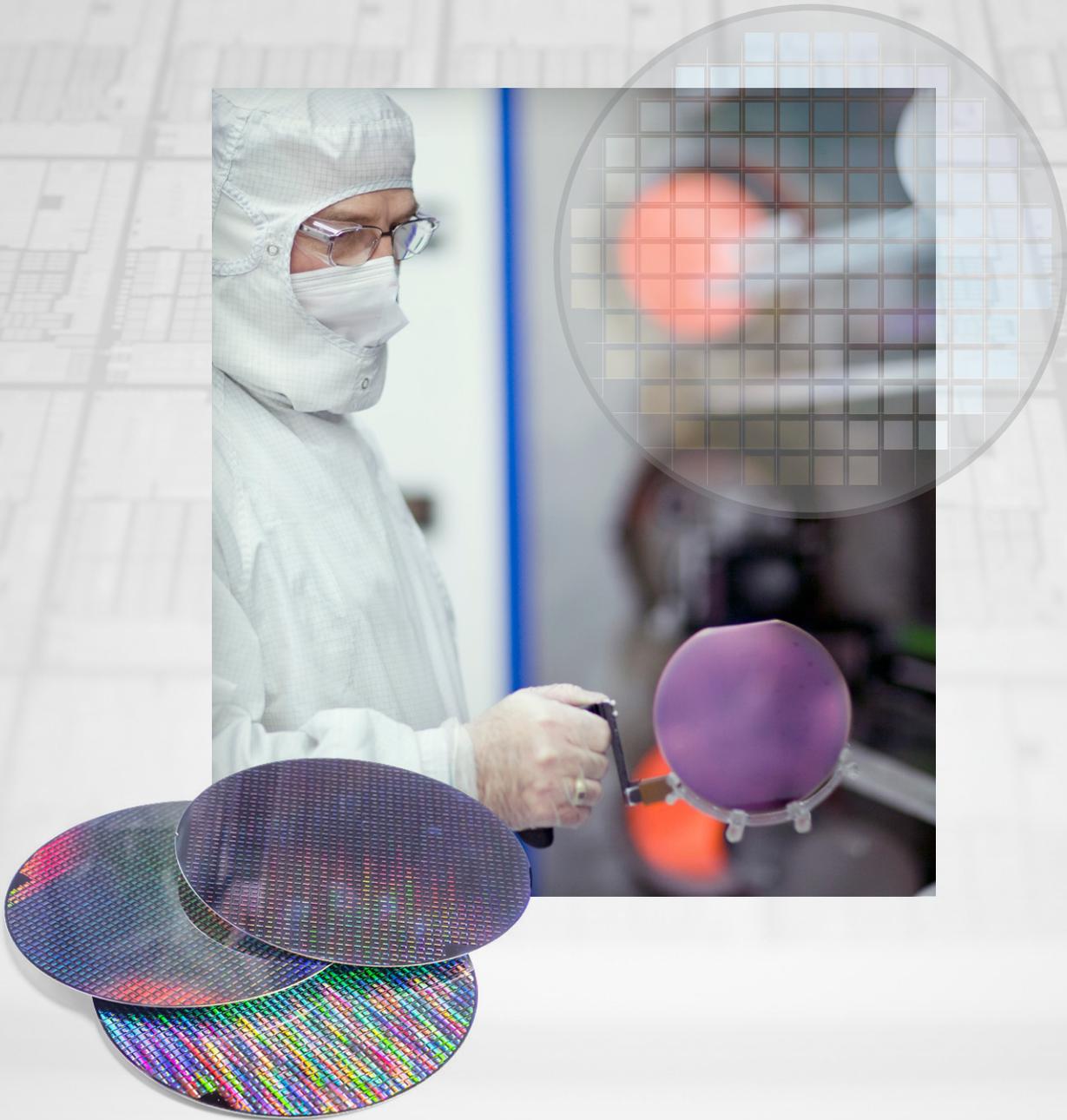


IC/SP industrial

Semiconductor workflows

Trace contaminant analysis





Improving yield in semiconductor manufacturing

Demand for semiconductor wafers will continue its vigorous growth as the demand for mobile devices, cloud computing, Internet of Things (IoT), automotive, artificial intelligence, and other uses increases. The complexity of the processes and costs of semiconductor fabrication (FAB) manufacturing are high, so the industry is always looking to improve production efficiencies.

