride, sulfate, bromide, nitrate, and phosphate – again 6 ions detected. Typical IC instrumentation is pictured in Figure 1, and typical IC scans are shown in Figure 2.

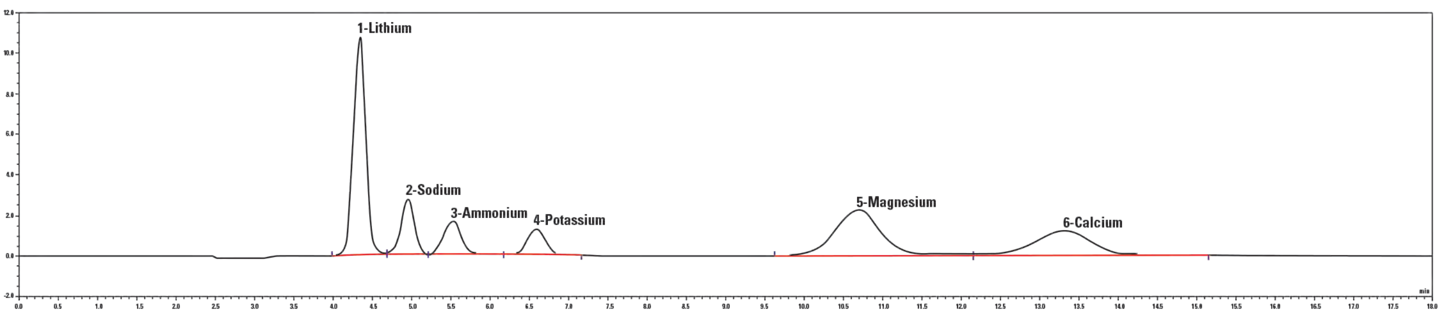
Figure 1.

Figure 2:

Anions



Cations



Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICPMS) is a more complicated technique. A liquid sample containing the ions of interest is introduced into the instrument. In a sequential series of steps, (i) the liquid is evaporated, leaving behind the ions in solid form, (ii) the metallic constituents of the solid are converted back to ions by the plasma, (iii) the metallic ions are separated based on their characteristic mass-to-charge ratio by a device known as a quadrupole, and finally, (iv) the ions are detected by a sensor that responds to the amount of ions present. Thus, ICPMS also provides qualitative and quantitative information as to the ion profile in the sample. While the ICPMS can provide analytical information only on the metals in the sample, it has greater sensitivity than the IC device and can provide measurement capability for the transition metals (iron, copper, chromium, etc.) as well as the alkali and alkaline earth metals.

Analyzing Ions in Wipers

Cleanroom wipers are ubiquitous in controlled environments. Cleanroom wipers do for surfaces what HEPA filters do for air – they keep the cleanroom clean. Cleanroom wipers must have an extremely low ion profile since they come into contact with environmental and production surfaces. The protocols for analyzing ions in wipers have been established over many years and are fairly well standardized.

For water-soluble ions – the alkali metals ions and alkaline earth ions described above – the wipers are extracted with ultrapure water for 30 minutes and then the water extracts are analyzed by IC or ICPMS. If transition metals are to be determined, then the wipers are extracted with a dilute acid in order to dissolve those metals. The acid extract is then analyzed by ICPMS.

Obviously, great care must be exercised in preparing the wiper extracts in order to prevent extraneous ion contamination from elevating the true ion levels originating from the wiper.

When wipers are processed to reduce ion levels to the greatest degree, it is possible to achieve ion profiles as follows:

Sodium	0.001 ppm
Potassium	<0.001 ppm
Calcium	0.007 ppm
Magnesium	<0.001 ppm
Chloride	0.042 ppm

These may well be the lowest ion values achieved for cleanroom wipers.

Summary

The issue of ion contamination in microelectronic manufacturing is of critical importance because electronic device failures have been directly linked to the presence of trace levels of ions. Because wipers are so widely used in the cleaning and maintenance of cleanrooms and production and test equipment, it is incumbent on the wiper manufacturer to provide products with the absolute minimum levels of detectable ions. As the data above illustrates, this has been accomplished through (i) comprehensive understanding of the sources of ion contamination, (ii) fine tuning the production process, and (iii) incorporating the most sensitive analytical technology for accurate and reproducible measurements.