Semiconductor wafer fabs environmental and quality control

Control of the process steps and wafer environment to meet the daily challenges of routine wafer compliance requires the use of many diverse characterization techniques, including many employing analytical instrumentation.

Thermo Scientific™ chromatography and spectrometry solutions are designed to monitor the semiconductor manufacturing process to ensure the highest possible yield.

Production environment induced wafer contamination

Monitoring the wafer manufacturing environment includes the evaluation and analysis of all media that the silicon wafers are exposed to that can adversely affect their manufacturing yield.

These include:

- Deionized (DI) water that is used as a rinsing agent throughout the fabrication of an integrated circuit
- Chemical reagents, acids, bases, and solvents that are used to clean wafer surfaces or etch wafer surfaces
- Inert and reactive gases that are used during ion implantation and deposition process steps
- Air in cleanroom and mini-environments throughout the entire manufacturing process

To minimize production environment induced wafer contamination, these gaseous and liquid media must be analyzed for particles, impurities, and specific contaminants including organics, trace metals, acids, and bases. Depending on the phase of the medium (gas, liquid, solid) and the nature of the contaminants to be monitored, different chromatography and spectrometry analytical techniques must be used.

Described below is an ion chromatographic method using the microbore Thermo Scientific™ Dionex™ IonPac™ Anion Exchange AS17 Column to determine trace concentrations of common inorganic anions, low molecular-weight organic acids, and acrylate, methacrylate, benzoate, and phthalate. These contaminants can come from some of the following sources: cleaning agents, adhesives, oils, mold release agents, and solder fluxes.

Column:	Dionex IonPac AG17, AS17, 2 mm	Peaks:	µg/L
Eluent:	1.0 mM potassium hydroxide for 3 min 1 to 12 mM from 3–10 min 12 to 20 mM from 10–14 min	1. Fluoride	0.61
Eluent source:	Dionex EG40	2. Acetate	7.0
Flow rate:	0.5 mL/min	3. Formate	1.5
Injection:	1 mL	4. Acrylate	3.7
Temperature:	30°C	5. Methacrylate	4.2
Detection:	Suppressed conductivity, Dionex ASRS ULTRA Gas-assisted recycle mode	6. Chloride	1.2
		7. Nitrite	2.0
		8. Bromide	3.1
		9. Nitrate	3.8
		10. Benzoate	7.0
		11. Carbonate	–
		12. Sulfate	2.1
		13. Oxalate	1.6
		14. Phthalate	10.8
		15. Phosphate	3.8

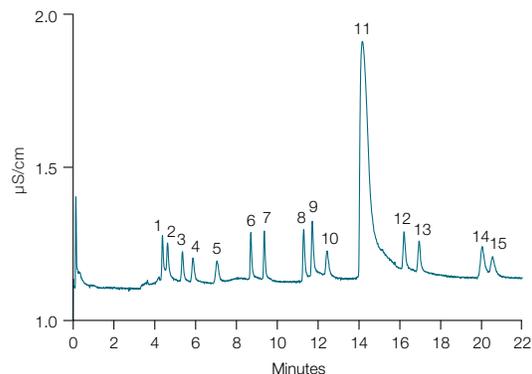
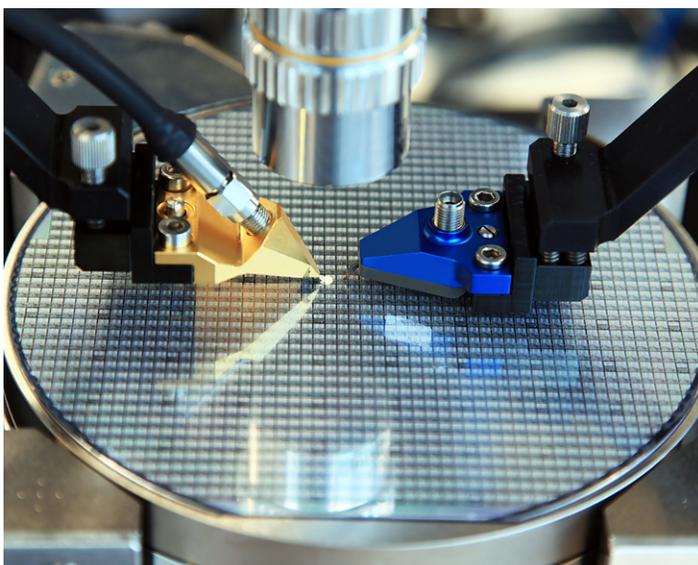


Figure 1. Trace anion determination using a Dionex IonPac AS17 column* with a separation time of 27 min.

* Newer equivalent columns may be used but must comply with its column manual, especially with the pressure limit.



Organic acid and inorganic residues from solder flux residues and other manufacturing processes can cause soft and hard failures in the printed circuit board (PCB). Below are two methods for improved determinations of residual anions and organic acids needed for printed circuit cleanliness. Method A and Method B shown here demonstrate alternative methods from those shown in Thermo Scientific Application Note AN1163 when it is not necessary to measure both succinate and malate.

Method A was optimized on a 2 mm i.d. Thermo Scientific™ Dionex™ IonPac™ AS11-HC Column without methanol, taking advantage of selectivity changes at 20°C and further optimizing the gradient to reduce the run time. Figure 2 shows the final conditions. All organic acids and inorganic anions of interest are fully resolved except succinate and malate (Peaks 8–9). These can be resolved using the conditions in Application Note 1163.

Method B demonstrates the impact of reducing the separation temperature or adding a methanol gradient on column selectivity. Method B followed the conditions in [Thermo Scientific Application Note AN1163](#) using a 2 mm i.d. Dionex IonPac AS11-HC column, but the methanol gradient was optimized to improve resolution. Figure 3 shows the final conditions. Adipate (Peak 8), nitrate (Peak 9), succinate (Peak 10), and malate (Peak 11) are not fully resolved.

Columns: Dionex IonPac AG11-HC guard,
Dionex IonPac AS11-HC analytical, 2 mm i.d.

Eluent source: Dionex EGC-500 KOH cartridge,
Dionex CR-ATC 600 trap column,
Dionex high pressure degasser

KOH gradient: 1 mM KOH (-5 to 9 min), 1–14 mM (9 to 16 min),
14 mM (16 to 23 min), 14–85 mM (23 to 30 min),
85 mM (30 to 32 min), 1 mM (32 min)

Methanol gradient: none

Flow rate: 0.38 mL/min

Injection volume: 5 µL

Column temp.: 20°C

Detector oven temp.: 20°C

Detection: Suppressed conductivity, Dionex ADRS 600, 2 mm,
external water mode by pump 2 @ 0.38 mL/min, 57 mA

System pressure: 2,600 psi (with ~800 psi backpressure tubing
between trap column and injection valve)

Run time: 38 min

Peaks:	mg/L		mg/L
1. Fluoride	2	9. Malate	10
2. Acetate	10	10. Carbonate	10
3. Formate	10	11. Bromide	10
4. Methanesulfonic acid	10	12. Nitrate	—
5. Chloride	10	13. Sulfate	10
6. Nitrite	10	14. Phosphate	20
7. Adipate	10	15. Phthalate	10
8. Succinate	10		

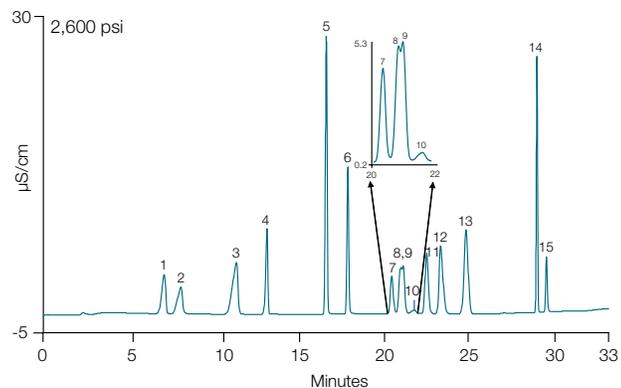


Figure 2. Separation of nine organic acids and seven inorganic anions within 38 min on a 2 mm i.d. Dionex IonPac AS11-HC column using a 20°C column temperature.

Columns: Dionex IonPac AG11-HC guard,
Dionex IonPac AS11-HC analytical, 2 mm i.d.

Pump 1 proportioning: A: DI water for eluent generation
B: Methanol for methanol gradient

Eluent source: Dionex EGC-500 KOH cartridge,
Dionex CR-ATC 600 trap column,
Dionex high pressure degasser

KOH gradient: 1 mM (-5 to 17 min), 1–15 mM (17 to 24 min),
15 mM (24 to 35.3 min), 15–60 mM (35.3 to 54.6 min),
1 mM (54.6 to 55 min)

Methanol gradient: 2% (-5 to 24 min), 2–10% (24 to 29 min),
10–15% (29 to 51 min), 15–2% (51 to 54.6 min),
2% (54.6 to 55 min)

Flow rate: 0.38 mL/min

Injection volume: 5 µL

Column temp.: 30°C

Detector oven temp.: 20°C

Detection: Suppressed conductivity, Dionex ADRS 600, 2 mm,
external water mode by pump 2 @ 0.38 mL/min, 57 mA

System pressure: ~2,100 (measured without backpressure tubing.)
~2,400 psi with 300 psi backpressure tubing

Run time: 60 min

Peaks:	mg/L		mg/L
1. Fluoride	2	9. Nitrate	10
2. Acetate	10	10. Succinate	10
3. Formate	10	11. Malate	10
4. Methanesulfonic acid	10	12. Carbonate	—
5. Chloride	10	13. Sulfate	10
6. Nitrite	10	14. Phosphate	20
7. Bromide	10	15. Phthalate	10
8. Adipate	10		

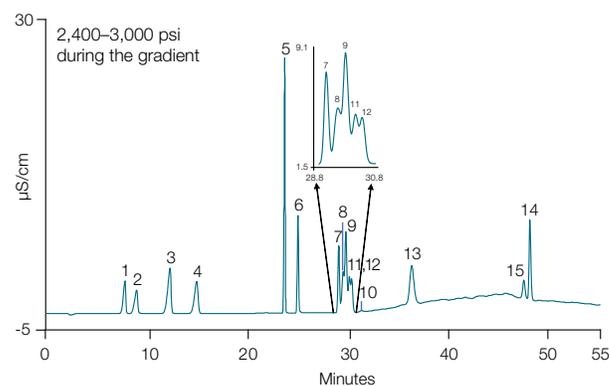


Figure 3. Separation of nine organic acids and seven inorganic anions on a Dionex IonPac AS11-HC column using methanol in the eluent.

The introduction of Thermo Scientific™ Dionex™ AutoNeutralization™ technology eliminated the need to dilute concentrated acids to avoid column overloading, and thus allowed the determination of µg/L and ng/L concentrations of anions and cations. Some cations can combine with anionic contaminants to form insoluble compounds that can cause plating and etching defects in plating and electronics manufacturing processes. The AutoNeutralization method was applied to determine trace cations in 25% phosphoric acid and 10% hydrofluoric acid (Figure 4). Spike recoveries were determined by standard addition using aliquots of diluted Thermo Scientific™ Dionex™ Combined Six Cation Standard-II.



Sample prep.	Analytical
Trap column: Dionex IonPac CTC-1, 9 x 24 mm	Column: Dionex IonPac CG16, CS16, 4 mm,
Carrier: Deionized water	Eluent: 28 mM Methanesulfonic acid
Carrier flow rate: 0.5 mL/min	Eluent source: Dionex EGC II MSA
Inj. Vol.: 100 µL	Flow rate: 1.0 mL/min
Temperature: 30°C	Temperature: 30°C
Neutralization: AutoNeutralize, Dionex CSRN II, external water mode, 500 mA	Detection: Suppressed conductivity, Dionex CSRS ULTRA II, recycle mode, 82 mA
	Concentrator: Dionex IonPac TCC-ULP1

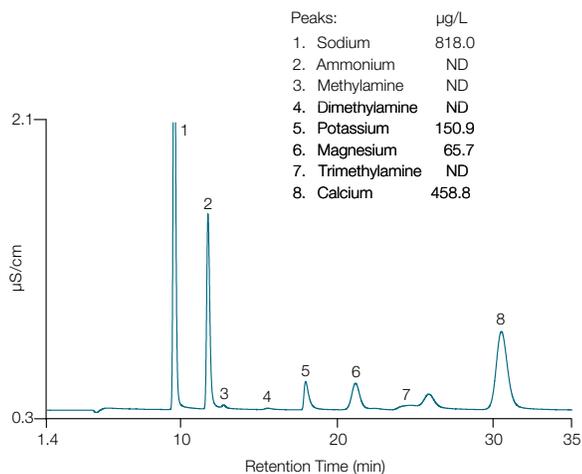
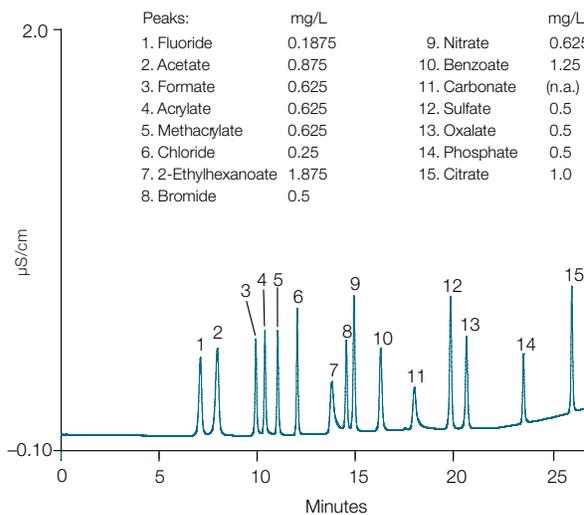


Figure 4. Trace levels of cations in 25% phosphoric acid and 10% hydrofluoric acid using the AutoNeutralization method.

Figure 5 illustrates the separation of a mixed inorganic and organic anion standard utilizing a Thermo Fisher™ Dionex™ Reagent Free™ Ion Chromatography (RFIC™) System on a Dionex IonPac AS17 column. Keeping the anionic contamination of electronic components low can reduce the incidence of component failure.



Separation of a mixed inorganic and organic anion standard.

Ion chromatography provides a convenient method for determining chloride in acid copper plating baths. These baths are used for the deposition of copper on semiconductor wafers. Monitoring chloride concentration is of interest because it plays an important role in the quality of copper deposition.

Column: Dionex IonPac AG15, AS15, 4 mm
 Eluent: 30 mM Potassium hydroxide
 Eluent source: Dionex EG40
 Flow rate: 1.2 mL/min
 Sample volume: 25 μ L of copper plating bath diluted 1:100
 Detection: Suppressed conductivity, recycle mode
 Peaks:
 1. Unidentified
 2. Chloride 0.47 mg/L
 3. Carbonate
 4. Sulfate

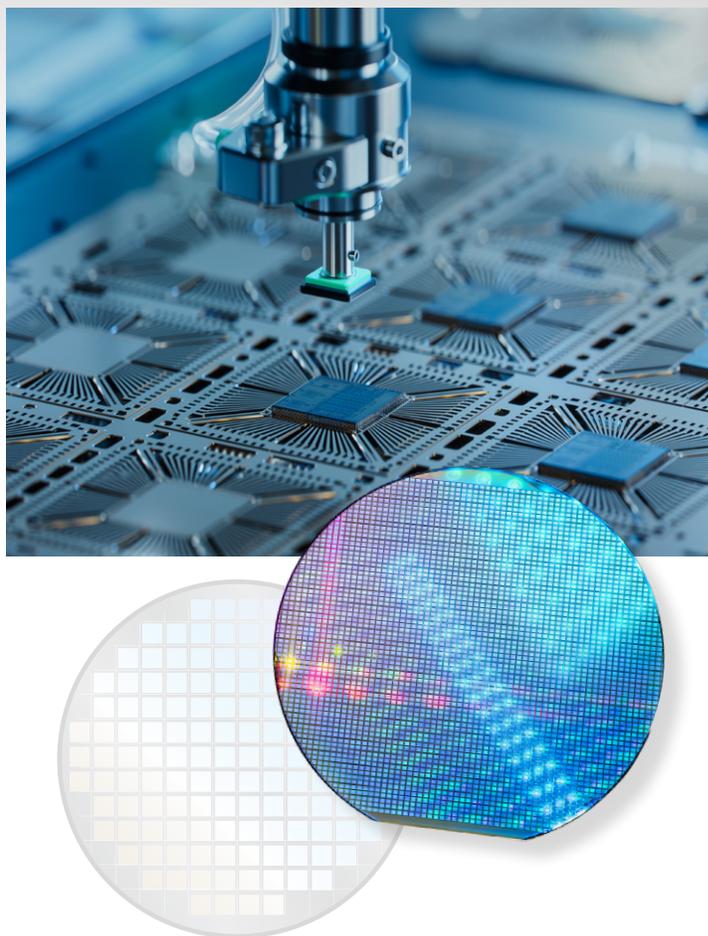
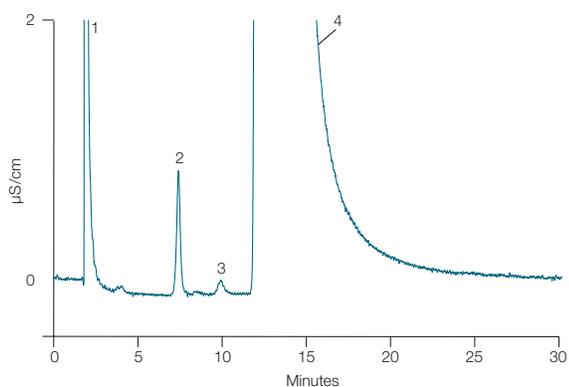


Figure 6. Determination of chloride in acid copper plating bath.

To improve the copper finish and enhance the electrodeposited film's appearance and quality, organic additives are incorporated into plating baths. High performance liquid chromatography (HPLC) methods for the determination of accelerator, leveler, and suppressor organic additives in acid copper plating baths provide reliable and fast determinations of the levels of these organic additives (Figure 7). Unlike cyclic voltammetric stripping (CVS) metrology which shows a cumulative signal related to all the additives and their impurities, actual quantities of additives can be reliably obtained.

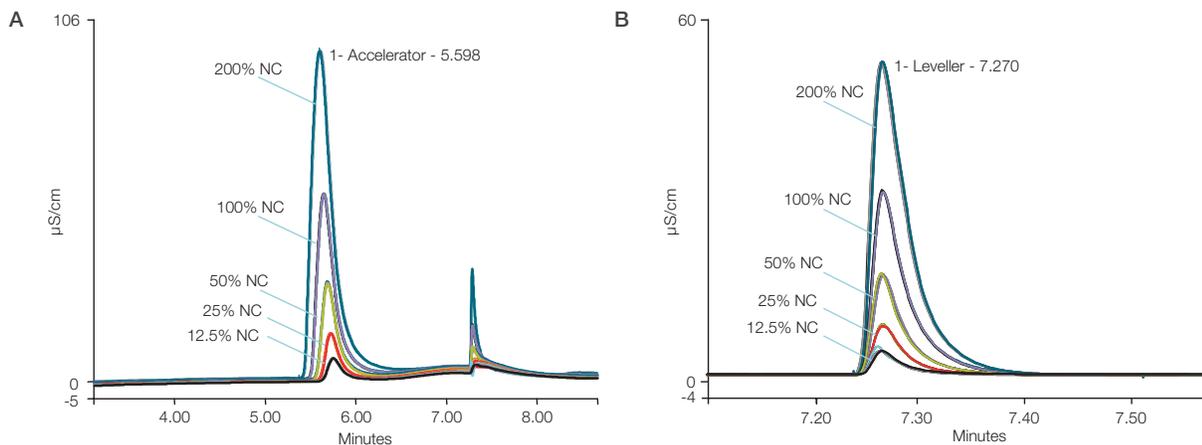


Figure 7. A) Overlaid HPLC-ECD (+900 mV) chromatograms of accelerator standards from 12.5 to 200% NC (nominal concentration), each analysis in triplicate. B) Overlaid HPLC-ECD (+650 mV) chromatograms of leveler standards from 12.5 to 200% NC, each analysis in triplicate.

Monitoring cleanroom environments for airborne molecular contamination

Airborne molecular contamination (AMC) is a concern for high-tech manufacturing processes, especially in the microelectronics industry and the production of semiconductors. Organic contamination can cause adverse effects on production tools and consequently increase costs.

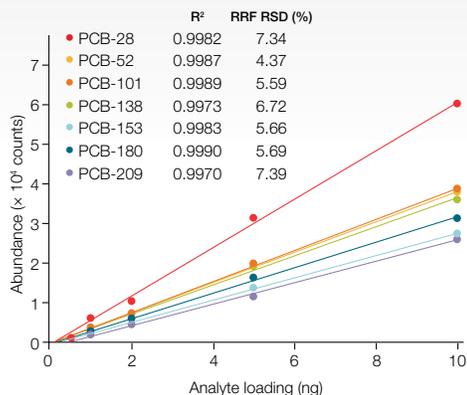
Localizing contaminant sources*

Condensable and organic contaminants—PCBs

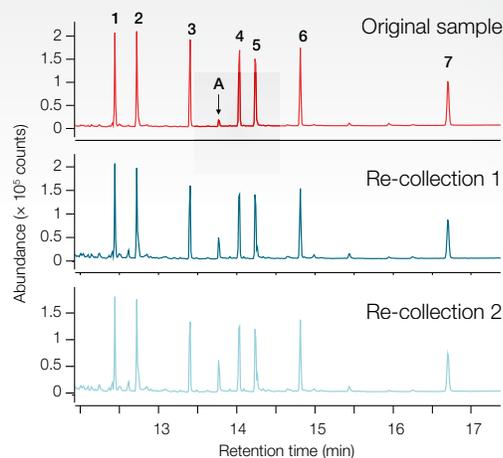
Thermal desorption is a powerful pre-concentration technique and as such can enable monitoring of organics such as polychlorinated hydrocarbons (PCBs) down to pg/m^3 limits of detection.

The analysis is robust and repeatable and enables confident monitoring of these chemicals of concern for the industry.

Compound	MDL (ng/m^3)
PCB-28	0.22
PCB-52	0.19
PCB-101	0.27
PCB-138	0.32
PCB-153	0.25
PCB-180	0.54
PCB-209	0.44



1. PCB-28	4. PCB-138	7. PCB-209
2. PCB-52	5. PCB-153	A. Sorbent Artefact,
3. PCB-101	6. PCB-180	2,6-Diphenylphenol

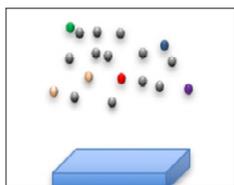


AMC Cleanroom monitoring*

On-line monitoring of volatile organic contamination in cleanroom environments



Cleanroom



Chamber/bag testing



Pre-concentration followed by analysis with UNITY-Air Server-xr™ GC/MS

SEMI E46: Test method for the determination of organic contamination from mini environments
SEMI F21: Classification of airborne molecular contaminant levels in clean environments

Systems solutions

Control of the process steps and wafer environment to meet the daily challenges of routine wafer compliance requires the use of many diverse characterization techniques, including many employing analytical instrumentation. Learn about semiconductor fabrication and how Thermo Fisher Scientific analytical instrumentation can help you control process steps and monitor the wafer environment throughout semiconductor manufacturing to ensure the highest yield possible.



Thermo Scientific™ Dionex™
ICS-6000 HPIC System



Thermo Scientific™ Dionex™
Integriion™ HPIC System



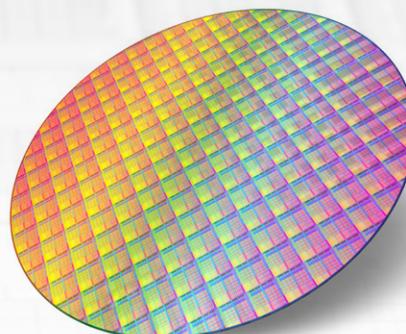
Thermo Scientific™
Vanquish™ Flex UHPLC
System



Thermo Scientific™
Vanquish™ Charged
Aerosol Detector (CAD)



Thermo Scientific™ ISQ™ 7610 Single Quadrupole GC-MS with
Markes Thermal Desorber TD System



Learn more at thermofisher.com/semicon-fab

General Laboratory Equipment – Not For Diagnostic Procedures. © 2023 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific and its subsidiaries unless otherwise specified. UNITY–Air Server-xr is a trademark of Markes International. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manner that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details. **BR002118-EN 0623M**